The Active Site Behaviour and Spontaneous Decoration of Electrodeposited Gold and Platinum Nanomaterials

A thesis submitted in fulfilment of the requirements for the degree of Doctor of Philosophy (Applied Chemistry)

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Declaration

I certify that except where due acknowledgement has been made, the work is that of the author alone; the work has not been submitted previously, in whole or in part, to qualify for any other academic award; the content of this thesis is the result of work which has been carried out since the official commencement date of the approved research program; and any editorial work, paid or unpaid, carried out by a third party is acknowledged.

Blake Plowman
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**Blake Plowman**
This thesis is dedicated to:

My parents, Robert and Alison,
And to Leigh, Alina and Ethan Plowman.

To God be the glory.
Proverbs 3:5-6
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Abstract

The formation of nanostructured materials is an important field of research in materials science. While attention has been placed on the synthesis of inorganic or carbon-based materials, including carbon nanotubes, graphene and other nanostructures, the fabrication of metallic nanostructures is another key area of study. This research is largely driven by the different properties shown by the metals in their nanostructured form, where altered optical, electronic, catalytic and electrocatalytic behaviour is displayed compared with the bulk metal structure. This is perhaps most clearly seen through the catalytic behaviour of gold nanoparticles towards the oxidation of carbon monoxide, which was unexpected as gold is known to be one of the most inert materials. Since this pioneering work by Haruta and co-workers in the late 1980s, the synthesis and behaviour of a range of metallic and metal oxide nanostructures have been intensively studied. This has involved a host of fabrication methods, including chemical, electrochemical and biological methods, as well as physical methods such as evaporation and vapour deposition. Amongst these methods the electrochemical synthesis route provides a facile means to fabricate surface-bound metallic nanostructures with control over the morphology, shape and crystallographic orientation of the deposited material. This method can also avoid the contamination of the surface with capping agents which may alter the behaviour of the nanostructures.

While much work has been performed on the synthesis, electrochemical behaviour and applications of electrodeposited metallic nanostructures, more research in this field is required to understand the complex nature of these nanomaterials. This includes the effects of the size, shape, crystallographic orientation, composition and porosity of the materials, and so the design of novel nanomaterials with properties tailored towards important applications requires a more complete understanding of these surface properties. Another important property of metal surfaces is the ability to oxidise at potentials lower than that expected for the bulk surface. This activity, known as premonolayer oxidation, has
been reported to occur in the double layer region of a number of metal surfaces such as gold, silver, platinum, palladium, copper and ruthenium, and has been postulated to be caused by the oxidation of low lattice coordinated atoms or clusters of atoms on the metal surface known as active sites. The premonolayer oxidation of these active sites is closely related to the electrocatalytic activity towards a range of important electrocatalytic reactions, however due to their often low coverage and complex nature further study is required to better understand and synthesise more effective materials for these applications.

The aims of this current research are to study the active site behaviour of gold and platinum nanomaterials, as these represent two important electrocatalytically active materials which are known to undergo premonolayer oxidation. As active sites are thought to be located at defects in the bulk surface structure and may be promoted at the disrupted surfaces present on nanostructures, the formation of novel gold and platinum nanostructures will be performed as a means to increase the presence of active sites. Electrodeposition is chosen as a means of fabricating these nanostructured materials, especially as uncapped metallic nanostructures may be formed and allow a direct study of the active sites present on the surfaces.

A number of materials are reported for the first time in this work, including the formation of gold nanospikes through a chemically templated electrodeposition method (Chapter III), platinum and platinum-lead dendritic nanostructures (Chapter IV) and highly porous gold surfaces formed through the in situ templating effect of hydrogen bubbles (Chapter V). The synthesis, electrochemical behaviour and application of these nanomaterials in electrocatalytic or surface enhanced Raman spectroscopy (SERS) applications are investigated, with active site behaviour demonstrated at each material. The premonolayer oxidation of these active sites is then extended to investigate the spontaneous decoration of these surfaces with metals such as silver, platinum and palladium, (Chapter VI) providing a facile means to both study the behaviour of these active sites as well as creating a range of active bimetallic electrocatalysts.
Chapter I

Introduction

Sections of this chapter have been published in the following peer-reviewed journal:

1.1. Introduction to Metallic Nanostructures

The study of metallic nanostructures is an area of intensive research efforts. These materials are broadly categorised by their feature size on the order of 1-100 nm, and at this size regime the materials may possess a range of unique properties not displayed by the bulk material. A classic example of this is the work of Haruta and co-workers, who observed that gold nanoparticles show enhanced catalytic activity towards the oxidation of carbon monoxide at temperatures as low as -70 °C. Such activity aptly demonstrates the altered behaviour which may occur on the nanoscale, as gold in its bulk form is known to be a weak chemisorber and remarkably inert.[2]

While the synthesis of nanostructured materials can be traced back over hundreds of years,[3-5] the realisation that these materials can revolutionise the fields of materials science and any associated fields has lead to their intensive investigation. This research has also been driven by the development of methods to probe the chemical and physical properties on this length scale, as well as the advancement of techniques to synthesise nanostructured materials.[5]

1.2. Electrodeposition of Metallic Nanostructures

As mentioned previously, electrodeposition provides an attractive method for the synthesis of metallic nanostructures. This involves the application of an appropriate electrochemical driving force to an electrode/electrolyte interface, resulting in the adherence of the metal species to the electrode surface. In the case of metal electrodeposition, this most commonly occurs by the reduction of a metallic salt to its elemental state, although variations such as the electrochemically driven precipitation of certain metal oxides or hydroxides is known.[6-7]

Electrodeposition is a widely studied field which is of keen interest in materials science applications as it can be used to synthesise a wide range of nanostructured materials.[8-9] Several benefits of this method of nanofabrication include the synthesis of materials of variable size, shape, crystallographic orientation, density and composition, which can be formed in the absence of capping agents.[10-12] This
can be readily achieved through the electrochemical parameters employed such as the applied potential (or current density) and the duration of the electrodeposition, as well as the nature of the electrode surface and the composition of the electrodeposition solution.\cite{10,13-14} A number of different electrochemical techniques also exist, including deposition at fixed, stepped or pulsed potentials or current densities, or by sweeping the applied deposition potential.\cite{15} These techniques provide a level of control over the reduction process not available in other methods such as the chemical synthesis of nanomaterials, as the reduction potential is carefully controlled through the use of a potentiostat rather than relying on the reduction potential supplied by the chemical reductant.\cite{9}

The electrodeposition of metallic nanostructures can be summarised under four categories, which are (i) the electrodeposition at unmodified electrodes, (ii) at modified electrodes or in the presence of (iii) physical or (iv) chemical templating agents. These methods are commonly employed for the formation of nanostructured metallic surfaces and are the subject of the following sections.

\section*{1.2.1. Unmodified Electrodes}

The electrodeposition of metals on untreated substrates provides the simplest system for the electrodeposition of nanostructures. This offers a number of benefits, with the maintenance of a clean surface increasing the coverage and reproducibility of the electrodeposited material as well as avoiding possible complications from surface capping agents in future applications. A wide variety of metallic nanostructures have been synthesised in this manner, including gold,\cite{16-22} silver\cite{23-27} and platinum.\cite{28-31} An example of this growth is shown in Figure 1.1, where Zhang and co-workers demonstrated the electrodeposition of gold nanostructures on an unmodified glassy carbon surface.\cite{21} By adjusting the pH and temperature of the plating bath a range of isolated nanostructures were formed, including berry-like nanostructures. The gold nanostructures formed in this manner showed activity towards the electrocatalytic reduction of oxygen, and after modification with \textit{n}-dodecanethiol the surface displayed superhydrophobic properties.
The electrodeposition of metallic nanostructures at unmodified surfaces can also be used to carefully control the shape of the electrodeposited structures. Chen and co-workers reported this for the synthesis of iron nanocrystals, where the shape of the nanostructures could be controlled from rhombic-dodecahedral (Figure 1.2a) or tetragonal bipyramidal nanostructures (Figure 1.2f) through to cubic structures (Figure 1.2e,j).\[32\] This was achieved by an initial nucleation step followed by prolonged growth at a higher potential from a solution of FeSO$_4$ in H$_2$SO$_4$. By altering the concentration of Fe$^{2+}$ in this solution as well as by careful control of the applied potential during the growth stage the various shapes were produced. The exposed crystal planes were found to be sensitive to the latter effect, with a greater number of (100) facets formed at lower potentials which lead to the growth of cubic nanostructures. The concentration of Fe$^{2+}$ similarly affected the growth of the exposed crystal planes, where the (110) facets grew slowly and isotropically at a

\[ Figure 1.1: \text{SEM images of berry-like gold nanostructures (Reprinted with permission from Ref. 21)}. \]
lower concentration of Fe$^{2+}$, while at higher concentrations the growth rate of several of the exposed (110) facets was increased, leading to the formation of tetragonal bipyramidal iron nanostructures.

![Figure 1.2: SEM images and schematics of electrodeposited Fe nanocrystals (Reprinted with permission from Ref. 32).](image)

A number of interesting reports on the electrodeposition at unmodified surfaces have recently been published by Sun and co-workers. This involved the electrodeposition of large, quasi-spherical platinum nanoparticles on a glassy carbon surface, following which the surface was washed and added into a solution containing ascorbic acid and H$_2$SO$_4$. A square wave potential perturbation was then applied, resulting in the formation of tetrahexahedral platinum nanostructures (Figure 1.3).[33] These highly faceted nanostructures were formed by selecting appropriate potentials during the square wave treatment, where the upper potential limit resulted in the oxidation of the platinum, which then underwent a place exchange reaction at the exposed lower index facets. The reduction of this oxide and any dissolved platinum species liberated during the upper limit pulse was then performed during the lower potential pulse, and repetition of this sequence lead to the growth of nanostructures rich in steps at the expense of the quasi-spherical seed particles. Similar procedures were also used to form platinum nanorods as well as concave hexoctahedral platinum and palladium nanostructures,[33-34] and the highly faceted nanostructured surfaces showed improved electrocatalytic activity towards reactions such as ethanol oxidation. In addition to this post synthesis treatment, the authors have also reported the direct electrodeposition of texahetrahedral
palladium nanostructures on a glassy carbon electrode through a nucleation step followed by a square wave treatment in PdCl$_2$ in HClO$_4$.\[35\]

**Figure 1.3:** Schematic and SEM images showing the electrochemical formation of tetrahexahedral platinum nanostructures (Reprinted with permission from Ref. 33).

As can be seen from the examples listed previously, a variety of metallic nanostructures may be electrodeposited at unmodified electrodes, and by modulation of the parameters involved in the electrochemical growth a range of nanostructured metallic surfaces may be formed.

### 1.2.2. Electrodeposition on Modified Electrodes

While much research has been performed at unmodified electrode surfaces, the electrodeposition of nanostructured metals is also commonly performed on modified electrodes. This technique involves the alteration of the underlying electrode with a conductive material prior to electrodeposition. This material is often a nanostructured support and can lead to the formation of high surface area materials and possibly alter the behaviour of the electrodeposited metal through metal-substrate interactions.\[36\]

The electrodeposition on modified electrodes is commonly reported in the case of carbon nanotubes, titania nanotubes or self-assembled monolayers of organic molecules (SAMs). Carbon nanotubes have been the subject of extensive research attention in recent years, owing to their interesting electronic and mechanical properties as well their high thermal stability and high surface areas.\[37-39\] However in order to tailor their activity for applications such as catalysis and sensing the
carbon nanotubes are often decorated with noble metal nanoparticles. This can be achieved through chemical or electrochemical methods, and the latter approach has been shown to be well suited to the formation of well-adhered nanoparticles.\[40-41\] The preparation of the nanotube surface is generally performed through chemical vapour deposition (CVD) on a conductive surface, which provides a well-defined composite substrate for electrodeposition onto either single (SWNT) or multi-walled (MWNT) carbon nanotubes. The electrochemical formation of CuO,\[^{42}\] Ag\[^{43}\] and TiO\(_2\) nanoparticles\[^{44}\] have all been performed on such surfaces, as illustrated in Figure 1.4 for the decoration of CuO nanoparticles. While these deposits are generally quasi-spherical in nature, the formation of a number of other morphologies has been reported. For example homogeneous coatings of MnO\(_2\) have been reported on MWNTs,\[^{43,45}\] while platinum nanoflowers have been electrodeposited on SWNTs.\[^{46}\] The electrodeposition of copper nanocubes has also been reported,\[^{47}\] although the shape direction in this case was the result of both the underlying MWNT support and a chemical templating effect (as will be discussed in Section 1.2.4.).

![Figure 1.4](image)

**Figure 1.4:** Schematic of electrodeposition on a MWNT array (Reprinted with permission from Ref. 42).

The preparation of CNT surfaces for electrodeposition is also routinely performed by drop-casting a suspension of CNTs on a conductive substrate from a liquid such as n-methylpyrrolidone (NMP) or sodium dodecyl sulphate (SDS). After allowing to dry a network of CNTs are formed on the surface of the electrode, although it should be noted that the alignment and adherence of the CNTs is lower in this case than for CNTs prepared on the substrate by CVD. Drop-cast films of CNTs
have been utilised as modified substrates for the electrodeposition of gold,[48-49] platinum,[50] copper,[51] ruthenium oxide,[52] zinc oxide,[53] iron oxide,[54] Prussian blue[55] and nickel hexacyanoferrate (HCF).[56] While quasi-spherical deposits are generally formed on these surfaces, similarly to the CVD approach other morphologies can be synthesised such as aggregated nanoparticles,[51, 57-58] continuous films[52, 59] or irregularly shaped nanoparticles.[51, 60] Another variation on the drop-cast method is to include additives in the CNT suspension such as chitosan.[61-62] The metal electrodeposition is in this case accompanied by the precipitation of the chitosan film, brought about by a local increase in the solution pH. The drop-cast method has been extended by Zheng and co-workers to the inclusion of ionic liquids in the suspension, as was reported for the electrodeposition of a number of alloys such as PtRu,[63] AuPt[64] and PtRuNi.[65] The inclusion of the ionic liquid in the modified surface was found to limit the agglomeration of nanoparticles and increase the density of electrodeposited nuclei. Additionally the ionic liquid acted as a chemical templating agent during the electrodeposition and also caused the MWNT bundles to cross-link together. This demonstrates the multi-functional nature that ionic liquids can exert on electrodeposition and shows the scope for further research in this area.

An alternative to the use of carbon nanotubes as a modified support are TiO₂ nanotubes. These nanotubes, unlike their CNT counterparts, are generally formed through electrochemical methods, including the oxidation of a titanium electrode in a fluoride solution with a number of other additives. This results in the formation of a surface-confined array of conductive nanotubes, which may be further functionalised through electrodeposition. Noble metal decoration of TiO₂ nanotubes have been investigated in the case of both gold[66-67] and platinum.[68] Other materials including cadmium telluride[69] and Prussian blue decoration on gold-sputtered TiO₂ nanotubes[70] have also been reported. As was the case for the decorated CNT films, the deposits on the TiO₂ nanotubes tend to be quasi-spherical in nature, with either isolated nanoparticles or aggregates seen depending on the electrodeposition parameters. Another interesting report on the electrochemical decoration of TiO₂ nanotubes was work performed by Huang et al., who modified a TiO₂ nanotube surface with a SAM as a mask prior to electrodeposition.[71] Defined
regions for electrodeposition were then exposed by selectively patterning the surface using photolithography to degrade the SAM in particular regions. Following this masking process silver electrodeposition was then performed on the exposed TiO₂ nanotubes.

While the latter example of the use of a SAM displayed a masking or inhibiting role for electrodeposition, it should be noted that not all SAMs behave in this manner. Instead, where a monolayer consisting of an appropriate molecule is selected, electrodeposition can take place at the solution-exposed tail of the molecule. One of the main criteria for selecting an appropriate SAM is the length of the molecule, as electron transfer from the underlying substrate to the exposed section of the SAM can be significantly impeded at extended lengths and inhibit the electrodeposition. The electrodeposition on SAMs is largely based on either gold or glassy carbon electrodes, as the surface chemistry of establishing smooth monolayers is well established in these cases. SAMs on gold electrodes are often based on the affinity between gold and sulphur to form thiol bonds, while on glassy carbon surfaces monolayers of either 3-aminopropyltriethoxysilane (APTES)¹⁷² or cystamine¹⁷³ have been reported. The electrodeposition of a range of metal nanoparticles on these surfaces has been studied, including gold,⁷²-⁷³ silver,⁷⁴ copper,⁷⁵ Prussian blue,⁷⁶ zirconia⁷⁷ and also platinum and AuPt alloys,⁷² with the deposits generally forming quasi-spherical structures. A significant advantage of electrodepositing at such a modified electrode is that the SAM can introduce functionality in the final material, for example by reducing non-specific binding in the case of biosensing.

### 1.2.3. Physical Templating

Another method of forming nanostructured metals through electrodeposition is the use of physical templating. While similar to the previous section on electrodeposition on modified electrodes, there are a number of distinctions between these categories. Physical templating involves electrodeposition through a non-conductive mould, which avoids the formation of nanoparticles on the template itself. This method defines the areas on the electrode available for nucleation and growth of the metal electrodeposit, and the presence of the template can also alter
the diffusion layer and hence the rate of reduction. Once the electrodeposition is terminated the template is then removed from the surface, leaving the metallic nanostructures adhered to the electrode surface.

One of the most important examples of physical templating is the use of anodised aluminium oxide (AAO) templates, which are formed by the electrochemical oxidation of aluminium surfaces, typically in a solution of hydrofluoric acid. This results in the formation of a large number of well-defined pores across the surface, as seen from the schematic and SEM image of an AAO surface in Figure 1.5. While a detailed description of the factors involved in forming such templates is beyond this current work, an excellent review on this topic is available from Poinern et al.[78]

![Figure 1.5](image)

**Figure 1.5: Schematic and SEM image of an AAO template (Reprinted with permission from Ref. 78).**

Due to the regular pore shape and size, as well as the long-range order exhibited by the pores across the surface, AAO templates may be used as a physical template during electrodeposition. In order for this to occur one side of the AAO membrane is modified by the sputtering of a conductive layer such as silver, allowing electrical contact to be made to each of the pores. The metal electrodeposition can then occur at the underlying conductive surface within the pores, and the reaction is terminated after the pores are filled to the desired extent. After electrodeposition the AAO template is then removed by dissolution in an alkaline solution, leaving an ordered array of nanowires on the electrode surface. If desired the conductive substrate may also be dissolved, producing free nanowires in solution (Figure 1.6), however most reports do not involve this last step.
The AAO templated electrochemical formation of nanowires with diameters below 150 nm have been reported for materials such as gold\cite{80-82} and Prussian blue\cite{83-84}. AAO templates can also be used to form ordered arrays of metallic nanoparticles, as opposed to the growth of nanowires. This has been reported for the electrodeposition of silver nanoparticles\cite{85-86} as well as the electrodeposition of gold nanoparticles\cite{87}. Several recent reports also highlight the novel approaches being applied to AAO templated electrodeposition. For example, multi-segmented nanowires have been synthesised by electrodepositing through the AAO template from successive electrodeposition baths, as shown in Figure 1.6 for the formation of gold-nickel-polypyrrole nanocomposite structures.\cite{79, 88} The synthesis of porous nanorods has also been investigated using AAO templates. Bai and co-workers achieved this by coating the template with a thin layer of cadmium sulphide prior to electrodeposition. The authors found that the affinity of metal salts to the $S^{2-}$ groups on the pore walls encouraged preferential growth along the walls, which they used to form both palladium\cite{89} and silver\cite{90} porous nanorods. The cadmium sulphide layer was crucial to the porosity of the electrodeposited nanostructures, with solid nanorods formed in the untreated AAO template.

Figure 1.6: Schematic and SEM images showing the electrodeposition of multi-component nanowires in an AAO template (Reprinted with permission from Ref. 79).
Polycarbonate templates offer another means of physical templating during electrodeposition. These act in a very similar way to AAO templates, and have been reported for the formation of tungsten oxide nanowires.\cite{91} However AAO templates are preferred to porous polycarbonate membranes as the synthesis of the AAO templates has been extensively studied and the morphology can readily be adjusted through factors such as the bath contents, the anodisation time and potential.\cite{78}

Besides electrodepositing through porous materials such as AAO or polycarbonate templates the physical templating can also be performed using beads of materials such as polystyrene, polycarbonate or silica in a process known as nanosphere lithography.\cite{92-94} These beads, with typical dimensions of several hundred nanometres, can form an ordered layer (or layers) on an electrode surface through either drop-casting or by a Langmuir-Blodgett method.\cite{95} Once the ordered array of beads are assembled, electrodeposition on the surface is restricted to the small voids present between the spherical particles.\cite{96} The templates may then be removed through dissolution or by sonication.

In addition to the more commonly used physical templating methods there are also a number of other methods which have been reported. This includes lithographic methods, where an electrically insulating layer is added to the surface, providing a barrier for electrodeposition. This layer is then irradiated with either light (photolithography) or electrons (e-beam lithography) in selected regions, causing the layer to degrade in these areas and become prone to dissolution. This selective masking of the surface allows the physical templating of electrodeposition, after which the removal of the remaining mask is performed. Lithographic methods are used extensively in the fabrication of electronic devices, and although they are not commonly reported for electrodeposition there are reports of both photolithography\cite{97} and e-beam lithography\cite{98} templated electrodepositions. Another approach to physical templating is nanoindentation.\cite{99} This involves the piercing of a non-conductive layer by a sharp tip attached to a cantilever, exposing small regions of an underlying conductive material for electrodeposition. However this method is not applicable for the bulk synthesis of nanomaterials and is generally used to study fundamental processes.
1.2.4. Chemical Templating

The final method of electrodepositing nanostructured metallic surfaces to be discussed here is chemical templating. This method involves the inclusion of a chemical species in the deposition bath which is capable of directing the growth of the electrodeposit, and can therefore alter the shape or crystallography of the growing deposit. One suitable class of chemical templates is the addition of a surfactant in the deposition solution. While this is commonly employed in the chemical formation of nanostructured materials, it is also slowly finding application in electrochemical syntheses.\textsuperscript{[100]} Examples of the use of surfactants as chemical templating agents during electrodeposition include cetyltrimethylammonium bromide (CTAB),\textsuperscript{[101]} cetyltrimethylammonium chloride (CTAC)\textsuperscript{[102-103]} or sodium dodecyl sulphate (SDS).\textsuperscript{[104]} The ability of these species to alter the growth of the electrodeposits is due to their preferential adsorption to particular exposed crystal facets of the electrodeposit which alters the growth rate along these directions.\textsuperscript{[103-104]} An example of the materials which can be formed in this manner is shown in Figure 1.7, where the electrodeposition of gold in the presence of CTAC formed gold nanoplates, nanothorns or nanowires, based on the concentration of CTAC and the applied potential during electrodeposition.

Another class of chemical templates are liquid crystal templates. These non-ionic surfactants behaves differently to the surfactants discussed previously, as they can self assemble into a hexagonal lyotropic liquid crystalline phase in the plating solution.\textsuperscript{[105]} The structure of the phase is then able to template the growth of the electrodeposition, restricting electrodeposition to within the regularly arranged pores in the liquid crystal phase. For this purpose Brij 56 is commonly used, with early reports related to the electrodeposition of mesoporous platinum surfaces with a well-ordered arrangement of pores.\textsuperscript{[105-109]} Mesoporous nickel has also been synthesised in this manner,\textsuperscript{[110]} and in order to improve the stability of the surface gold plating was also performed on the mesoporous nickel surface.\textsuperscript{[111]}

Electrodeposition from eutectic solvents has also been reported, although this remains a relatively unexplored area. Sun and co-workers investigated the electrodeposition of platinum from a solution containing choline chloride and urea,
observing the growth of platinum nanoflowers.[112] Interestingly the morphology of the electrodeposit was noted to be highly sensitive to the temperature of the electrodeposition bath, with 80 °C found to be optimal. Further studies on such systems is required in order to investigate the nature of the growth direction effect and to identify other nanostructures which can be formed by this method.

**Figure 1.7**: SEM images showing the growth of nanoplates (a-b), nanothorns (c-d) and nanowires (e-f) in the presence of CTAC (Reprinted with permission from Ref. 103).

The chemical templating of metal electrodepositions is also commonly influenced by the inclusion of inorganic anions in the plating solution. Feng and co-workers have studied the effect a number of common anions in the form of chloride, bromide, iodide, sulphate and perchlorate anions on the electrodeposition of platinum nanostructures.[113] It was found that monodisperse, quasi-spherical nanostructures were synthesised in the presence of these anions, in contrast with the polydisperse, irregular structures formed without the addition of these anions.
to the deposition bath. It was suggested that this altered growth was the result of anion adsorption on the growing electrodeposit, causing electrostatic repulsion with the reactant PtCl$_6^{2-}$ species. This interaction altered the electrodeposition kinetics at the growing nanostructures and favoured the growth of quasi-spherical particles. The choice of anion was also found to alter the size of the nanostructured platinum, with larger anions promoting the formation of smaller nanoparticles, due to both the electrostatic repulsion and the steric hindrance of these larger species.

The shape directing effect of anionic species is an important consideration in electrodeposition, especially as such species may be present as a background electrolyte or as they are liberated from the metal salt during electrodeposition.\textsuperscript{114} This latter case may be especially important, as the localised concentration of the liberated anions will be higher at the electrode surface than in the bulk solution, which may allow the anions to influence the growth of the electrodeposit.

The chemical templating of electrodepositions has also been explored in the case of a number of other anionic species. For example, the addition of cysteine to a deposition bath for gold electrodeposition was found to form a bumpy surface, while smooth deposits were formed in the absence of cysteine.\textsuperscript{115} This altered growth was attributed to the potential-dependent adsorption/desorption of cysteine to particular facets of the gold electrodeposit. This affinity of cysteine for the gold surface is related to the formation of thiol bonds with the surface, and resulted in preferential growth along the (111) direction. Nitrate has also been reported as a chemical templating agent in gold electrodeposition, with Yang and co-workers speculating that it can lead to the oxidation of less stable gold facets in a similar mechanism to etching by aqua regia.\textsuperscript{103} However the presence of CTAC in the deposition solution (as discussed previously) meant that the exact influence of the nitrate on the electrodeposition was not determined. Citrate has also been used as a chemical templating agent, for example in the electrodeposition of platinum\textsuperscript{116-117} or bismuth.\textsuperscript{118} In the latter case the authors observed that the presence of citrate lead to the formation of aggregates of bismuth nanoparticles, whereas a less homogeneous surface was formed in its absence.
While the adsorption of anions on the electrodeposit has been widely found to influence the growth of the electrodeposit, in certain cases the altered growth may instead be related to the speciation of the metal salt prior to electrodeposition. For example, Yang and co-workers reported the electrodeposition of copper nanocubes on MWNTs, where the formation of these cubic structures was attributed to the stabilisation of a Cu(I) chloride intermediate species during electrodeposition and its interaction with the growing electrodeposit.\textsuperscript{[47]} Sun and co-workers reported a similar situation in the electrodeposition of copper, where local enrichment of Cu\textsuperscript{2+} occurred by complexation with the carboxyl groups of proline.\textsuperscript{[119]} This speciation effect resulted in the formation of pillar-like structures.

The inclusion of a heavy metal salt such as lead acetate in the plating bath has also been found to influence the morphology of electrodeposited materials. Electrodeposition in the presence of lead acetate has been reported in the formation of platinum black\textsuperscript{[120]} as well as gold black\textsuperscript{[121-123]} although the surface structure of these materials was not widely reported. Van Noort and Mandenius,\textsuperscript{[124]} as well as Bonroy \textit{et al.}\textsuperscript{[125]} electrodeposited gold from solutions containing lead acetate and HAuCl\textsubscript{4}, and although the shape directing effect of the lead salt was not addressed it was noted that the procedure formed a porous surface. More recently O’Mullane and co-workers electrodeposited from similar solutions, forming highly dendritic nanostructured gold surfaces.\textsuperscript{[114]} The dendritic nature of the electrodeposits was attributed to both the applied deposition potential as well as the underpotential deposition (UPD) of Pb on the growing electrodeposit.

Another means of chemical templating is through the use of dynamic hydrogen bubble templating. In this method a strongly cathodic potential is applied to an electrode in an acidic solution containing a metallic salt. This results in both the reduction of protons as well as the reduction of the metal salt (Equations 1 and 2, respectively).

\[
2H^+ + 2e^- \rightleftharpoons H_2(g) \quad (1)
\]

\[
M^{n+} + ne^- \rightleftharpoons M^0(s) \quad (2)
\]
While the evolution of hydrogen during metal deposition under appropriate conditions has been known for some time, and indeed viewed as an undesirable side reaction,\textsuperscript{[126]} recent investigations have shown that under suitably vigorous conditions the reduction of hydrogen alongside the metal salt can provide a novel means of templating the electrodeposition. This occurs as the evolved H$_2$(g) coalesces into bubbles at the electrode surface, as shown in Figure 1.8. The electrodeposition of the metal is then templated by these evolved hydrogen bubbles, and as these bubbles then escape the surface this templating is a dynamic process, forming a highly porous three-dimensional metallic network. The hydrogen bubbles are then readily removed from the structure after the electrodeposition is terminated and the sample is washed. An added advantage of this method is that the electrodeposited surface is free from any capping agents.

\textbf{Figure 1.8: Schematic showing the electrodeposition of copper using the dynamic hydrogen bubble templating method (Reprinted with permission from Ref. 127).}

Much of the early work on the dynamic hydrogen bubble templating method was focused on the electrodeposition of copper.\textsuperscript{[128-133]} As shown in Figure 1.9, this results in the formation of a highly porous surface, with pore sizes typically on the order of tens of micrometres due to the vigorous formation and release of hydrogen bubbles from the surface during the electrodeposition.\textsuperscript{[128]} Closer examination of the pore walls (Figure 1.9d) reveals the prevalence of dendritic nanostructures. This combination of a highly porous surface, which may aid the mass transport processes involved in catalytic or electrocatalytic applications, along with a highly
nanostructured morphology demonstrate why this synthesis procedure is of interest.

![SEM images of copper electrodeposited using the dynamic hydrogen bubble templating method](image)

**Figure 1.9:** SEM images of copper electrodeposited using the dynamic hydrogen bubble templating method (Reprinted with permission from Ref. 128).

The dynamic hydrogen bubble templating method has also been extended beyond copper surfaces, including porous silver,[134-135] bismuth,[136] platinum,[137] and palladium materials.[138-139] Bimetallic porous materials have also been demonstrated, with the electrodeposition of nickel[140] or tin[129, 141] on a porous copper support, as well as Co(OH)₂ on a porous nickel surface.[142] Galvanic replacement of porous support materials has also been reported, with the replacement of porous copper with platinum,[143-144] gold,[145] silver[146] or palladium,[146] along with the replacement of porous Cu-Au with platinum.[147] In addition bimetallic porous materials may be fabricated by direct electrodeposition with Cu-Au,[147-148] Cu-Pd,[149] Cu-Sn[150] and Ni-Co[151-152] formed in this manner. In combination with the unique morphologies attainable, showing both a high degree of nanostructured growth as well as a highly porous network, the compatibility of this templating method with the electrodeposition of a range of metallic and
bimetallic materials provides scope for the creation of novel materials for catalytic and electrocatalytic applications.

1.3. Importance of Developing Novel Nanomaterials

1.3.1. Electrocatalytic Applications in Fuel Cells

One of the most important applications of nanostructured metal surfaces is in the field of electrocatalysis. Electrocatalytic reactions involve the transfer of electrons between an electrode and a reactant species, where the reaction kinetics and reaction mechanism may be altered to give enhanced performance.[153] Such electrocatalytic process are of vital importance in industrial processes, as the reduced overpotential required for an electrocatalytic process may result in substantial cost savings.[154] It has been known for a long time that electrocatalytic reactions can be highly sensitive to the surface structure of the electrode, having been observed during research on electrocatalysis at single crystal surfaces.[155-157] This remains an ongoing and challenging area of research, as the study of nanostructured materials has shown varied electrocatalytic activity in comparison with their bulk counterparts, driven by factors such as the altered size, shape and crystallography of the materials.[33,158-161]

One of the major applications of nanostructured electrocatalysts is in fuel cells. These are devices which convert the chemical energy stored in a fuel directly into electrical energy, eliminating the relatively inefficient combustion process used in other forms of power generation.[162] In a fuel cell a continuous supply of reactants allows the constant generation of electrical energy without the need for storage. While the first working fuel cell was constructed by Sir William Grove some 170 years ago[163] much research on this field continues to the present day. This research is largely driven by the need to reduce the greenhouse gas emissions caused by other forms of energy conversion including combustion engines and coal-fired power plants, as well as the limited supply available of these fossil fuels.[164] Recent estimates place these fossil fuel reserves as depleting within the next 70-150 years,[163] highlighting the need for alternative power sources such as fuel cells.
Research to date has been performed on a number of different fuel cells, including alkaline, phosphoric acid, molten carbonate, solid oxide, polymer electrolyte membrane, direct alcohol and microbial fuel cells. While these technologies have been shown to successfully act as power sources, there are several technical issues which may limit their practical application. This includes the limitation of alkaline fuel cells to space applications, as the presence of even trace quantities of CO\textsubscript{2} in the electrolyte can result in the formation of alkali carbonates and lead to significant performance loss, and the inability to generate sufficient power densities in microbial and phosphoric acid fuel cells. While solid oxide fuel cells can provide a suitable means for bulk power generation, their operation at elevated temperatures (approx. 800 °C) decreases their lifetime and requires the use of expensive housing materials. One of the more promising choices for transport applications are polymer electrolyte membrane fuel cells (PEMFCs). Shown in Figure 1.10 is a schematic of such a fuel cell, where an anode and a cathode are separated by a polymer electrolyte membrane. Two electrochemical reactions occur at this assembly, with the oxidation of hydrogen occurring at the anode and the reduction of oxygen at the cathode. The polymer electrolyte membrane prevents the unit from short-circuiting while also allowing the protons produced by the reaction at the anode to migrate to the cathode, where they are involved in the reduction of oxygen. The other product from the reaction at the anode are electrons, and by connecting the fuel cell to an external grid and returning it at the cathode these electrons are able to do work, as illustrated by the illumination of the light bulb in the schematic. As the reactants for this reaction are only hydrogen and oxygen, the emission from this fuel cell is water vapour, showing that this is a clean method of converting chemical energy into electrical energy. In practice a number of these fuel cells are then added into a larger unit, known as a stack, increasing the total power output available.
Research on electrocatalysts for the oxidation of hydrogen in PEMFCs has largely centred on platinum-based nanomaterials, especially as this reaction is facile on these materials.\cite{164} However in order to reduce the platinum loading of these materials and to decrease the poisoning which can occur from CO still present in the H\textsubscript{2} feed gas a variety of bimetallic electrocatalysts have been investigated for this application. These include platinum-based bimetallics with Ru, Co, Mo, Sn and W,\cite{173-175} however PtRu appears to be the best candidate of these bimetallic surfaces.\cite{164,176}

While the use of hydrogen as a fuel source offers many advantages, it should be noted that there are several technical issues in this system. These include difficulties in the safe storage of hydrogen at the relatively high pressures required to extend the range of the vehicles as well as the economical production of hydrogen gas.\cite{169,177} There are several approaches to this latter issue, including the formation of hydrogen through the reforming of hydrocarbons\cite{178} and the electrolysis of water.\cite{179} A large number of studies have been devoted to the identification of electrocatalysts for the hydrogen evolution reaction,\cite{180-181} as these surfaces can reduce the overpotential required for the reaction and may therefore make the synthesis of large quantities of hydrogen more economically viable.
As an alternative to hydrogen-based fuel cells a range of other fuels have been investigated. The most important of these is methanol, which is the basis of the direct methanol fuel cell (DMFC). In this case oxygen reduction is again employed at the cathode, as it is readily available and provides a suitable overpotential for fuel cell applications. The use of methanol has received attention as it provides a higher energy density than hydrogen and involves easier storage and transport compared with hydrogen. While platinum-based materials display enhanced activity towards methanol oxidation over a range of other materials, this reaction is more complicated than the oxidation of hydrogen as carbonaceous species including CO are produced during this reaction. It is well known that CO ads can readily poison platinum electrodes by blocking available reaction sites, and this has driven the research of bimetallic nanostructures for methanol oxidation, as these surfaces can show reduced poisoning through either bifunctional or electronic effects. These platinum-based bimetallic surfaces include Pb, Au, Ni, Ir, Pd, Sn, Fe and Co, however the most practical bimetallic electrocatalyst developed appears to be PtRu. A further challenge for DMFCs is the cross-over of methanol from the anode through the polymer electrolyte membrane to the cathode which can limit the efficiency of the fuel cell by competing with oxygen for binding sites. Research is currently being undertaken on alternative membranes to reduce the extent of methanol cross-over, as well as the formation of cathodes which are less sensitive to the presence of methanol.

Similarly to the DMFC, a number of other fuels are being considered for use at the anode. Ethanol is one such fuel, with an increased energy density and ease of production compared with methanol. Like methanol oxidation this reaction is also prone to poisoning by species such as CO, and so the formation of bimetallic electrocatalysts for the oxidation of ethanol has been focused on, including PtSn, PtIr and PtRu, as well as PtRu modified with W and Pd. A wide range of other fuels have also been considered for fuel cell applications, including formic acid, borohydride, glucose and dimethyl ether.

As has been referred to a number of times, the electrocatalytic reduction of oxygen remains one of the most important reactions involved in fuel cells, finding application in the majority of fuel cells. Oxygen is chosen for the reaction at the
cathode as is abundant and its positive redox potential provides a suitable overpotential for the fuel cell.\cite{164, 182} However the reduction of oxygen can be problematic in these reactions as the slow reduction kinetics associated with this reaction can be a limiting factor in a fuel cell.\cite{206} The reduction of oxygen has received much attention in the literature, and it has been found to occur mainly through either the four-electron reduction of oxygen to water or by the formation of hydrogen peroxide in a two-electron step, followed by another two-electron reduction to water.\cite{207} The development of electrocatalysts for the oxygen reduction reaction has been guided by computational work, which revealed that platinum was a more active electrocatalyst than other monometallic systems, while in the case of bimetallic electrocatalysts materials such as PtFe, PtCo and Pt Ni were found to be more active than monometallic platinum.\cite{207-208} Other research on electrocatalysts for the reduction of oxygen include the dispersion of platinum nanoparticles on high surface area supports or the formation of nanostructured platinum or platinum-based bimetallic surfaces,\cite{176} as well as research towards alternative materials to platinum.\cite{209-211}

From the discussion above it can be seen that the study of the electrocatalytic reactions involved in fuel cells is an area of ongoing importance, especially in light of the complexity involved in many of these reactions. This research involves attempts to both improve the electrocatalytic activity of platinum nanostructures and the development of other materials which may provide viable alternatives for these applications.

\subsection*{1.3.2. Electroanalytical Applications}

The electrochemical formation of metallic nanostructures has also been performed for applications in the field of electroanalysis, where electroactive target species may be detected at electrode surfaces. While this covers a broad range of analytical targets, two of the most important categories are the detection of environmental or biological analytes.

\textbf{Environmental Sensing}

One of the most commonly studied analytes in the field of environmental electroanalysis is hydrogen peroxide, as it is of interest in the paper, textile and food
industries\textsuperscript{[212]} and also as it can be used to indirectly sense glucose. The detection of hydrogen peroxide occurs via either an enzymatic route, where the electrode surface is modified with an enzyme which acts as a recognition element, or by a non-enzymatic route, where the hydrogen peroxide is detected by its interaction with the electrode surface. The enzymatic sensing of hydrogen peroxide is often achieved by drop casting horseradish peroxidase (HRP) on an electrode, with sensing of the analyte achieved through the electrochemical detection of the reaction products formed through the enzymatic reaction. The drop casting of the enzyme is often performed in the presence of a support material such as chitosan, adding to the stability of the sensing platform. The electrodeposition of metals, often on a modified electrode surface, is often carried out prior to the addition of the enzymatic layer. For example the electrodeposition of polyaniline nanofibres followed by the electrodeposition of platinum nanoparticles was reported by Chen \textit{et al.}, after which suspensions of gold nanoparticles, chitosan and HRP were drop-cast on the surface, creating a composite surface for the electroanalysis of hydrogen peroxide.\textsuperscript{[213]} Similar work has been reported in the case of gold on drop cast chitosan,\textsuperscript{[214]} as well as gold/platinum on a MWNT/polyaniline nanotube surface,\textsuperscript{[215]} where HRP was then introduced after the electrodeposition steps. In these cases the limits of detection for hydrogen peroxide were reported as 0.1 µM and 2.8 µM, respectively. These values are in keeping with other HRP-based systems,\textsuperscript{[216-217]} and one of the key advantages of this enzyme-based electroanalysis is that the selectivity of the sensor is largely controlled by the inherent selectivity of the enzyme.

While enzyme-modified electrodes may be used to detect hydrogen peroxide, they possess several limitations such as the expense of enzyme purification, the limited adherence of the enzyme to the surface and also that care must be taken to store and operate the system in appropriate solvents with the correct pH and temperature ranges.\textsuperscript{[44, 218]} This has lead to research on the non-enzymatic detection of hydrogen peroxide at nanostructured surfaces. A further benefit of this strategy is that lower detection limits have been reported in certain cases\textsuperscript{[95, 219-222]} which may be related to an increased number of binding sites for hydrogen peroxide, especially as the chitosan matrix is not present in this instance.
Amongst the non-enzymatic hydrogen peroxide sensors, much attention has been focused on the use of hexacyanoferrate (HCF) materials including nickel,[56, 223] copper,[224] copper-palladium,[225] copper-cobalt[226] and ruthenium oxide HCFs.[227-228] Amongst these materials, an iron-based HCF (Prussian blue) has been utilised to detect hydrogen peroxide to a limit of detection (LOD) of 1 nM,[95, 219] demonstrating the improved LODs which can be found at the non-enzymatic sensors. Prussian blue is also referred to as an artificial peroxidase due to its high activity for sensing hydrogen peroxide.[76] However, Prussian blue has several limitations, as its stability is reduced in highly alkaline solutions[229] or in the presence of cations including Na⁺, H⁺, Ca²⁺ and Mg²⁺, as these species may slow the mass transport of hydrogen peroxide into the PB lattice.[227]

The electroanalysis of hydrogen peroxide may also be achieved at electrodeposited copper or copper oxide surfaces. The latter material was formed by Lin et al. by electrodepositing copper on a glassy carbon electrode, which was then electrochemically oxidised to copper oxide.[222] Separately Selvaraju et al. detected hydrogen peroxide at electrochemically deposited copper surfaces, although X-ray photoelectron spectroscopy revealed the existence of native copper oxides.[221] Both of these methods were capable of detecting hydrogen peroxide at low concentrations, with LODs of 25 nM and 10 nM, respectively. The electroanalysis of hydrogen peroxide has also been investigated by Compton’s group, with hydrothermally synthesised copper oxide nanorods[230] and silver nanoparticles electrodeposited on glassy carbon[212] used to detect hydrogen peroxide to 0.22 µM under alkaline conditions and to 2 µM in phosphate buffer, respectively.

Another important class of analytes in the electroanalysis of environmental samples is the detection of metal species, with lead,[118, 231-232] cadmium,[231-232] mercury,[233] arsenic[234-235] and chromium[27, 235-236] as common targets due to their high toxicity and potential for environmental damage. Of the electroanalytical methods used to sense these metal species, the anodic stripping voltammetry (ASV) at bismuth-modified electrodes presents one of the most common approaches. This is shown schematically in Figure 1.11,[237] where metallic species such as Pb²⁺ can accumulate at the electrode surface before being electrochemically deposited. After
this deposition is performed at a fixed potential for a given time the concentration of
the metallic species is then determined by ASV, where the species are quantitatively
removed from the surface by oxidative stripping. This technique also allows the
simultaneous detection of multiple elements, as the oxidation peaks for these
individual elements may be resolved (as shown in Figure 1.11).

![Figure 1.11: Schematic and anodic stripping voltammogram for heavy metal detection at bunch-like bismuth nanostructures (Reprinted with permission from Ref. 237).](image)

Bismuth provides an appropriate electrode for the anodic stripping voltammetry
of heavy metals as it may form fused alloys with heavy metals, in a similar manner
to mercury.[238] Bismuth however does not share the same sensitivity towards
dissolved oxygen as mercury electrodes,[239] making it more practical for routine
analysis. The electrodeposition of bismuth for these electroanalytical procedures
may be performed by *ex situ* electrodeposition,[240-241] where the electrodes are
modified prior to addition to the sample solution, or by *in situ* electrodeposition,[231,
242-243] where the sample solution is doped with a bismuth salt and the
preconcentration step involves the electrodeposition of both bismuth and the target
metal species. It should be noted that the structure of the electrodeposited materials
is not often the focus in such work, which is instead directed to the sensing performance and stability of the materials.

A range of other metallic surfaces have also been reported for the electroanalysis of heavy metals, with gold films detecting Pb$^{2+}$ to concentrations of 0.8 ng mL$^{-1}$,[20] while electrodeposited silver surfaces were used to sense Cr$^{6+}$ to 0.65 ppb.[27] The electrodeposition of gold on organic nanofibres modified with Pt$^{2+}$ has also been reported,[233] with a LOD of 8 ppt towards Hg$^{2+}$. Another novel approach to heavy metal sensing was reported by Choudhry et al.,[244] where palladium, platinum and gold were electrodeposited on screen printed electrodes, which were then sprayed with a commercially available deodorant to form a polymeric matrix. The pores formed in this matrix altered the electrochemical behaviour to resemble that of microelectrodes, and for the electrodeposited gold sample a LOD of 0.48 µM was found for As$^{3+}$. Metal oxide electrodes have also been employed for the detection of heavy metals, with cobalt oxide able to detect As$^{3+}$ to 11 nM,[234] and iridium oxide able to sense Pb$^{2+}$ and Cd$^{2+}$ to 0.7 nM and 8 nM, respectively, in the presence of Cu$^{2+}$.[231]

The electroanalytical detection of insecticides and pesticides is another area of application for electrodeposited metal surfaces. These chemicals are often in the form of organophosphates, and the electroanalysis of methyl parathion is used as a model case. Zirconia nanoparticles have been presented as an option for this purpose, as the adsorption of phosphoric groups on zirconia is well known. The zirconia nanoparticles have been electrodeposited on screen printed electrodes[245] as well as SAM-modified electrodes,[77] with the latter surface allowing the formation of smaller, more uniform nanoparticles with increased stability compared with the unmodified surface. Organophosphates have also been detected at Cu decorated MWNTs[51] as well as at an electrode drop cast with a suspension of chitosan, acetylcholine and free gold nanorods.[246] These gold nanorods were synthesised electrochemically through AAO templating and then released from the surface by dissolution of the template and the underlying electrode film, as illustrated in Figure 1.6.
Nitrites represent another important class of environmental analytes in the wastewater management and agricultural sectors, as they are known to convert to carcinogenic nitrosamines in the presence of amines.\cite{53, 75, 247} Again a variety of approaches have been employed, however the electrodeposition of copper has received much attention. This electrodeposition has been carried out on a drop cast suspension of Nafion and MWNTs,\cite{248} DNA-SWNT hybrids\cite{247} and on a SAM covered gold electrode,\cite{75} where this latter example was shown to detect nitrite to a LOD of 0.1 nM. Iron nanocrystals electrodeposited on glassy carbon electrodes (as shown in Figure 1.2) have also been reported for nitrite detection.\cite{32} This study highlights the link between the electrocatalytic activity of the material with the structure of the electrodeposit, showing that a thorough understanding of the structure of the electrode can result in the formation of more effective materials for electroanalysis.

**Biological Sensing**

The detection of biological species is another significant field of electroanalysis, however as this represents a broad area of research this discussion is limited to the more important examples. One of the most widely studied areas of biological electroanalysis is the detection of glucose, especially in light of the need for portable and reliable glucose sensors for diabetes management. Similarly to the previous section on hydrogen peroxide detection, the electroanalysis of glucose can be achieved by both enzymatic and non-enzymatic methods. The enzymatic detection of glucose is performed by the modification of an electrode with an enzyme such as glucose dehydrogenase, although glucose oxidase (GOx) is more commonly reported. Electroanalytical sensing of glucose involving GOx is based on the enzymatic oxidation of glucose to gluconolactone and hydrogen peroxide, with the detection of the latter species used to determine glucose concentrations.\cite{249} The electroanalysis of by-products formed through enzymatic reactions is illustrated in Figure 1.12, where the electroanalysis of gluteraldehyde was performed by monitoring the hydrogen peroxide generated at the surface bound glutamate oxidase.\cite{250} In this instance a modified surface was employed, formed by electrodepositing platinum nanospheres or palladium nanocubes on a SWNT
surface, with improved electroanalysis observed at the platinum nanosphere modified surface.

A range of electrodeposited nanostructured surfaces have recently been used for the enzyme mediated electroanalysis of glucose, including gold,[81, 251-252] platinum[50, 253-254] and PB,[55, 61, 70, 229, 255] as well as composites of these materials including PB/Au[101, 256] and Au/Pt.[64] These materials have been investigated due to their electrocatalytic activity towards hydrogen peroxide, although it should be noted that the stability of the enzymes and electrodes must be considered prior to the electroanalysis. For example the pH of the solution can impact the choice of materials, as GOx activity decreases in acidic conditions and PB becomes less stable under alkaline conditions. The electroanalysis of glucose at such enzyme-modified electrodes has been reported at sub-millimolar concentrations,[229, 254, 257] which is below the analytically relevant range of 3-8 mM.[21]

**Figure 1.12:** Schematic of a glutamate sensor at an enzyme modified decorated nanotube surface (Reprinted with permission from Ref. 250).
The electroanalysis of glucose at non-enzymatic electrodes is also attracting a significant research effort. Amongst these reports copper based electrodes have been found to be effective materials, especially under alkaline conditions. In these cases LODs are commonly in the sub-micromolar range\cite{42,119,258-259} and even as low as 50 nM\cite{249} illustrating the high degree of sensitivity which can be achieved at copper electrodes. Porous copper films have also been reported for this application\cite{260} while copper oxide is also known to be active towards glucose electroanalysis\cite{42}.

The electrodeposition of nickel may also be used to create effective glucose sensors, with detection limits reported in the sub-micromolar range. A variety of approaches have been employed for this purpose, such as the electrodeposition of Ni(II)-curcumin\cite{261}, NiHCF\cite{223} and nickel hydroxide nanoparticles\cite{262}. This research on a variety of different nickel based surfaces may be related to the ready oxidation of nickel surfaces, as this has been found to be detrimental to the oxidation of glucose\cite{111} and ethanol\cite{110,263} at mesoporous nickel electrodes after exposure to air. To solve this issue the electrodeposition of alloys such as CuNi has been reported\cite{263}, which also showed synergistic effects towards glucose oxidation\cite{258} as well as the electrodeposition of a thin layer of gold on a mesoporous nickel surface, limiting the oxidation of the nickel\cite{111}.

It should be noted that while both copper and nickel electrodes have demonstrated promising glucose electroanalysis under alkaline conditions\cite{102} their application under physiological pH conditions has not been widely reported. Several sampling strategies have been employed to overcome this issue, such as the dilution of a sample with NaOH prior to sensing\cite{47} although this places additional sample preparation requirements and can lead to poorer LODs. An alternative to these materials is gold, which has been used to sense glucose under alkaline conditions after electrodeposition on TiO$_2$ nanotubes\cite{66} or mesoporous nickel surfaces,\cite{111} as well as by co-deposition with MnO$_2$\cite{264}. Rassaei and Marken applied an interesting approach to the electroanalysis of glucose, electrodepositing gold on neighbouring electrodes until the distance between the gold electrodeposits was approximately 500 nm\cite{265}. Glucose electroanalysis was then performed under quasi-alkaline...
conditions at one electrode by electrochemically generating OH⁻ at the other electrode, resulting in an increased sensitivity towards glucose electroanalysis.

Glucose electroanalysis may also be performed at or near physiological pH, especially at noble metal electrodes such as gold, platinum decorated nanoporous gold, platinum decorated SWNTs and porous palladium nanotubes. Although such metals possess several limitations for glucose sensing, for example the poisoning of platinum by carbonaceous species or the low selectivity of glucose oxidation at gold electrodes in the presence interfering species such as ascorbic acid, uric acid or dopamine, these limitations may be reduced at nanostructured electrodes. This can occur as platinum nanostructures may not be as susceptible to poisoning as a bulk platinum surface and large shifts in the onset potential of electrocatalytic reactions at nanostructured gold can increase the selective oxidation of species such as glucose.

The detection of neurotransmitters represents another important field within electroanalysis. One of the major analytes studied is dopamine, where the presence of uric acid and ascorbic acid can provide false readings of dopamine due to their similar oxidation potentials. As discussed in the case of glucose electroanalysis, a range of nanostructured materials have been studied to avoid this interference in the case of dopamine sensing. This has been achieved by the electrodeposition of palladium nanoparticles on polymer-modified electrodes by Atta et al, who reported LODs of below 50 nM for dopamine detection. Other work has been reported by Shaidarova et al, including the electrodeposition of gold nanoparticles on a cystamine modified electrode, as well as the addition of a Nafion layer on an electrodeposited iridium oxide surface. This addition of Nafion was performed in order to screen potentially interfering species through electrostatic repulsion, caused by the sulfonate groups present within the Nafion structure. Nitric oxide is another neurotransmitter studied by electroanalysis, although it is also involved in a range of other biological functions such as regulating blood pressure, controlling platelet activity and also various immune responses. Marken’s group have extended their work on junction electrodes (as described previously for glucose electroanalysis) to the detection of nitric oxide. In this work nitric oxide was oxidised at one of the gold electrodes with the by-product being reduced at the
opposite gold electrode, providing information about the nitrosonium phosphate intermediate species as well as a LOD of 10 µM for nitric oxide. Nitric oxide detection has also been reported at nickel oxide electrodeposited on MWNT/chitosan surfaces,[275] as well as a AuHCF material,[272] where LODs as low as 10 nM for solution based sensing or 1 nM for gaseous sensing were achieved.

Another important electroanalytical application of nanostructured materials is the detection of therapeutic drugs, especially as knowledge of how these drugs metabolise in the body can lead to modified drug delivery strategies and ensure the correct dosages of medication. The electroanalysis of a range of drugs has been reported, covering analgesics such as morphine[18], aspirin,[276] antibacterial agents[277] and non-steroidal anti-inflammatory drugs.[278-279] This has been performed at number of different nanostructured electrodes, including platinum,[31] gold[18, 277] and cobalt hydroxide nanomaterials,[276] electrodeposited Ni(II)-curcumin[278] and palladium nanoparticle decoration on polymer films.[269]

1.3.3. Surface Enhanced Raman Spectroscopy

A further area of application for nanostructured metallic surfaces is as surface enhanced Raman spectroscopy (SERS) substrates. Raman spectroscopy is based on the inelastic scattering of light after interaction with an analyte, resulting in a difference in the frequencies of the incident and scattered light, which provides information on the vibrational structure of the analyte. While Raman spectroscopy may be used for the identification of analytes, a major limitation is that the relatively infrequent Raman interactions can provide a low signal to noise ratio, especially for an analyte present in low concentration. In order to overcome this limitation, the analyte may be adsorbed on a nanostructured metal, where the Raman signal can be greatly enhanced through the increased local electromagnetic field as well as by charge transfer between the analyte and the surface. This is schematically represented in Figure 1.13, where the adsorption of pyridine at a nanostructured silver surface can be monitored by the change in frequency of the light. The use of such SERS substrates offers a number of advantages for analytical purposes, as is it is non-invasive, can be extremely sensitive (with reports of sensing single molecules) and requires minimal sample preparation. As such SERS substrates have
been employed across a wide range of applications, such as the detection of narcotics, chemical warfare agents, trace chemicals and explosives, as well as being used to monitor industrial chemical processes.[280-284] SERS has also been extensively studied for biosensing applications, with analytes covering amino acids, peptides, proteins, deoxyribonucleic acid (DNA), ribonucleic acid (RNA), neurotransmitters, antigens and fungicides.[281-282, 285] The in vivo detection and targeting of tumours has also been explored in mice, demonstrating the wide range of practical applications for SERS.[286]

![Figure 1.13: Schematic showing the SERS effect for pyridine on a silver surface (Reprinted with permission from Ref. 287).](image)

While there are a wide variety of approaches for the synthesis of SERS substrates, including the chemical synthesis of nanoparticles or the roughening of surfaces through electrochemical redox cycling methods, the electrodeposition of metallic nanostructures has also been widely reported.[288] Amongst the electrodeposition methods the use of physical templates has been favoured, with nanosphere lithography receiving much attention. This electrodeposition in the voids present between colloidal particles includes the use of polystyrene,[289-293] latex[294-295] and even nickel phosphate[296] templates, with much of the work in this area reported by Bartlett’s group. In the case of polystyrene spheres the surface is often first modified with a layer of cysteamine as this leads to a more regular arrangement of spheres.[291] Electrodeposition in AAO templates has also been reported, with the electrodeposition of fine nanowires showing activity for SERS applications.[297-303]
Other strategies for the electrodeposition of SERS substrates include the electrodeposition on surfaces modified by carbon nanotubes,[43,304] TiO₂ nanotubes,[305] graphitic petals[306] or a layer of polydopamine.[307] An inventive approach to this method was employed by Giallongo et al., who used the silver coated polycarbonate tracks present on a digital versatile disc (DVD) as a substrate for silver electrodeposition.[308] The electrodeposition on unmodified electrodes[309-316] or in the presence of chemical templating species such as citric acid,[317-318] citrate,[319] PVP,[320] citrate/PVP[321] and gelatin[322] has also been used to create SERS active substrates. Clearly a broad range of electrodeposition methods have been investigated for this purpose, showing the importance of this technique for SERS based analytical applications.

1.4. Active Site Behaviour of Metallic Surfaces

1.4.1. Active Sites and Premonolayer Oxidation of Metallic Surfaces

As discussed previously, nanostructured metallic surfaces may find applications across a wide range of areas. While nanostructuring often leads to an increased surface area compared with a planar surface, the increased activity of the modified surfaces may also be influenced by a number of different factors such as the size, shape and crystallographic orientation of the nanostructured surface or the nature of the support material.[10,161,323] Another factor which is becoming more recognised is the presence of defects on the surfaces. This concept was first introduced in the field of heterogeneous catalysis by Taylor, who attributed the enhanced catalytic activity to the incomplete crystallisation of a metallic surface.[324-325]

The concept of surface defect sites showing altered behaviour was later extended to the field of electrochemistry by Burke and co-workers. The authors postulated the presence of two types of surfaces (Figure 1.14), known as equilibrated metal surfaces (EMS) and metastable metal surfaces (MMS). In the first case the surface consists of a well-ordered and regular arrangement of atoms, minimising the
surface energy of the system. In the second case the surface differs from this regular arrangement of atoms, with low lattice coordinated atoms or clusters of atoms on the surface. These surface defects, known as active sites, were found to significantly alter the electrochemical behaviour of a material, with oxidation of the surface beginning at potentials much lower than the oxidation potential of the monolayer oxide at the bulk metal. For this reason the oxidation of active sites was termed ‘premonolayer oxidation’.

![Equilibrated Metal Surface (EMS) and Metastable Metal Surface (MMS)](image)

**Figure 1.14:** Schematic showing an equilibrated metal surface (EMS) and a metastable metal surface (MMS).

While it has been postulated that defects are present on all surfaces,[326] the electrochemical study of these sites has proved difficult due to the relatively low coverage of active sites, which has been estimated to be as low as 1% of surface atoms.[327] A number of surface treatments have been utilised to disrupt the ordered nature of the surfaces, including thermal treatments, electrochemical activation or even mild abrasion with emery paper.[328] The thermal treatment involves heating the electrode, either by exposure to a flame[329-331] or by resistive heating through the application of a large current.[332-334] This heating allows the surface atoms to rearrange, and depending on how the surface is cooled back to room temperature the less thermodynamically favoured surface defects can be retained in the final structure.[335] Electrochemical activation was also investigated, and it was found
that the application of a cathodic potential in an acidic solution could promote the magnitude and extent of premonolayer oxidation.[329,331,333,336] This activation was related to the evolution of hydrogen at the electrode surface resulting in an embrittlement process, where the insertion of hydrogen into the metallic lattice can dislodge atoms within the top few layers of the surface.[335] Electrochemical activation can also be performed by the growth and subsequent stripping of a thick oxide, perturbing the ordered nature of the metallic lattice.[337] These activation processes were found to promote the number of active sites for a given surface to the extent that the premonolayer oxidation behaviour of the materials could be studied by cyclic voltammetry.

Gold provides an attractive material for the study of premonolayer oxidation, as the electrochemical behaviour of gold in its bulk form has been well studied, with relatively few redox processes occurring across its potential window. This is demonstrated by the voltammogram of a gold wire electrode in 1 M H₂SO₄ (Figure 1.15a),[338] where the double layer region extends from the initial potential of 0 V (vs RHE) until approximately 1.36 V (vs RHE), during which the capacitive charging of the surface produces a small current response. The peak observed at 1.36 V (vs RHE) is assigned to the formation of a bulk Au₂O₃ oxide on the surface, forming a monolayer oxide.[339] Several features can be seen in this region, relating to the oxidation of different exposed crystal facets on the gold surface[340] as well as the formation of a hydrous or anhydrous Au₂O₃ oxide.[339] On the reverse scan a reduction peak is observed with a peak potential just below 1.2 V (vs RHE), relating to the reduction of the monolayer oxide formed in the forward sweep. Once this oxide is reduced no further redox peaks can be detected until the end of the sweep, with the reduction of hydrogen occurring at slightly lower potentials. However after cathodic polarisation (Figure 1.15b) significantly altered electrochemical behaviour can be seen, with intense redox processes visible well within the double layer region. These processes, centred at ca. 0.4 V and 0.5 V (vs RHE) are attributed to the oxidation of active sites formed on the gold surface during the cathodic polarisation treatment. This response is diminished on the second cycle (Figure 1.15b, dashed line), although this may be related to surface restructuring occurring during the formation and stripping of the monolayer oxide. The clear presence of redox
features within the double layer region of gold provides evidence that this region is not void of Faradaic redox processes, as had been assumed.

![Cyclic voltammograms](image)

**Figure 1.15:** Cyclic voltammograms for a gold wire electrode in 1 M H$_2$SO$_4$ recorded at 50 mV s$^{-1}$ before (a) and after cathodic polarisation at -0.6 V for 20 min (b), with the second cycle in (b) shown by the dashed line (Reprinted with permission from Ref. 338).

Studies have also been performed on the pH dependence of premonolayer redox processes. While the reduction of a monolayer oxide peak typically shifts by (2.3 RT/F) V/pH unit, altered behaviour was observed for the reduction of oxides formed under premonolayer oxidation conditions. Larger shifts were observed in the case of gold, with shifts of -88.5 mV per pH unit observed (1.5 times larger than the expected shift). These super-Nernstian shifts were attributed to the behaviour of a metallic hydrous oxide under conditions of varying pH. Since the super-Nernstian shifts indicated a ratio of hydrogen or hydroxide ions to electrons transferred of 3:2, and as Au$^{3+}$ is the most stable configuration of ionic gold, the oxidation product of the active sites was postulated to be in the form of the complex
\[\text{[Au}_2\text{(OH)}_3]\text{^3\text{–}},\text{ possibly in the form of a polymeric or aggregated structure. After examining the reduction of this species by the Nernst equation, it was found that this species was consistent with the super-Nernstian shifts observed experimentally, adding further support of the nature of the oxidised product of the active sites. Similar studies have also been performed in the case of platinum, with the premonolayer oxidation product attributed to the formation of Pt(OH)\text{^6\text{–}}.}\text{[342-343]}

In addition to the studies on gold\text{[329-334, 336, 339, 344-351]} and platinum,\text{[342, 352-358]} Burke and co-workers also investigated the formation of hydrous oxides on silver,\text{[359-361]} palladium,\text{[362-367]} copper,\text{[368-373]} cobalt,\text{[374]} and nickel.\text{[375-376]} These hydrous oxides formed prior to the onset of the monolayer oxide and displayed similar super-Nernstian shifts to gold and platinum, again suggesting the involvement of high energy surface states on the materials.

While the concept of premonolayer oxidation has attracted controversy in the literature, with the assignment of these processes as either impurities in the electrolyte or as the chemisorption of anionic species from the electrolyte,\text{[342, 362]} these concerns were addressed by observing premonolayer oxidation in a variety of solvents which adsorb to different degrees on an electrode surface.\text{[377]} The oxidation of metallic nanostructures at unexpectedly low potentials is also receiving a number of reports in the literature,\text{[378-380]} as illustrated by the oxidation of gold nanoparticles in a halide solution shifting by 850 mV to lower potentials.\text{[381]} In addition a growing number of researchers have also reported the premonolayer oxidation of metallic electrodes, including silver,\text{[382-383]} gold,\text{[384-389]} copper,\text{[390-393]} nickel,\text{[394]} palladium,\text{[395-399]} and platinum surfaces.\text{[377, 400-403]} Amongst these studies a variety of non-electrochemical methods have been used to observe premonolayer oxidation, for example Savinova et al. employed \text{ex situ XPS} to study the premonolayer oxidation on a silver electrode.\text{[382]} The authors observed evidence of this oxidation at potentials approximately 1 V below the reversible potential of Ag\text{\textsubscript{2}}O formation. \text{Ex situ XPS} has also been used by Tian et al. in the case of nickel electrodes, where the formation of a hydrated oxide was observed as a result of premonolayer oxidation.\text{[394]} Other examples of the study of premonolayer oxidation include Petrović et al.,\text{[384]} who observed premonolayer oxidation on gold surfaces by the combination of an electrochemical quartz crystal microbalance (EQCM) and
cyclic voltammetry, and Desilvestro et al.\textsuperscript{[404]} and more recently Zhumaev et al.\textsuperscript{[405]} have observed premonolayer oxidation of gold by vibrational spectroscopic methods. The premonolayer oxidation of copper has been examined by Marcus’ group, where scanning tunnelling microscopy (STM) was used to observe the premonolayer oxidation of Cu(111) surfaces.\textsuperscript{[406-407]} This work was later re-examined by thermodynamic calculations, and the stability of hydroxyl species was found to exceed either Cu$_2$O or H$_2$O$_{ads}$ at premonolayer oxidation potentials.\textsuperscript{[390]} Premonolayer oxidation on gold and platinum electrodes has also been reported recently by Bard and co-workers, where scanning electrochemical microscopy (SECM) was used to generate a redox mediator at the metallic surface.\textsuperscript{[408]} The presence of incipient oxide species was observed by a redox mediator process, with electrochemical reduction of Ru(III) hexamine to Ru(II) hexamine at the SECM tip. These Ru(II) species then diffused to an adjacent gold or platinum electrode, where their chemical oxidation to Ru(III) hexamine was coupled to the reduction of incipient oxides formed electrochemically at the metallic electrode. A feedback loop could then be attained, with the electrochemical generation of fresh Ru(II) hexamine and metallic hydrous oxide species, allowing the detection of these latter species.

Alongside this work on premonolayer oxidation there have been a number of interesting studies on the presence of active sites on metallic surfaces. Scholz and co-workers investigated the structure and electrochemical behaviour of metallic surfaces after exposure to Fenton’s reagent.\textsuperscript{[409-410]} This reaction is known to produce hydroxyl radicals, and it was found that these species could selectively remove asperities, or active sites, from the surface. This ability to ‘knock out’ the active sites provided a means of examining the electrochemical properties of the active sites. In the case of gold this treatment lead to a decrease in the electrocatalytic activity towards the reduction of oxygen, as observed by a cathodic shift in the peak reduction potential.\textsuperscript{[411]} The surface was also examined with both an outer sphere electrochemical reaction (Ru$^{III}$/Ru$^{II}$) and inner sphere reactions (quinone/hydroquinone and the hydrogen evolution reaction). It was found that the outer sphere reaction chosen was insensitive to the presence of active sites, whereas significant decreases on the rate of inner sphere reactions were observed with the removal of active sites. A number of other metallic surfaces were also
studied, including silver, palladium and platinum,[412] and while silver demonstrated similar behaviour to gold this was not the case for palladium or platinum. The electrocatalytic activity of these materials towards the quinone/hydroquinone reaction was instead attributed to reaction at the regular surface atoms.

The study of premonolayer oxidation at metallic surfaces has also been reported using Fourier transformed ac (FT-ac) voltammetry. This technique provides a more sophisticated approach to the investigation of premonolayer oxidation processes than dc cyclic voltammetry, as it allows the separation of the Faradaic processes from the capacitive background typically observed by cyclic voltammetry. The discrimination between these processes provides a powerful tool for the study of premonolayer oxidation processes, as these processes may be masked by the capacitive current in cyclic voltammetry owing to their low surface coverage. FT-ac voltammetry has been employed to examine the active site behaviour of polycrystalline gold electrodes, which revealed significant premonolayer oxidation occurring well within the double layer region.[328] The cathodic polarisation of the gold electrodes was also studied, with this activation process promoting the extent of premonolayer oxidation. FT-ac voltammetry has also been applied to copper under alkaline conditions, where clear Faradaic processes were again observed within the double layer region.[327]

1.4.2. The Importance of Premonolayer Oxidation in Electrocatalysis

The study of premonolayer oxidation represents an important area of research in electrochemistry as it was found to have practical relevance in electrocatalytic reactions. This was discovered by Burke and co-workers, who found that the onset potentials of a range of electrocatalytic processes coincided with potentials at which premonolayer oxidation of the surface was observed in the absence of the reactant.[343, 413] In light of this data the authors proposed the incipient hydrous oxide adatom mediator (IHOAM) model of electrocatalysis. Shown schematically in Figure 1.16, an active site on a metallic electrode (M*) can undergo premonolayer oxidation to a hydrous oxide species (M[OH]_{ads}). In the case of an electrocatalytic oxidation reaction, this hydrous oxide species can mediate the electron transfer
process as its chemical reduction back to the metallic active site provides the electrons for the oxidation of the reactant species. However as the applied potential for this reaction is at or above the premonolayer oxidation potential the active sites are again electrochemically oxidised and the electrocatalytic process continues. Similarly, electrocatalytic reduction processes may also be promoted by the presence of active sites. In this case the electrocatalytic process is reversed, with the chemical oxidation of the active site coupled to the reduction of the reactant species. The hydrous oxide species is then electrochemically reduced to the metallic active site, allowing the electrocatalytic reduction to continue.

**Figure 1.16:** Schematic showing the participation of premonolayer oxidation in the IHOAM model of electrocatalysis (Reprinted with permission from Ref. 414).

The electrocatalytic reaction of a wide range of reactants has been studied at surfaces such as gold,[114, 329, 331, 333-334, 344-345, 349] silver,[359-360] platinum,[353, 415] palladium[362, 366-367] and copper,[368-373, 416] showing the importance of the IHOAM model of electrocatalysis for commonly employed electrocatalytic materials. In the case of gold a thorough comparison between premonolayer oxidation processes and the onset potentials of electrocatalytic oxidation or reduction reactions was presented by Burke and Nugent.[344] The authors observed the apparent involvement of IHOAM processes in the oxidation or reduction of aldehydes, carbohydrates, organic acids, hydrocarbons, nitrogen-containing molecules (including amino acids) and inorganic species. This demonstrates the importance of the IHOAM model of electrocatalysis at gold surfaces across a range of important
electrocatalytic process, which may be applied to areas such as biosensing and electrosynthesis. The involvement of the IHOAM model of electrocatalysis was also demonstrated for a variety of alcohols (including methanol and ethanol) as well as dissolved gases (including H₂, O₂ and CO), which as discussed in Section 1.3.1. are all important electrocatalytic processes in fuel cells.

The correlation between premonolayer oxidation and electrocatalytic processes is further demonstrated in Figure 1.17 for a gold electrode activated by cathodic polarisation. Here a number of premonolayer oxidation processes can be observed from the CV in 1 M H₂SO₄ (Figure 1.17a), and upon the addition of H₂O₂ (b,d) or N₂H₄ (c) the onset of the electrocatalytic reactions can be found at potentials close to the premonolayer oxidation processes (indicated by the dashed lines). It should be noted that these coupled reactions appear to take place in distinct potential ranges. This may be related to the oxidation of active sites with differing levels of activity,[114,328] with the electrocatalytic process occurring in a potential range where both the adsorption of the reactant and the formation or reduction of the premonolayer oxide occur.
1.5. Research Aims

The broad aims of this work are to investigate the active site behaviour of electrodeposited gold and platinum nanomaterials, as well as planar evaporated films. This will be achieved by investigating the electrodeposition of gold and platinum in the presence of lead acetate, as well as by testing if gold can be electrodeposited through the dynamic hydrogen bubble templating technique.

After synthesising these gold and platinum nanomaterials their electrochemical behaviour will be tested in aqueous solutions with a range of pH values, especially in relation to any premonolayer oxidation which occurs. This will involve the use of
both dc cyclic voltammetry as well as FT-ac voltammetry, which may be useful in extracting the Faradaic premonolayer oxidation components from the capacitive current contribution in cyclic voltammetry.

Possible applications of these nanomaterials will then be explored including their electrocatalytic activity towards a number of technologically important reactions as well as testing their activity as SERS substrates. For the electrocatalytic reactions focus will be placed on whether the electrocatalytic activity is related to the presence of premonolayer oxidation processes, indicating an IHOAM type electrocatalytic mechanism.

A further possible area of research at the electrodeposited nanomaterials is the spontaneous decoration of the surfaces with a secondary metal from a solution of an appropriate metallic salt. This formation of bimetallic nanomaterials is an important research topic, and the possibility of driving a spontaneous decoration process based on the active site behaviour of the synthesised nanomaterials will be explored.

1.6. Thesis Outline

The experimental methods employed in this work are outlined in Chapter II. This is separated into both the electrochemical methods used to synthesise and characterise the gold and platinum nanomaterials, as well as the methods used to physically characterise the materials, including techniques such as electron microscopy, X-ray diffraction and X-ray photoelectron spectroscopy.

The electrodeposition of gold was investigated in the presence of lead acetate, which was found to act as a shape-directing agent and resulted in the formation of gold nanospikes (Chapter III). The electrochemical behaviour of the gold nanostructures was then tested by cyclic voltammetry and FT-ac voltammetry, showing substantial premonolayer oxidation processes. The gold nanospikes were also investigated towards a range of electrocatalytic reactions including the oxidation of glucose and the evolution of hydrogen, where improved electrocatalytic responses were attributed to the formation of a premonolayer oxide on the gold nanospikes and the presence of the surface defects, respectively. Additionally, the
use of these surfaces for the electroanalysis of dopamine in the presence of interfering species was studied, as was the application of the gold nanospikes as SERS substrates.

Having observed the ability of lead acetate to promote the formation of active sites in the case of gold electrodeposition, the ability of this shape-directing agent to control the electrodeposition of platinum was then investigated (Chapter IV). While quasi-spherical particles were found in the absence of lead acetate, electrodeposition in the presence of lead acetate was found to create highly branched platinum-lead nanostructures. Unlike in the case of gold, the electrodeposition of lead on platinum was found to be the cause of this altered morphology. The electrochemical behaviour of both the platinum and platinum-lead nanostructures were investigated by cyclic voltammetry and FT-ac voltammetry, which revealed the presence of premonolayer oxidation behaviour. Significantly a correlation was observed between a particular premonolayer oxidation peak and the electrocatalytic activity of the materials towards the oxidation of methanol. The platinum-lead surface was also tested as a SERS substrate, with the fine tips and overlapping structures creating a SERS active material.

While the templated electrodeposition of gold using hydrogen bubbles generated in situ was reported to be unachievable,[418] we demonstrate for the first time the fabrication of highly porous materials in this manner (Chapter V). In addition the vigorous electrodeposition conditions resulted in the formation of a surface displaying significant premonolayer oxidation activity. These high surface area materials were then tested towards a number of electrocatalytic processes as well as SERS applications.

Although the spontaneous reduction of metal salts to their metallic state on noble metal surfaces has attracted a few reports in the literature, the underlying mechanism of this process remains largely unexplored. In this work (Chapter VI) the presence of active sites was found to be responsible for the spontaneous reduction process, as the facile oxidation of active sites provided an appropriate driving force for the reaction. Spontaneous decoration was studied in detail for the
honeycomb gold surfaces and evaporated gold films, and the study was extended to the gold nanospikes and the platinum/platinum-lead nanostructures.

Lastly, a summary of the findings of this work are presented in Chapter VII. Also covered in this chapter are areas for future study in the fields of electrodeposition, active site behaviour and spontaneous decoration.

1.7. References


Chapter II

Experimental Section
2.1. Electrochemical Fabrication and Characterisation Techniques

2.1.1. Electrochemical Instrumentation and Experimental Arrangement

The electrochemical experiments performed in this work share a number of common features and are therefore described here. A glass vial was filled with approximately 5 mL of the electrolyte solution, and unless otherwise stated these solutions were purged for between 5-10 mins with nitrogen prior to performing experiments in order to remove dissolved gases such as oxygen from the solution. This is a necessary procedure as the presence of oxygen can be problematic in electrochemical experiments,\textsuperscript{[1]} for example where the reduction of dissolved oxygen can compete with other electrochemical processes and either interfere with a material deposition or alter the electrochemical signature from a process and complicate the analysis of the data obtained from an experiment.

Electrochemical experiments were all performed by the use of a three-electrode system, consisting of a working electrode, a reference electrode and a counter electrode (Figure 2.1). This setup offers a greater degree of control and repeatability as compared to a two-electrode system as is sometimes used in electrodeposition work, as this latter system requires the careful positioning of the electrodes.\textsuperscript{[2]} A variety of different working electrodes were employed in this work, ranging from evaporated metallic films and commercially available electrodes (as described in Section 2.3.2) to nanostructured surfaces formed through electrodeposition. The reference electrode used is a Ag/AgCl electrode, which consists of a silver wire coated with AgCl contained in a glass vial filled with 3 M NaCl, with a porous Vycor frit at the bottom attached with Teflon heat shrink. By using a standard electrode such as this the overpotential between the working electrode and the reference electrode can be measured, providing a means to standardise the potentials measured. Unless otherwise stated all potentials are quoted against this Ag/AgCl (3 M NaCl) reference electrode. A commercially available graphite rod (6 mm diameter,
Johnson Matthey Ultra ‘F’ purity grade) was chosen as the counter electrode. While metallic wires such as platinum wires are often employed as counter electrodes, graphite was chosen so that when a reductive potential was applied to the working electrode the oxidation at the counter electrode would not involve the dissolution of platinum into the deposition solution. This is significant as the presence of trace quantities of foreign metal salts may interfere with the electrodeposition at the working electrode by templating or being incorporated into the electrodeposit.[3] This selection of counter electrode material is especially important for the honeycomb gold electrodepositions carried out at high current density (Chapter V) where an appreciable level of platinum dissolution may occur.

Figure 2.1: Photograph of a typical three-electrode system employed in this work.

The three electrodes were positioned in solution using either a Teflon cap with defined positions for the electrodes or a glass vial as shown in Figure 2.1. The electrochemical experiments were carried out with a CH Instruments Bipotentiostat (CHI 760c) unless otherwise stated. By controlling the bipotentiostat with a support computer this allowed the electrochemical behaviour of the electrode/solution interfaces to be analysed using the techniques described in the following sections (Sections 2.1.2 to 2.1.6.).
2.1.2. Cyclic and Linear Sweep Voltammetry

One of the most widely employed electrochemical techniques is cyclic voltammetry (CV). This method involves altering the potential applied to the working electrode between initial value and an upper or lower limit, at which the potential is cycled back to the initial potential (Figure 2.2). Depending on the nature of the experiment information can be gained by repeating this process over a number of sweeps, as is often the case for cyclic voltammetry, or otherwise a single sweep from the initial value to the lower or upper limit may provide the required information, as is the case for linear sweep voltammetry (LSV). For either of these techniques the applied potential between the working electrode and the reference electrode is altered in a linear manner with respect to time, and when the current between the working electrode and the counter electrode is measured as a function of the applied potential a voltammogram can be constructed.

![Figure 2.2: Schematic showing a typical potential sweep program used in cyclic voltammetry.](image)

Cyclic voltammetry is commonly used to reveal the nature of a wide variety of oxidation and reduction processes which occur at the working electrode/electrolyte interface, such as those found in electrocatalytic reactions.[4-5] This information can include the onset potential of the reaction, the peak potential and peak current, which may be used to indicate the promotion of a reaction through an electrocatalytic mechanism. The peak shapes obtained by cyclic voltammetry are known to be the result of factors including the reaction kinetics, including the diffusion of the electroactive species to the electrode surface and the rate and type
of electron transfer mechanism involved. For example, the shape of the peak given
by cyclic voltammetry for a reversible electrochemical process at a planar electrode
is described by Nernst’s law (Equation 1) and Fick’s second law of diffusion
(Equation 2). The first of these equations, Nernst’s law, describes the ratio of
oxidised (A) to reduced (B) species at the electrode surface (that is, where the
distance from the electrode surface, x=0) for the reaction of A + ne⁻ ⇌ B:

\[
\frac{[A]_{x=0}}{[B]_{x=0}} = e^{\frac{nF}{RT}(E(t)-E_c^{\circ})}
\]  

(1)

where \( n \) is the number of electrons transferred per mole, \( F \) is the Faraday constant,
\( R \) is the ideal gas constant, \( T \) is the temperature, \( E(t) \) is the applied potential at time \( t \)
and \( E_c^{\circ} \) is the formal reversible potential for the reaction.\(^6\) When the applied
potential is equal to the formal reversible potential of the reaction the right hand
side of the equation simplifies to \( e^0 \), or 1, meaning that the species \( A \) and \( B \) are in
equilibrium at the electrode surface. As this applied potential is shifted to less
positive potential (i.e. the reducing power increases) the exponential is raised to a
negative value, giving a low value for the ratio of \([A]:[B]\), indicating that the reaction
has resulted in the reduction of species \( A \) to species \( B \).

In the absence of species \( A \) being replenished from solution the reaction would
eventually terminate as all the reactant was consumed at the electrode surface.
However this is overcome by the action of diffusion, whereby unreacted species \( A \)
approaches the electrode from the bulk of the solution and product \( B \) moves
towards the bulk solution. This is described by Fick’s second law of diffusion
(Equation 2), which states that the increase in species \( A \) with respect to time
brought about by diffusion is related to the spatial distribution and the diffusion
coefficient (\( D \)) of species \( A \).\(^6\)

\[
\frac{d[A]}{dt} = D \frac{d^2[A]}{dx^2}
\]  

(2)

While the above example describes one of the simplest electrochemical processes
possible, sophisticated electrochemical models are being developed to better
understand more complicated scenarios. One such area is the electrochemical
behaviour of nanostructured electrodes, where effects such as the size, shape and
separation between electrode elements require more careful attention.\textsuperscript{[7-8]} By finding an appropriate model the nature of the electrochemical processes can then be confirmed, highlighting the importance of these voltammetric techniques.

Another source of information that can be gained from voltammetric studies involves altering the timescale of the measurement and seeing how this influences the electrode response. This can be readily achieved by varying the rate at which the potential is scanned, known as the sweep rate. As these sweep rates are typically between 5 mV s\textsuperscript{-1} and 1 V s\textsuperscript{-1},\textsuperscript{[9]} a range of different reaction timescales can be observed. The Randles-Sevcik equation\textsuperscript{[10]} (Equation 3) relates the peak current ($I_p$) observed by voltammetry with the square root of the scan rate ($\sqrt{v}$) for a given bulk concentration of electroactive species ($C_0$) and an electrode with surface area $A$:

$$I_p = 0.4463(nF)^{3/2}(RT)^{-1/2}AD^{1/2}C_0\sqrt{v}$$ \hspace{1cm} (3)

When a number of voltammograms are carried out with differing sweep rates and the results are plotted as $I_p$ versus $\sqrt{v}$ the Randles-Sevcik equation may be used to readily determine experimental unknowns such as the diffusion coefficient of the redox species of interest.

In this work the cyclic and linear sweep voltammetry experiments were performed using a CH Instruments potentiostat (CHI 760C) using the three-electrode set up as described previously. All potentials are quoted against the Ag/AgCl reference electrode unless otherwise stated.

2.1.3. Chronoamperometry

The technique of chronoamperometry involves applying a fixed potential to a working electrode for a defined period of time. This technique is often used in electrocatalytic applications, where the potential is fixed at a value which will maximise the production of the desired species over an extended period of time while maintaining the activity of the surface. Chronoamperometry is also used in the field of electroanalysis, where it can be used to monitor the presence of a known species by recording the current passed as a function of time. The Faradaic
component of this current for a planar electrode at time $t$ is described by the Cottrell equation:[11]

$$i = \frac{nFAD^{1/2}C_0}{\pi^{1/2}t^{1/2}}$$  \hspace{1cm} (4)

Chronoamperometry is also used extensively in the electrochemical formation of a variety of materials. This materials synthesis aspect is generally performed once the electrochemical behaviour of the working electrode/plating solution interface has been determined through the use of other electrochemical techniques such as cyclic voltammetry. These supporting techniques allow the parameters for the chronoamperometry to be determined, including the initial potential and the appropriate potential range required for electrodeposition to occur. The deposition time can then be varied in consideration of the initial electrode surface as well as the desired size, shape and coverage of the electrodeposit.

Chronoamperometry is a powerful tool, not only for the generation of nanostructured surfaces but also as it can shed light on the growth of nanostructures formed through other protocols. This is especially true for the chemical synthesis of nanoparticles and core-shell materials, where one of the rate determining steps for the reduction of the metallic salts is the chemical composition of the solution and in particular the choice of the chemical reductant. While many investigations have been performed into the chemical growth of such nanostructures, chronoamperometry is a facile method to understand the reduction behaviour of metallic salts as a function of the applied potential. This applied potential is of vital importance to the growth of the nanostructures as it can influence the shape, size, crystallographic orientation and nucleation behaviour of the nanostructures.[12] Additionally, as the electrochemical reaction can be terminated by controlling the deposition time, intermediate structures can easily be isolated and studied, providing a means of studying the growth of the nanostructured materials.

Chronoamperometry has been used in this work for the synthesis of both gold and platinum based nanomaterials, as well as for the investigation of the materials towards electrocatalytic applications. These experiments were performed using a
CH Instruments bipotentiostat (CHI 760C) using the three-electrode configuration described earlier.

2.1.4. Rotating Ring-Disk Electrode Studies

While the electrochemical techniques described so far are all performed under hydrostatic conditions (that is, with no external mixing of the electrolyte solution during experiments), much information can be gained by studying electrochemical processes under hydrodynamic conditions, where forced convection is induced. While in principle this could be achieved by stirring the solution through the use of a stirring bar or rod, a more controllable method is to instead rotate the electrode during the experiment, generating a laminar flow from the centre of the electrode to the edges. This is performed using a rotating ring-disk electrode (RRDE), which consists of two electrodes fabricated within the one body. As their name suggests, these are comprised of a disk electrode in the centre, often similar to commercially available polycrystalline electrodes, with an insulating region around this disk followed by another electrode in the shape of a thin ring (Figure 2.3). The leads for these two components are insulated from each other allowing electrochemical experiments to be performed on each electrode independently. This electrode assembly is then attached to a spinning head which may be controlled to give a desired rotation rate.
Figure 2.3: Schematic showing a rotating ring-disk electrode.

Unlike typical CV experiments performed on stationary electrodes, where mass transport to the electrode is governed by the diffusion of the electroactive species, the solution is agitated in RRDE experiments by rotating the electrode and increased mass transport is seen under these conditions. This information can be used to gain a greater understanding of the electron transfer mechanisms of redox processes, for example the Levich equation (Equation 5)\(^{[13]}\) may be used to calculate the number of electrons transferred per mole of product \((n)\) for a fast redox process:

\[
    i_d = 0.62nFA C_0 D_0^{2/3} v^{-1/6} \omega^{1/2}
\]  

(5)

where \(i_d\) is the current under diffusion limiting conditions, \(F\) is the Faraday constant, \(A\) is the surface area of the electrode, \(C_0\) is the bulk concentration of the electroactive species, \(D_0\) is the diffusion coefficient of the electroactive species, \(v\) is the kinematic viscosity of the solution and \(\omega\) is the rotation rate of the electrode (in radians per second). When a plot of \(i_d\) versus \(\omega^{1/2}\) is constructed a linear relationship can be observed for a reaction involving fast electron transfer kinetics, where the slope of the curve \((B)\) is given by Equation 6:\(^{[13]}\)

\[
    B = 0.62nFA C_0 D_0^{2/3} v^{-1/6}
\]  

(6)
In cases where the electron transfer kinetics are slower, a modified version of these plots may be used, known as the Koutecky-Levich equation:[13]

\[
\frac{1}{i} = \frac{1}{i_k} + \frac{1}{i_d}
\]  \hspace{1cm} (7)

where \(i_k\) is the kinetic current, \(i_d\) is the diffusion limited current and \(i\) is the experimentally observed current. Unlike the case for the Levich equation, a linear relationship can be observed from a plot of \(1/i\) against \(1/\omega^{1/2}\). The number of electrons transferred in this case may again be calculated from the slope of the curve, which is given here by \(1/B\).

In addition to analysing the electrochemical reactions at the disk electrode alone, the production of intermediate species formed in electrochemical reactions at the disk electrode may be detected at the ring through the laminar flow created by the electrode rotation. Such information can provide evidence of the electrochemical pathways involved in reactions at the disk electrode. For instance, the formation of hydrogen peroxide during oxygen reduction can be monitored by sweeping the potential at the disk electrode while the ring electrode is polarised at a potential where hydrogen peroxide known to oxidise. This ability to monitor the products formed by an electrochemical reaction at the disk electrode is therefore an important tool in understanding electrochemical reactions and has been used to study a wide variety of systems.[14-15]

RRDE studies in this work were performed using an ALS Rotating Ring Disk Electrode Rotator (RRDE-3A) with a CH Instruments bipotentiostat (CHI 760C), which allowed simultaneous control of the disk and ring electrodes. The gold disk, platinum ring RRDE electrode was purchased from ALS and cleaned prior to experiments by polishing with an alumina slurry on a polishing cloth, followed by sonication in water to remove any adsorbed alumina and then drying under a stream of nitrogen.

2.1.5. Differential Pulse Voltammetry

Another voltammetric technique which finds application in electroanalytical situations is differential pulse voltammetry (DPV). The aim of this technique is to reduce the contribution of the capacitive current to the detected current. Since this
contribution can often be sizeable it can interfere with the detection of electroactive species, especially at the low concentrations which are typically of interest.[16]

DPV differs from the other electrochemical techniques described previously such as linear sweep voltammetry as the potential is not ramped in a linear manner. The applied potential is instead in the form of a staircase waveform on which small pulses are superimposed (Figure 2.4). The current is sampled both before and after a pulse and as the name suggests the differential between these values is then plotted as a function of the applied potential. This technique has been widely applied in electroanalytical applications, where it provides a facile method of sensing a wide range of analytes at levels of analytical interest. DPV may also provide voltametric discrimination between similar analytes by the peak-to-peak separation, further highlighting the advantages of this approach for electrochemical sensing.

![Figure 2.4: Schematic showing the individual potential programs and the resulting potential pulse profile utilised in differential pulse voltammetry. (Reprinted with permission from Ref. 17)](image)

All DPV experiments performed in this work were recorded on a CH Instruments potentiostat (CHI 760C) using the standard three-electrode setup.
2.1.6. Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy (EIS) is a technique which can be used to investigate the electrical and electrochemical behaviour of an electrode/electrolyte interface. Impedance is similar in concept to the more familiar notion of resistance, however impedance is not restricted by several definitions placed on an ideal resistor, such as that the response is independent of the frequency, the current and voltage through the resistor are in phase, and it follows Ohm’s Law for all currents and voltages.\textsuperscript{[18]} In the complex setting of an ac signal applied to an electrode/electrolyte interface impedance therefore provides a more adequate measure of the opposition to the flow of current.

The study of electrochemical impedance is performed by the application of an ac signal of a fixed amplitude and a set potential to the working electrode, and the frequency of the ac signal is then varied between typical values of 0.001 Hz to 50 kHz.\textsuperscript{[19]} The impedance (Z), or dynamic resistance to the sinusoidal current flow, is then calculated as the ratio of the applied potential to the current passed at time $t$ (Equation 8), which is analogous to the measurement of resistance in linear systems. This relationship is then calculated using the right hand side of Equation 8,\textsuperscript{[18]} which is expressed as a function of the maximum voltage ($V_0$), the maximum current ($I_0$), the angular frequency of the signal ($\omega=2\pi f$, where $f$ is the frequency of the ac signal), the phase difference between the voltage and current ($\theta$) and the time ($t$).

\begin{equation}
Z = \frac{V(t)}{I(t)} = \frac{V_0 \sin(\omega t)}{I_0 \sin(\omega t + \theta)}
\end{equation} \tag{8}

The impedance may also be written in the Cartesian form shown in Equation 9,\textsuperscript{[18]} where the impedance at a given angular frequency is the sum of a real impedance value ($Z_r$) and an imaginary impedance value ($Z_i$) multiplied by $j$ ($\sqrt{-1}$).

\begin{equation}
Z(\omega) = Z_r(\omega) + jZ_i(\omega)
\end{equation} \tag{9}

This equation is the basis of the Nyquist plot, in which $-Z_i$ is plotted against $Z_r$ (also referred to as $-Z''$ and $Z'$, respectively). These plots may contain a number of different elements including hemispherical or depressed hemispherical regions as
well as linear sections. While the analysis of these plots is often not a trivial matter, a great deal of information can be gained about the system. Typically these spectra are analysed by matching the different features present with the electrical behaviour of an equivalent circuit, often composed of elements such as resistors, capacitors and inductors which may be connected in series or in parallel. This combination of elements describe a number of basic processes, including Ohmic resistance, capacitance, constant phase elements (CPEs), and Warburg impedance.\cite{20}

EIS has been used in this work to investigate whether nanostructured materials showed altered impedance behaviour to that of bulk materials. EIS spectra were recorded using the CH Instruments potentiostat described previously (CHI 760C) using a standard three-electrode setup.

\subsection*{2.1.7. Fourier Transformed Alternating Current Voltammetry}

Fourier transformed alternating current voltammetry (FT-ac) is a powerful electrochemical technique for the detection of Faradaic redox processes. FT-ac shares similarities with the technique of cyclic voltammetry, however instead of altering the applied potential with a linear ramp rate a sinusoidal waveform is superimposed on this signal as shown in Figure 2.5.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig2.5.png}
\caption{Schematic showing the variation between a typical potential sweep program used in FT-ac (red) and cyclic voltammetry (black).}
\end{figure}

This potential scanning method results in the applied potential sweeping between redox processes while the average potential value is steadily changed,
producing a current-time plot which is comprised of a number of superimposed sinusoidal waves. The individual sinusoidal waves may then be extracted from this plot using a fast Fourier transform (FFT), producing a plot known as a power spectrum (Figure 2.6). The different components, comprising of the fundamental wave and its harmonic components (often down to the fifth or sixth harmonic waves), are then selected before an inverse Fourier transform brings each component back from the frequency domain to the time domain. As the sweep rate is known this data may then be converted to a plot of current versus potential for each component, resulting in an FT-ac voltammogram.

The ability to generate and identify the harmonic waves is one of the key strengths of FT-ac, as the linear capacitive components are diminished in the lower harmonics and effectively absent from the fourth and fifth harmonics.\textsuperscript{[21-22]} As discussed in the previous section on differential pulse voltammetry (Section 2.1.5) this capacitive current is often encountered in electrochemical experiments and can result in the masking of Faradaic processes, especially those of low magnitude. A further advantage of the FT-ac technique is that it allows a more precise analysis of voltammetric features such as peak potentials, which may be problematic when studied with cyclic voltammetry due to the contribution of capacitive current to the recorded signal.\textsuperscript{[23-24]}
Figure 2.6: An example of a power spectrum produced by FT-ac voltammetry, showing the inverse Fourier transforms of the first to fourth harmonic responses. (Adapted from Figure 3 in Ref. 25 and Figure 6 in Ref. 26)

In light of the advantages offered by this technique, FT-ac is a very useful tool to study electron transfer behaviour and has been applied to the study of a number of varied systems. These include 7,7,8,8-tetracyanoquinodimethane (TCNQ), ferrocene, ferrocenemethanol, uric acid and surface bound proteins such as myoglobin, azurin, cytochrome c peroxidase and heme-containing enzymes. The study of electron transfer at bare electrodes has also been conducted for copper and gold surfaces as well as carbon-based electrodes including screen printed carbon ink based electrodes and pyrolitic graphite.

Much of the pioneering work and further development of the FT-ac technique was completed by Prof. Alan Bond and co-workers. This work has determined the effect of various parameters involved in the technique. For example, the behaviour of the FT-ac voltammograms relative to the dc scan rate as well as the frequency and amplitude of the applied sinusoidal waveform have been examined. One important finding from these studies was that when a large amplitude sinusoidal
potential perturbation is chosen (on the order of 100 mV) that the signal-to-noise ratios for the higher harmonic components can be improved, allowing a more careful study of these higher harmonic responses.\[35\] The validity of the FT-ac technique has also been established from the similarities between the dc response and a conventional CV response for a given electrode/electrolyte interface, and experimentally observed FT-ac results have been found to be in agreement with simulated results.\[24-25\]

All FT-ac experiments in this thesis were obtained using an instrument\[36\] at the Electrochemistry Research Group at Monash University, with access and guidance kindly provided by Prof. Bond. All solutions were purged with nitrogen prior to testing in order to remove dissolved gases. Due to the large amount of data generated with each experiment the data was binned (1 in 16) to minimise file sizes whilst maintaining the integrity of the data. The FT-ac voltammograms presented in this work have all been separated into their forward and reverse components for their dc and first to fourth harmonic responses for clarity.

### 2.2. Materials Characterisation Techniques

While the electrochemical formation and behaviour of electrodeposited films is of critical importance in the creation of materials for electrocatalytic applications, it is often just as important to understand the physical structure of the material. This stems from the well-reported connection between the electrochemical behaviour and factors such as the size, shape, porosity, crystallography and chemical composition of the electrodeposited material. A number of different materials characterisation techniques were employed in this work, including scanning electron microscopy, transmission electron microscopy, energy dispersive X-ray spectroscopy, X-ray photoelectron spectroscopy, X-ray diffraction, Raman spectroscopy and inductively coupled mass spectrometry and are outlined in the following sections.
2.2.1. Scanning Electron Microscopy

One of the most common methods for characterising the morphology of electrodeposited materials is scanning electron microscopy (SEM). While based on similar principles to conventional optical microscopy, SEM offers a number of advantages for the analysis of electrodeposited surfaces, foremost amongst them the greater resolution power which can be achieved by SEM. Imaging in optical microscopy is based on the illumination of the sample with visible light, which is reflected towards one or more lenses where the image is magnified. However one of the largest limitations on the application of optical microscopy to study electrodeposited materials is the resolution limit brought about by the wavelength of the illuminating light. This limit is known as the Abbé diffraction limit and is approximately equal to $\lambda/2$, where $\lambda$ is the wavelength used to investigate the sample.\textsuperscript{[37]} As the wavelength of visible light is on the order 400-700 nm this places a theoretical limit on the workable resolution of optical microscopy on the order of hundreds of nanometres.

Considering these limitations on conventional optical microscopy, the use of the SEM becomes attractive for imaging the morphology of electrodeposited materials. In this technique the sample is probed using a beam of electrons rather than visible light, where the former has a considerably smaller wavelength of 0.4 Å for an electron with an energy of 1000 eV.\textsuperscript{[38]} The Abbé diffraction limit is therefore no longer a limiting factor for the imaging of materials on the nanoscale. Imaging is achieved by directing a beam of electrons from an electron gun source down an evacuated chamber through the use of magnetic lenses which collimate and focus the beam to a fine point.\textsuperscript{[39]} When this electron beam is incident upon the sample a number of outcomes are possible, including the release of secondary electrons, where the excitation of a surface electron causes its emission from the surface, or the release of X-rays, light or heat. The incident electrons, known as primary electrons, may also be detected, either through their reflection from the surface as backscattered electrons or after their transmission through the surface.\textsuperscript{[40]} The emission of secondary electrons is a surface sensitive phenomenon and is used in the case of SEM to provide a three-dimensional image of the surface by scanning (or rastering) the electron beam across the surface and correlating the intensity of the
detected secondary electrons with the position of the beam on the surface. Imaging in this method can be used to resolve surface features smaller than 10 nm, even down to 1 nm.[41]

SEM has been used in this work to characterise the morphology of the electrodeposits in order to understand how the deposition parameters affect the coverage, shape and size of the deposits. All SEM images presented were obtained with an FEI Nova SEM instrument. Imaging was performed with the sample at a working distance of between 4-5 mm from the pole piece, with an accelerating voltage of either 10 kV or 15 kV. Charging of the samples was generally not encountered due to the conducting nature of the electrodeposited materials and the use of carbon tape which both physically secured the samples to the aluminium stub as well as providing a means to conduct any excess charge to ground.

2.2.2. Transmission Electron Microscopy

Another form of electron microscopy which can be used to examine electrodeposits is transmission electron microscopy (TEM). This follows similar principles to the SEM, in that the sample is analysed by interaction with a beam of electrons which are incident upon the surface in an evacuated chamber.[39] As was mentioned in the previous section this interaction can lead to a variety of phenomenon, and rather than detecting the secondary electrons emitted from a surface as in SEM the TEM is instead based upon the transmission of electrons through the sample. These transmitted electrons are then detected at either a photographic plate or more commonly by a digital detector below the sample. The incident beam of electrons is a relatively wide compared to the beam used in SEM and does not require the surface to be rastered with the beam. In order to ensure that a significant number of electrons are transmitted through the sample the electrons are accelerated to a much higher voltage (between 100-200 kV) than is used for SEM (typically between 5-30 kV). This transmitted beam of electrons contains much useable information about the surface, with the identification of individual atoms within lattices possible and the ability to collect diffraction patterns which reflect the crystallographic orientation of the sample.[42] However one of the major limitations for the study of electrodeposited materials with TEM is
that the sample must be very thin in order to allow the transmission of a sufficient number of electrons through the sample where they may be detected.\cite{38} In many cases this requires specific sample preparation, such as the dispersion of nanoparticles on a holey (or lacy) TEM grid or in the case of adhered nanostructures they may first need to be removed from the surface by a method such as sonication or mechanical scraping. Unfortunately these methods may not necessarily be representative of the deposited material (in terms of the distribution or surface arrangement of such nanostructures) and may also lead to the degradation of the nanostructures prior to imaging.

In this work TEM studies were performed on platinum nanostructures (Chapter IV) and a decorated gold TEM grid (Chapter VI), with SEM being routinely used to provide information on the structure of the electrodeposited metals. The TEM studies were performed using a JEOL 2100 high resolution instrument with an accelerating voltage of 200 kV.

### 2.2.3. Energy Dispersive X-ray Spectroscopy

While electron microscopy provides a valuable method of characterising the morphology and crystallography of an electrodeposited surface, these techniques may also be used to provide elemental analysis of the samples. As previously mentioned, the interaction of the primary beam of electrons with a sample can lead to a number of different emissions, one of which is the excitation of a core shell electron to an excited state, where its decay to back to its ground state leads to the emission of an X-ray. The energy of these X-rays is characteristic of the atomic shells from which they were released, and can therefore be used to provide qualitative and quantitative information on the elemental composition of a surface.\cite{40, 42} As both the TEM and SEM rely on the investigation of the sample by a beam of electrons, both of these techniques lead to the generation of X-rays and so energy dispersive X-ray spectroscopy (EDX, also referred to as EDS) may be used on either instrument.

It is important to note that when the beam of primary electrons is incident upon the sample these electrons tend to penetrate into the surface in a tear-drop like shape.\cite{39} While only the surface and near-surface atoms are able to release secondary electrons which can be recorded at the detector as these electrons
undergo fewer collisions on their way to the detector, the X-rays generated are not hindered as easily and can reach the detector from further into the sample. This property means that the information given from EDX is reflective not only of the immediate surface layer but also to a larger degree of the sub-surface layers. EDX can therefore be considered to be more representative of the bulk composition of the material rather than as a surface sensitive technique. In addition to acquiring information from a particular spot on a surface, an EDX map of a surface can also be generated by rastering the electron beam across the surface and correlating the emitted X-rays with the position of the beam, showing elemental distribution across a surface.

EDX measurements on the Nova SEM were recorded with an AMETEK EDX system. The accelerating voltage of the electron beam was kept at 30 kV in order to excite a higher proportion of inner electron shells and provide confirmation of elemental identification using multiple peaks. When this EDX system was used the detector was wound further into the sample chamber in order to maximise the proportion of X-rays reaching the detector. The entrance to this detector was biased at 20 kV in order to inhibit the interference of secondary electrons on the detection of X-rays. EDX measurements on the 2100 TEM were recorded with a Jeol Si(Li) X-ray detector, with the primary electrons accelerated at a voltage of 200 kV.

### 2.2.4. X-ray Photoelectron Spectroscopy

Another form of elemental analysis is X-ray photoelectron spectroscopy (XPS). The general principle of this technique is that a beam of incident X-rays excite electrons from atoms in the surface, which can lead to the emission of these electrons from the surface.\[43\] This technique of detecting electrons emitted after excitation from an X-ray beam is opposite that of EDX, where an electron beam is used to excite the surface and generate the detected X-rays. The detection of emitted electrons has a few important consequences for XPS, such as the need to operate under a high vacuum\[44-45\] so that the mean free path of the emitted electrons is increased. The use of a high vacuum is also required in order to minimize any losses in the energy of the emitted electrons. Since the energy of the X-ray beam ($h\nu$) is known, the kinetic energy of the emitted electrons ($E_k$) can be measured and a
correction for the work function of the solid \((E_W)\) can be made the characteristic binding energies \((E_B)\) of the elements present on the surface can be determined,[45] as given by Equation 10.[46] Any loss in these kinetic energies due to collision with gases in the chamber will lead to alterations in the recorded binding energies and intensities, and so a high vacuum is required to obtain reliable results.

\[
E_K = h\nu - E_B - E_W \tag{10}
\]

The analysis of a sample by XPS is a particularly surface sensitive technique, with electrons emitted from approximately the top 10 nm of the surface.[44, 47] Although the incident X-rays may penetrate further into the sample, the emitted electrons from these regions do not possess enough energy to overcome the inelastic collisions which take place as they travel to the surface of the material and are therefore not used to provide information on the surface composition.[43] Importantly, this property makes XPS a complementary analytical technique to EDX, as the former is a surface sensitive technique while the latter contains a greater extent of information on the bulk of the material.[48] The comparison of these results may then provide useful information on the elemental composition of the surface.

Another advantage of XPS as an analytical tool compared with EDX is that it offers a greater amount of information than just the elemental composition of the surface. For example, the electronic configuration of the electron orbitals can be observed at defined binding energies as separate peaks, such as the \(5/2\) and \(3/2\) orbitals of the Ag 3d shell. The binding energies of the outermost electron shells are often of interest in XPS as they are more susceptible to change with respect to their chemical environment. For example in the case of a native oxide on a silver film the binding energy of the Ag 3d\(_{5/2}\) and 3d\(_{3/2}\) orbitals will shift to higher binding energies, as the more electronegative oxygen atoms withdraw the electron density of these silver orbitals and the emission of electrons from these partially positive silver atoms becomes increasingly difficult. These properties allow the detection of surface oxides, alloying (where the altered electronic configuration shifts the binding energy of the constituent atoms) and the oxidation states of elements, demonstrating the power of XPS for the chemical analysis of a wide variety of surfaces.[46]
In this current work XPS has been used in a number of different ways, for example to examine whether Pb is present on the gold nanospikes and to determine whether the electronic structure of the Pt-Pb samples shows alloyed or segregated behaviour. XPS has also been used in the case of the spontaneous decoration work to both confirm the presence of the decorated metal and to investigate whether the metal is present as an adsorbed salt or whether it has been reduced onto the surface. All XPS results presented here were recorded using a Thermo K-Alpha instrument with a pressure better than $1 \times 10^{-9}$ Torr. In order to correct for anomalous charge shifting of the surfaces and to compare the results to those in the literature all data was referenced to the adventitious C 1s binding energy of 285 eV.[47]

2.2.5. X-ray Diffraction

It is well known that metals can exist in a variety of different crystallographic orientations, whether they be single crystal surfaces or polycrystalline materials with a range of different exposed crystal facets. As these orientations are known to affect a wide variety of phenomenon such as the adsorption and desorption of chemical species from the surface[49-50] and the electrocatalytic and catalytic activity of the materials[51-53] it is important to understand the crystallographic nature of the such materials. This is also an important part of understanding the growth of nanostructured surfaces, which may be directed by the specific interaction of different species with particular crystallographic planes of the growing surface, acting to template their growth by slowing the kinetics of metal reduction along these planes.[54-55]

In order to characterise the crystallographic orientation of a material a convenient technique is X-ray diffraction (XRD). While it was previously noted that electron diffraction patterns obtained using a TEM can provide valuable information on the localised crystallography of a sample, this technique is limited by the requirement for thin samples. In addition this is not a bulk analytical method as the sample size is small, and it is therefore not practical for the analysis of large amounts of material, let alone their routine analysis.
The principle behind XRD is similar to that used in electron diffraction, where the incident beam undergoes diffraction when it impinges upon atoms within the sample, and the diffracted beams are then detected as a function of their deviation from the incident angle. In XRD the X-rays are generated by impacting a metal target with high energy electrons,[56] as was discussed for EDX analysis. Rather than generating X-rays with a range of different wavelengths a monochromatic wavelength is produced by using a known metal target (commonly a Cu Kα source[57] giving a fixed wavelength of 1.5418Å), with these X-rays directed towards the fixed sample. Although the exact penetration depth varies for different materials,[58] these X-rays are able to diffract from within the surface and thus increase the volume of interaction. Importantly for the analysis of materials when these X-rays see randomly arranged atoms within a surface they will scatter without a preferred direction, however when the X-rays see atoms arranged in ordered planes they will diffract at a particular angle. This angle is known as the Bragg angle and is given by:

\[ n\lambda = 2dsin\theta \]  

(11)

where \( \lambda \) is the wavelength of the incident X-rays, \( \theta \) is the angle of the diffracted X-rays (in degrees), \( n \) is an integer value representing the number of planes in the lattice, and \( d \) is the reciprocal spacing of the atoms in units of Å\(^{-1}\).[59] The inverse of this reciprocal spacing (1/\( d \)) can then be used to provide structural information about the physical separations between the atoms.

The data from an XRD pattern may give information on a number of different properties of the material, including elemental or phase identification based on the peak positions, and deviations from these ideal peak positions indicate a compression or expansion of the crystal lattice. This latter effect is commonly found in the case of alloyed materials which have significant mismatches in their crystal lattices, and the peak shift can be correlated to the percentage composition of the components.[60-61] The broadening of diffraction peaks may also provide useful information on the material, as broader peaks can indicate the presence of small grain sizes, according to the Scherrer equation:
\[ t = \frac{K\lambda}{B\cos\theta} \]  

(12)

where \( K \) is a numerical constant between 0.85-0.9, \( B \) is the full width half maximum of the peak and \( t \) is the particle size.\(^{[57]}\) The XRD patterns of polycrystalline materials may also be analysed with reference to the relative intensities of the crystal planes, indicating whether preferential growth has occurred or been inhibited along particular crystal planes.

The XRD patterns reported in this thesis were all recorded using a Bruker AX 8: Discover instrument with a General Area Detector Diffraction System (GADDS). This instrument was preferred over a traditional powder diffraction system as the X-rays could be directed to an elliptical area on the surface with a height of approximately 1.5 mm and a length of approximately 0.5 mm, so that X-ray diffraction was avoided from the unmodified areas of the surfaces. In order to obtain a more representative picture of the surface orientation the sample was rotated during all measurements using a custom-made spinning device.

2.2.6. Raman Spectroscopy

Raman spectroscopy is a characterisation technique used to study the vibration of molecules which may be present as a gas, liquid or solid phase, including an adsorbed layer on a solid support. This technique involves the irradiation of a sample with light of a known wavelength and detecting whether this wavelength is altered after interaction with the sample. Two possible outcomes of this interaction are the elastic scattering of the photons, in which the wavelength of the light is unperturbed, or the inelastic scattering of the photons where the wavelength of the scattered light is altered compared to the incident beam. The former case is known as Rayleigh scattering, while the second gives rise to the Raman process. This transfer of energy between the sample and the incident light can result in either the sample gaining energy, known as a Stokes transition, or it can result in the sample transferring energy to the photons, known as an anti-Stokes transition. For either of these cases the gain or loss in energy will alter the wavelength of the photons, and this shifted wavelength is recorded as a Raman shift. These anti-Stokes transitions occur much less frequently than Stokes transitions and it is usually these latter transitions which are observed by Raman spectroscopy. It should also be noted that
Rayleigh scattering occurs more frequently than Raman scattering (by a factor of approximately $10^6$), and therefore the instruments must filter these Rayleigh scattered photons in order to provide clear Raman spectra.

Raman spectroscopy is a widely used analytical technique for examining the molecular nature of known or unknown samples. This is especially the case as Raman spectroscopy can be complementary to Fourier transform infrared spectroscopy (FTIR), where the former is more suited to the identification of non-polar bonds and the latter more readily identifies polar bonds. Raman spectroscopy is also gaining popularity through the field of surface-enhanced Raman spectroscopy (SERS), where the Raman signal of molecules adsorbed to solid supports may be effectively amplified. This phenomenon is being widely studied as it can greatly increase the detection limit of the molecules, even to single molecule detection, and it therefore shows great promise for the fabrication of sensors. While there is still much debate in the literature over the exact mechanism of the SERS effect, it is generally accepted to occur as a result of electromagnetic and chemical enhancement effects, although the contributions from these effects are still being investigated and may differ from case to case.

In this work the fabricated nanostructures were investigated for their application as SERS materials. This was performed by immersing the materials in a solution of Rhodamine B for one hour after which they were thoroughly washed in milli-Q water in order to remove any weakly adsorbed species. The samples were then air dried and tested with a Perkin Elmer RamanStation 400 with an excitation wavelength of 785 nm. All data was then background corrected using the Spectrum software.

### 2.2.7. Inductively Coupled Plasma Mass Spectrometry

Inductively coupled plasma mass spectrometry (ICP-MS) provides a powerful analytical tool to study the composition of a variety of samples, and has been applied in fields such as environmental science, archaeology, biology, analytical chemistry and industrial applications. This technique is based on the ionisation of a sample prior to its detection at a mass spectrometer, where the ionised sample is detected on the basis of its mass-to-charge ratio (m/z). The ionisation is achieved
by the use of a plasma, formed by the interaction of an oscillating magnetic field (created by an applied high frequency electric field) with an appropriate gas.[72] Argon is often chosen for this purpose, and after an initial spark is provided a self-sustaining plasma is created by collisions within this gas. After the sample is injected into the plasma through a nebuliser, the high temperature of the plasma (which can be between 6,000-10,000 K) then ionises the sample species to a 1+ ion prior to its detection at the mass spectrometer.[73]

ICP-MS has proven to be a popular analytical tool, with the analysis of at least 65 elements possible with limits of detection below one part per trillion, with rapid quantification and information available on the different isotopes present.[73-74] In this work ICP-MS was used to examine a 1 mM AgNO₃ solution after an evaporated gold film was immersed in this solution (Chapter VI), in order to examine if gold species were liberated from the surface during this immersion. This was performed with an Agilent 7700x instrument with an ASX-520 autosampler.

2.3. Materials

2.3.1. Chemicals

Solutions were made with deionised water (resistivity of 18.2 MΩ cm) purified with a Milli-Q reagent deioniser (Millipore). HAuCl₄, Pb(CH₃COO)₂·3H₂O, potassium ferrocyanide, potassium ferricyanide, NaH₂PO₄·2H₂O, dopamine (Sigma), ascorbic acid, uric acid, hydrogen peroxide, Pd(NO₃)₂, Ni(NO₃)₂ (BDH), H₂SO₄, NaOH, glucose, KAuBr₄, KNO₃ (Ajax), Nafion 117 (5% solution in low aliphatic alcohols, Fluka), Rhodamine B, methanol, ethanol, AgNO₃ (Merck), Na₂HPO₄·12H₂O (May & Baker) K₂PtCl₄, K₂PtCl₆, ferrocenemethanol (Aldrich) and HCl (Rowe Scientific) were used as received.

Oxygen reduction experiments were conducted by bubbling high purity oxygen (Coregas 5.0) into 1 M solutions of H₂SO₄ or NaOH for at least 15 minutes prior to testing, and fresh O₂ was regularly bubbled into the solutions in between testing samples. All other electrochemical experiments were degassed with a stream of nitrogen for at least five minutes prior to testing.
2.3.2. Electrode Materials

Evaporated gold and silver films were prepared by e-beam evaporation using a Balzers system, providing a 10 nm Ti adhesion layer to a clean Si (100) wafer (Montco Silicon Technologies), followed by 150 nm of gold or silver. These surfaces were then cut as required and cleaned using immersion in acetone followed by methanol, after which they were thoroughly dried under a stream of nitrogen. In order to control the exposed geometric areas of these films, polyimide tape (ATA Distributors) was added to the surface, with a precut circular region (4.5 mm diameter) exposing reproducible geometric areas of the underlying film.

Indium tin oxide (ITO) coated glass (With a quoted sheet resistance of 4-8 Ω/sq, Delta Technologies Ltd.) were cut as required and cleaned and masked using the procedure outlined for the evaporated films.

Glassy carbon plates (Sigradur G, HTW) were cut in house, with reproducible surfaces obtained by polishing the smooth faces on a polishing pad (Microcloth, Buehler) with an aqueous 0.05 μm alumina slurry. These surfaces were then thoroughly washed with milli-Q water and dried under a stream of nitrogen. Reproducible geometric areas were again obtained by masking with polyimide tape.

Polycrystalline gold, silver and platinum electrodes (BAS) were cleaned using the same procedure as described for glassy carbon surfaces, with separate polishing pads used for each material in order to avoid cross-contamination. The geometric area of the polycrystalline electrodes was maintained by the electrode casing material, with an exposed diameter of 1.6 mm.

2.4. References


Chapter III

The Synthesis of Gold Nanospikes
Using a Chemically Templated Electrodeposition Protocol

Sections of this chapter have been published in the following peer-reviewed journals:


3.1. Introduction

3.1.1. Electrochemical Fabrication of Gold Nanostructures

The electrodeposition of gold is a well-known field of research and has received much attention in the literature. This covers the formation of smooth gold deposits through to nanostructured gold surfaces,[1-2] including reports on the electrodeposition from a range of different gold salts including cyanide, sulphite, thiosulfate and halide based salts.[3-5] In addition to the electrodeposition from a variety of metallic salts, a range of solvents have also been studied. Aqueous systems are the most widely reported but the use of organic solvents[6] or room temperature ionic liquids are also attracting attention,[7-9] especially for the latter case due to the unique physico-chemical properties of these solvents.[10]

The electrochemical formation of gold nanostructures is further separated into four distinct regimes, which are the electrodeposition at (i) untreated surfaces, (ii) modified surfaces, (iii) in the presence of physical templates or (iv) chemical templating agents, as discussed in Chapter I. Given that electrodeposition methods are better established in aqueous systems attention is turned to the electrochemical formation of nanostructures from these systems.

The electrodeposition of gold at untreated surfaces presents the simplest option for the formation of nanostructured gold materials through electrochemical methods. This involves the electrochemical reduction of a gold salt, often in the form of the bromide or chloride salt, at a clean surface such as a metallic or metal oxide film or a carbon-based electrode such as glassy carbon or highly oriented pyrolitic graphite (HOPG). A variety of materials can be formed with this simple protocol, including flower-like or quasi-spherical structures, where the morphology is controlled by factors such as the concentration of metal salt present or the deposition parameters including the applied potential or current density.[11-19]

Another approach to the electrochemical formation of gold nanostructures is to electrodeposit on a pre-existing nanostructured support, where this support is retained in the final material. Examples of this approach include the electrodeposition of gold nanoparticles on arrays of aligned nanowires[20] or carbon
nanotubes,[21] polymer-modified surfaces[22-23] and metal oxide nanoparticles,[24] as well as by electrodepositing gold over a surface of drop-cast gold coated microspheres.[25] The use of such modified electrodes for electrodeposition can be advantageous for the formation of gold nanostructures, especially for nanowire or nanotube-like materials which provide a large number of possible nucleation sites for the growth of gold.

Beyond altering the electrodeposition process through the choice of electrode surface, other common electrodeposition methods for the fabrication of nanostructured gold surfaces include either physical or chemical templating. Physical templating has been achieved by the use of anodised aluminium oxide (AAO),[26-30] porous silica or polycarbonate surfaces[31-32] and electrodepositing in the free spaces between a layer of polystyrene or silica spheres.[33-34] This method of physical templating acts by separating regions where electrodeposition is required with a material of poor conductivity, limiting growth to the unmasked regions. After the deposition step a post-synthesis treatment is used to remove the physical template, such as chemical etching[35] or sonication.[36]

Chemical templating is another commonly employed method for achieving growth control at electrodeposited nanostructures, and shares much in common with established growth direction routes in the chemical synthesis of nanomaterials, where growth agents preferentially adsorb to particular exposed crystallographic planes and control the rate of growth in these directions. Notable examples of chemical templating agents used for gold electrodeposition include organic species (cysteine, citric acid and CTAB),[19, 37-40] polymeric species (polyvinylpyrrolidone (PVP)),[32, 39] and inorganic species (including iodide as well as a range of metallic ions such as Pb$^{2+}$, Hg$^{2+}$, Tl$^+$ and Cu$^{2+}$).[19, 41-42] While the use of such metallic ions for altering the electrodeposition of gold has been reported, it should be noted that there are often limited descriptions on how they impact the growth of the gold nanostructures, and further work on this topic is required.

### 3.1.2. Research Aims

The electrochemical formation of gold nanostructures in this work was performed for a number of reasons. Firstly, while there are numerous reports in the
literature on the chemical synthesis of gold nanostructures, there are fewer reports on the electrochemical formation of surface bound gold nanomaterials. Since it is well known that in its bulk form gold is an inert material and that this reactivity increases dramatically at the nanoscale, the investigation of surfaces modified with gold nanostructures through electrodeposition adds the promise of application across a wide variety of areas. Specifically, the influence of including a heavy metal salt such as lead acetate in the deposition solution is examined, along with a number of different parameters which can alter the size and shape of the electrodeposited nanostructures.

Further to understanding the growth of these surfaces is a study of the premonolayer oxidation that occurs at these materials. While active site behaviour has previously been reported for a number of different gold surfaces, this activity was often promoted by post-synthesis modification involving thermal or electrochemical treatments,[43-49] however the possibility of creating nanostructured gold surfaces rich in active sites provides a means of negating this additional step. If this aim of forming materials with enhanced active site responses can be achieved then a wide range of applications may be possible. This will be explored by testing the electrocatalytic activity of the materials towards glucose oxidation and hydrogen evolution, along with the electroanalysis of dopamine and the surface enhanced Raman spectroscopy activity of the materials.

3.2. Results and Discussion

3.2.1. Synthesis of Gold Nanospikes

In order to study the electrodeposition of gold in the presence of a lead salt, cyclic voltammetry was performed in an aqueous solution of 6.9 mM HAuCl₄ and 0.5 mM lead acetate at a gold electrode (Figure 3.1a-b). After beginning the negative going scan at 0.75 V, a broad cathodic peak is observed which is attributed to the three-electron reduction of AuCl₄⁻. The peak potential for this reduction is found at 0.62 V, after which the current magnitude decreases as the process becomes diffusion limited. Two quasi-reversible processes are then observed towards the lower
potential limit, as are highlighted in the expanded section in Figure 3.1b. These processes are located at ca. -0.13 V and -0.3 V and relate to the under potential deposition (UPD) of lead on the gold surface. This process has previously been studied in detail, and it was shown that the peak at more positive potential (-0.13 V) relates to the formation of Pb islands, while the peak at lower potential (-0.3 V) relates to the coalescence of these Pb islands.\cite{50-51} A large anodic peak is also observed on the positive going sweep, with a peak potential at 1.1 V and a shoulder at 1.2 V. These processes are related to the formation of a gold oxide as well as the dissolution of gold, which is aided by the Cl\textsuperscript{-} anions liberated during the electrodeposition process in the negative sweep.\cite{52}

\textbf{Figure 3.1:} Cyclic voltammograms recorded at a gold electrode in a solution containing 6.9 mM HAuCl\textsubscript{4} and 0.5 mM Pb(CH\textsubscript{3}COO)\textsubscript{2} showing the overall scan (a) and a magnified image of the Pb UPD region (b). The HAuCl\textsubscript{4} reduction peak is shown in (c) for a solution containing 6.9 mM HAuCl\textsubscript{4} with (black) or without (red) the addition of 0.5 mM Pb(CH\textsubscript{3}COO)\textsubscript{2}. Scan rates in each case were 50 mV s\textsuperscript{-1}. 
The inclusion of lead acetate in the deposition solution can also be seen to alter the HAuCl₄ reduction peak as seen in Figure 3.1c, where the red curve was obtained from a solution containing 6.9 mM HAuCl₄ and the black curve shows an experiment obtained under similar conditions but with the addition of 0.5 mM lead acetate. This shift in the reduction potential is attributed to a cathodic depolarisation process, whereby the reduction of the HAuCl₄ occurs at slightly more favourable potentials as seen by a shift in the peak potential of 47 mV towards more positive potentials. This result indicates that the addition of lead acetate into the deposition solution results in an increased rate of gold electrodeposition.

The cyclic voltammetry of the HAuCl₄ and lead acetate solution (Figure 3.1a) reveals a relatively large electrochemical window for the electrodeposition of gold, with the reduction of HAuCl₄ beginning at ca. 0.8 V and continuing to -0.5 V, at which point the sweep direction was reversed. However previous work by this group has investigated electrodeposition at potentials below 0 V in a HAuCl₄/Pb(CH₃COO)₂ solution on a glassy carbon electrode, and it was found that the concurrent reduction of both HAuCl₄ and Pb(CH₃COO)₂ resulted in the formation of highly dendritic surfaces. While materials formed in this manner may prove to be an advantageous method of forming dendritic structures, this region was avoided in the current work in order avoid the possibility of Pb being retained in the structure. While Pb has been reported as an effective material for bimetallic surfaces such as PtPb (as will be investigated in the following chapter) it was decided that the presence of lead in the current study would further complicate the study of the active site behaviour and electrocatalytic activity of gold nanostructures.

The electrodeposition of gold was then performed by the application of a constant potential, starting just positively of the Pb UPD region at 0.05 V and then at the more positive potentials of 0.15 V and 0.25 V. The SEM images of these samples are presented in Figure 3.2, where the formation of gold nanospikes can be seen in Figure 3.2a, forming an even coverage of fine gold rods which taper to thin points to give the nanospike structure. The electrodeposition at 0.15 V (Figure 3.2b) shows the growth of some spike-like objects, however it is apparent that these structures are not as well defined as in Figure 3.2a, and the growth of a large number of crystallites on the underlying evaporated gold film can be seen. This trend extends
to the sample electrodeposited at 0.25 V (Figure 3.2c), where no gold nanospikes are evident and the growth predominantly occurs as fine crystallites. It should be noted that more well defined nanostructures could be achieved at this more positive potential by increasing the electrodeposition time, as demonstrated in Figure 3.2d. This resulted in the growth of plate-like structures with an under layer of small crystallites, where the growth of the former structures appears to result from the growth of the relatively large crystallites formed at shorter electrodeposition time (Figure 3.2c).

![Figure 3.2: SEM images of gold nanospikes electrodeposited from a solution containing 6.9 mM HAuCl₄ and 0.5 mM Pb(CH₃COO)₂ for 600 s at 0.05 V (a), 0.15 V (b), 0.25 V (c), and 40 min at 0.25 V (d).](image)

While it is clear that a number of different surfaces may be synthesised by controlling the applied potential, further work was conducted at 0.05 V as the gold
nanospikes provided an interesting surface with a large number of fine nanostructures. This surface was further investigated by SEM as shown in Figure 3.3, where imaging at an angle of 40° shows the growth of these nanospikes away from the surface (Figure 3.3a). This image also confirms that the gold nanospikes grow to sharp tips and form a dense, uniform coverage across the surface, as was also observed at lower magnification (Figure 3.3b). This degree of nanostructuring is in keeping with the aim of creating surfaces rich in active sites, which are assumed to be more densely populated at steps, kinks and edges of surfaces. These surface features are thought to exist at the surface of the gold nanospikes.

![SEM images of electrodeposited gold nanospikes](image)

**Figure 3.3:** SEM images of electrodeposited gold nanospikes showing an image recorded at an angle of 40° (a) and a low magnification image taken without sample rotation (b).

The effect of the deposition time was also studied for the gold nanospikes, and SEM images for surfaces deposited at 0.05 V for 150 s to 1000 s are shown in Figure 3.4. At shorter deposition times (Figure 3.4a- c) the initial growth of the nanospikes occurs, although the growth of these structures appears to occur alongside the growth of a large number of grains on the gold film. Increasing the deposition time to 600 s increases the size of the gold nanospikes and appears to provide enough time for the gold nanospikes to grow from the underlying crystallites, giving a more even coverage of nanospikes across the surface. Increasing the electrodeposition time beyond this value resulted in the over-growth of the nanospikes, leading to
much thicker nanospikes with larger tips as well as the growth of nodules along the backbone of the nanospikes.

Figure 3.4: SEM images of gold nanospikes electrodeposited at 0.05 V from a solution of 13.8 mM HAuCl₄ with 0.5 mM Pb(CH₃COO)₂ for 150 s (a), 300 s (b), 450 s (c), 600 s (d), 750 s (e) and 1000 s (f).
Another important parameter in the growth of the nanospikes is the concentration of HAuCl₄ in the deposition solution, as it leads to altered mass transport rates to the electrode under conditions of constant applied potential and therefore to different electrodeposition rates. Gold electrodeposition was performed from solutions containing 0.5 mM lead acetate and 3.5, 6.9, 13.8 and 20.7 mM HAuCl₄ for 600 s at 0.05 V (Figure 3.5). The sample electrodeposited from a solution containing 3.5 mM HAuCl₄ was seen to form a number of small nanospikes, although the growth of smaller structures is prevalent (Figure 3.5a). This is perhaps not surprising, as the lessened amount of HAuCl₄ available at the surface to undergo electrodeposition is akin to the limitation placed on the growth of the gold nanospikes by electrodepositing for relatively short times (Figure 3.4a). Of these materials electrodeposited from varying concentrations of HAuCl₄ the sample electrodeposited at 6.9 mM HAuCl₄ (Figure 3.5b) produced thinner nanospikes with smaller tips. Higher concentrations formed dramatically larger nanospikes, and in order to maximise the number of fine nanostructured features present while reducing the amount of HAuCl₄ required, 6.9 mM HAuCl₄ was selected for the growth of the nanospikes.
Figure 3.5: SEM images of gold nanospikes electrodeposited at 0.05 V for 600 s from a solution containing 0.5 mM Pb(CH₃COO)₂ and HAuCl₄ at 3.5 mM (a), 6.9 mM (b), 13.8 mM (c) and 20.7 mM (d).

The effect of altering the concentration of lead acetate was also examined, with SEM images of the materials formed presented in Figure 3.6. Shown in Figure 3.6a is a sample deposited in the absence of lead acetate, which consists of a large number of crystallites with a variety of shapes and sizes present. The presence of 0.125 mM lead acetate (Figure 3.6b) leads to the growth of a number of nanospikes, although the density of these structures is low and the nanospikes have not grown to the same size as seen previously (Figure 3.2). Further addition of lead to 0.25 mM (Figure 3.6c) increases the density of nanospikes, with the lengths of the structures increasing, and at a concentration of 0.5 mM lead acetate (Figure 3.6d) the best coverage is seen, with the nanospikes growing to a more even size distribution. Further increases in the concentration of lead acetate up to 1 mM (Figure 3.6e) do not result in appreciable differences from the sample deposited at a lead acetate concentration of 0.5 mM.
Figure 3.6: SEM images of gold nanospikes electrodeposited at 0.05 V for 600 s from a solution containing 6.9 mM H\(\text{AuCl}_4\) and \(\text{Pb(CH}_3\text{COO)}_2\) at concentrations of 0.125 mM (a), 0.25 mM (b), 0.5 mM (c) and 1 mM.

From the above results on the effect of lead acetate it is apparent that this species plays an important role in the formation of gold nanospikes. In order to investigate the role of the lead ions in solution, XPS characterisation was performed on the gold nanospikes formed from a deposition solution of 6.9 mM H\(\text{AuCl}_4\) and 0.5 mM lead acetate after thoroughly washing the sample in Milli-Q water to remove any loosely adsorbed reactants. The results of the survey spectrum (Figure 3.7a) reveal the
presence of C, Au, and O, however as a relatively large pass energy of 200 eV was used in obtaining this spectrum a more precise probing was performed on the Pb 4f region (Figure 3.7b) at a pass energy of 40 eV. It can be seen that no Pb is detectable from these scans, which is in agreement with the survey spectrum. This is an interesting result as it sheds light on the action of the lead acetate in forming the gold nanospikes. It indicates that lead is not electrodeposited during the synthesis, which concurs with the cyclic voltammetry data (Figure 3.1a and Figure 3.1b) where it was concluded that the applied potential of 0.05 V is not sufficiently negative to cause the UPD of lead. The XPS result also indicates that the surface is free of physisorbed lead acetate, showing that this electrodeposition protocol is adequate for the formation of gold nanostructures in applications where the presence of lead is undesirable.

![Figure 3.7](image.png)

**Figure 3.7:** XPS survey spectrum (a) and a spectrum recorded in the Pb 4f region (b) at gold nanospikes electrodeposited at 0.05 V for 600 s from a solution containing 6.9 mM HAuCl₄ and 0.5 mM Pb(CH₃COO)₂.

The gold nanospikes were also analysed by XRD (Figure 3.8). While not a conclusive result in itself, the absence of any extra peaks or shifts in peak positions due to the presence of lead is in agreement with the XPS results. While several additional peaks from the silicon substrate are present (as indicated with asterisks), a clean pattern showing the commonly observed crystal planes of gold (as indicated in brackets) can be seen. It is immediately apparent that the surface is highly oriented in the (111) crystal plane, well above the commonly reported 3:1 ratio for polycrystalline gold. However a number of the higher energy facets such as the
(220) and (311) planes are also notable, and present at higher levels than typically seen for polycrystalline gold samples. The presence of these higher energy facets is interesting as they can be indicative of the presence of kinks and steps on the material, which may have further implications on the active site behaviour and applications of the materials.

**Figure 3.8:** XRD pattern of gold nanospikes electrodeposited from a solution of 6.9 mM HAuCl₄ and 0.5 mM lead acetate for 600 s at 0.05 V, with the inset showing a magnified image of the higher 2θ region. Peaks from the underlying substrate are indicated with asterisks.

From the evidence presented it can be concluded that lead acetate does not reduce on the surface of the growing nanostructures during the electrodeposition. The most likely explanation for the altered growth seen when lead acetate is present in the deposition solution is that the lead acetate physisorbs to the gold surface and acts as a chemical template. It has previously been reported that lead has an affinity for the (100) and (110) crystal facets of gold, while HAuCl₄ shows an increased affinity towards adsorption on the (111) crystal facets in preference to the (100) and (110) crystal facets. This physisorption leads to the preferential growth of the (111) crystal planes, which is what was observed from the XRD results. This templated growth appears to take place on both the evaporated gold substrate and then on the growing electrodeposit, as previous studies on a glassy carbon surface did not result in the growth of gold nanospikes. From the studies of electrodepositions conducted with differing concentrations of lead acetate (Figure 3.6) it can be seen that as the concentration of lead acetate is increased to 0.5 mM
that the quality of nanospikes increases, after which a threshold value seems to have been reached and further addition of lead acetate results in negligible changes. This may occur as a particular concentration of lead acetate is required to adsorb to the growing electrodeposit, and below this concentration the electrodeposition of gold results in the growth of somewhat random crystallites. However once the concentration of lead acetate is sufficiently high as to adsorb to the exposed (100) and (110) gold crystal facets the templating effect occurs. This process is unhindered by the addition of higher quantities of lead acetate as this species appears to have a lower affinity for the (111) crystal planes of the growing electrodeposit than the HAuCl4 present. The ex situ XPS results do not reveal the presence of physisorbed lead acetate, indicating that it is removed from the surface either as the sample is removed from the deposition solution or during the subsequent washing step.

3.2.2. Electrochemical Behaviour of Gold Nanospikes

Having formed the gold nanospikes their electrochemical behaviour was then investigated in a number of commonly employed conditions. The cyclic voltammetry of an evaporated gold film (black) and gold nanospikes (red) in 1 M H2SO4 are presented in Figure 3.9. These scans consist of a number of different features, with the scan starting at 0 V and the double layer region extending to the onset of the monolayer oxide at 1.17 V on the gold nanospikes. This monolayer oxide is then stripped on the reverse sweep at 0.91 V, before the scan is ended at 0 V. However comparison of the CVs for the different materials reveals some interesting features. It can be seen that for comparable geometric areas the electrochemically active surface area is increased at the gold nanospikes, as illustrated by the increased magnitude of the monolayer oxide formation and stripping processes. Estimations based on the charge required to strip this monolayer oxide, using a value of 400 μC cm−2,59 indicate that this electrochemically active surface area increases from a value of 0.27 cm2 to 0.76 cm2, or an increase of approximately 2.8 times. It can also be seen that the monolayer oxide formation on the evaporated gold films is a relatively sluggish process, with a peak potential shifted by approximately 0.21 V to more positive potentials, which is in contrast to the rapid monolayer oxide formation process which occurs on the gold nanospikes. Another interesting feature
from the gold nanospikes is the appearance of an oxidation process centred at 1.1 V. This feature, with an onset potential of 0.99 V, is evidence that the gold nanospikes undergo premonolayer oxidation in H₂SO₄ solutions. While a minor, ill-defined oxidation process can be seen to occur at the evaporated gold surface, this feature is clearly enhanced as a result of the formation of the gold nanospikes. This tendency to undergo premonolayer oxidation may be related to the presence of gold atoms or clusters of gold atoms in a metastable metal surface configuration, as could be expected at the roughened tips and edges of the gold nanospikes.

![Figure 3.9: Cyclic voltammograms of gold nanospikes (red) and an evaporated gold film (black) in 1 M H₂SO₄, recorded at a sweep rate of 100 mV s⁻¹.](image)

While clear evidence of premonolayer oxidation events could be observed by cyclic voltammetry, large amplitude Fourier transformed ac voltammetry was also used to investigate the electrochemical behaviour of the gold nanospikes (Figure 3.10). This method has previously been shown to be a powerful tool to investigate surface confined electrochemical reactions, especially in instances where the typical capacitive nature of the double layer region masks the Faradaic responses within this region. Having separated the forward and reverse components for the dc and first to fourth harmonic responses, it can be seen that a typical response is seen in the dc component for gold in acidic conditions. It should be noted that the premonolayer oxidation seen at 1.1 V from cyclic voltammetry (Figure 3.9) is not observed as a distinct peak on the dc response from the FT-ac voltammogram. This may be related to a broadening of the peaks, which has previously been reported for an FT-ac voltammogram of an EC-type reaction.
While the first and second harmonic components still show a contribution from the capacitance at the electrode, as seen by the non-zero background current, this capacitance is much lower at the third harmonic and is negligible in the fourth harmonic. The results from the fourth harmonic show numerous peaks within the double layer region, with the major peaks located around 0.58 V and 0.41 V, however a small response can be seen at potentials as low as 0.12 V, which is dramatically lower than the onset potential of the monolayer oxide formation at 1.17 V. Such large shifts in the oxidation potential of gold has been reported previously for isolated gold clusters\[64\] which are not stabilised in a bulk lattice and may show different crystallographic orientations to their bulk counterparts. As can be seen from the fourth harmonic response, there are a number of different redox processes within the double layer region, which vary not only in their peak potential but also in their magnitude. This may be attributed to the presence of a range of different active sites on the gold nanospikes which oxidise at different potentials based on the structure of the gold atoms or clusters of atoms present. While it was previously mentioned that the major premonolayer oxidation peak visible by CV could not be seen from the dc response reconstructed from the FT-ac data, this oxidation is visible in the fourth harmonic, with a broad response beginning at 1.05 V and a peak potential visible at 1.16 V which is just prior to the onset of the monolayer oxide formation (Figure 3.9), confirming that FT-ac is a valuable tool for the study of the Faradaic responses encountered in premonolayer oxidation studies.
Figure 3.10: FT-ac voltammogram of gold nanospikes in 1 M \( H_2SO_4 \) recorded at a sweep rate of 67.06 mV s\(^{-1}\) with a sinusoidal perturbation of 100 mV amplitude and a frequency of 21.20 Hz.

The electrochemical behaviour of the gold nanospikes was also investigated in 1 M NaOH. Gold is known to often be a more effective electrocatalyst under basic conditions, and a possible explanation is that the product of the premonolayer
oxidation process is a hydrous oxide species, in the form of $[\text{Au}_2(\text{OH})_9]^3-$, which may be more stabilised under these conditions.\cite{48} The cyclic voltammetry of the evaporated gold film (black) and gold nanospikes (red) in 1 M NaOH is shown in Figure 3.11. This displays a number of features similar to the voltammograms recorded in 1 M H$_2$SO$_4$, however in this case a redox couple is immediately noticed within the double layer region. These processes, with peak potentials at -0.36 V and -0.43 V for the oxidation and reduction processes, respectively, are indicative of premonolayer oxidation occurring on the surface. The presence of a relatively large reduction component appears to be the result of the enhanced stability of the oxidation product in 1 M NaOH.

![Cyclic voltammograms](image)

**Figure 3.11**: Cyclic voltammograms of gold nanospikes (red) and an evaporated gold film (black) in 1 M NaOH recorded at 50 mV s$^{-1}$.

FT-ac studies were also performed on the gold nanospikes in 1 M NaOH (Figure 3.12). The presence of a large quartet is immediately evident, which is centred at -0.357 V. This is in close agreement with the dc cyclic voltammetry of the surface (Figure 3.11), where the visible premonolayer oxidation response had a peak potential of -0.36 V. As was also seen by cyclic voltammetry, the FT-ac results suggest that the oxidation products of the surface possess enhanced stability in 1 M NaOH, as evident by the reversible nature of the peaks between the forward and reverse scans. The oxidation of active sites also occurs at potentials far below the onset of the monolayer oxide formation (0.12 V from cyclic voltammetry), with redox processes occurring as early as -1.2 V. As was discussed previously for the FT-
ac voltammetry in 1 M H₂SO₄, the large number of premonolayer oxidation processes, which occur across a wide potential window, suggests that the active sites present on the gold nanospikes exist in a range of different structures.

Figure 3.12: FT-ac voltammogram of gold nanospikes in 1 M NaOH, recorded at a sweep rate of 70.78 mV s⁻¹ with a sinusoidal perturbation of 100 mV amplitude and a frequency of 21.16 Hz.
3.2.3. Electrocatalytic and SERS Activity of Gold Nanospikes

Having investigated the underlying electrochemical behaviour of the gold nanospikes in both acidic and basic conditions, the extension of these materials towards a number of different applications was then investigated. Shown in Figure 3.13 are cyclic voltammograms of an evaporated gold film (black) and gold nanospikes (red) in 1 M NaOH with 10 mM glucose. The electrooxidation of glucose at the evaporated gold film proceeds at an onset potential of -0.53 V before reaching a peak potential at -0.40 V. The reverse scan shows another oxidation peak of comparable magnitude to the forward scan, which has been attributed to the recommencement of glucose oxidation after the removal of surface oxides formed in the forward sweep.[65] Upon examining the response of the gold nanospikes to this reaction (red curve) clear differences can be seen. The onset potential begins at approximately -0.75 V, which is shifted by 350 mV to less positive potential compared to the evaporated gold film, demonstrating the electrocatalytic effect of the gold nanospikes. It is also important to note that this reaction is in keeping with the incipient hydrous oxide adatom mediator (IHOAM) model of electrocatalysis, which states that the onset potential of a variety of electrocatalytic reactions are linked to the onset potential of the premonolayer oxidation processes at the surface. In this instance the onset potential of glucose oxidation occurs at a slightly more positive value than an active site response at -0.79 V as seen from the FT-ac voltammogram in 1 M NaOH (Figure 3.12). In addition with the increased current magnitude at the gold nanospikes this provides evidence that the formation of nanostructured materials provides a valuable method to increase the electrocatalytic activity of materials through the enhanced degree of premonolayer oxidation which occurs at the nanostructured surface.
**Figure 3.13:** Cyclic voltammograms of gold nanospikes (red) and an evaporated gold film (black) in 10 mM glucose in 1 M NaOH recorded at a sweep rate of 50 mV s\(^{-1}\) and normalised for the electrochemically active surface areas of the materials.

The electrocatalytic activity of the gold nanospikes was also tested towards the hydrogen evolution reaction. Shown in Figure 3.14 are linear sweep voltammograms recorded in 1 M H\(_2\)SO\(_4\) for an evaporated gold film (black) and gold nanospikes (red). The increased electrocatalytic activity of the gold nanospikes can be seen through a shift in the onset potential of approximately 40 mV to higher potential as well as an increase in current magnitude at -0.40 V from -20.8 μA for the evaporated gold film to -150.2 μA for the gold nanospikes. This reaction follows a different mechanism to the electrocatalytic oxidation of glucose as it occurs in a potential range where premonolayer oxidation has not been observed and active sites are therefore likely to be in their elemental state. These active sites may increase the electrocatalytic activity towards hydrogen evolution as they provide exposed surface atoms which aid the adsorption, reaction and desorption of the relevant species.
Having observed the sharp metallic tips which are present at the gold nanospikes and in light of previous reports that gold can be used as an effective material for surface enhanced Raman spectroscopy (SERS), the gold nanospikes were tested for possible application in this field. Figure 3.15 shows Raman spectra recorded at both an evaporated gold film (black) and gold nanospikes sample (red) after immersion in a 1 mM Rhodamine B solution, which was used as a model compound for this application. Following this immersion period the samples were thoroughly washed in Milli-Q water to remove any loosely adhered Rhodamine B. The evaporated gold film did not perform well as a SERS substrate, not displaying the peaks which are indicative of Rhodamine B. This performance was clearly enhanced at the gold nanospikes sample, where clear peaks with good peak resolution and a high signal-to-noise ratio were recorded. The peak positions were compared with the literature and showed good agreement with previously reported spectra.[66] This activity towards SERS applications presents an interesting option for the application of the nanospikes, owing to the homogeneous distribution of gold nanospikes across extended areas which can be achieved through this synthesis route.
Figure 3.15: SERS spectra recorded for Rhodamine B on an evaporated gold film (black) and gold nanospikes (red).

3.2.4. Electroanalysis of Neurotransmitters With Gold Nanospikes

In addition to the applications presented in the previous section for the gold nanospikes, these materials were also investigated towards the electroanalysis of several neurotransmitters. This represents an important field, where an accurate method of determining the concentrations of molecules such as dopamine may aid the diagnosis of a number of neurological disorders including Parkinson’s disease, ADHD and drug addiction.\cite{67} One of the major problems with this detection is the presence of ascorbic acid and uric acid, which are known interferents in the electrochemical sensing of dopamine due to their similar oxidation potentials.\cite{68} However, in light of the shifted onset potentials for the electrocatalytic reactions shown in Section 3.2.3, this material was investigated as a possible electrocatalyst for dopamine electroanalysis.

As the intended application involves electroanalysis at physiological pH (pH 7.4), the voltammetry of the gold nanospikes was first tested in a 0.1 M phosphate buffer solution (PBS) to determine how the electrode behaves in the absence of analyte. Figure 3.16 shows the resulting voltammograms for a polycrystalline gold electrode (black) and a gold nanospike surface (red), where typical monolayer oxide formation and reduction processes dominate the response. It can be seen that the
onset potential for formation of the monolayer oxide on the gold nanospikes is located at 0.68 V, which is shifted by approximately 90 mV to less positive potentials when compared with the unmodified surface, with its onset potential at 0.77 V. This promoted oxidation process is indicative of active sites on nanostructured gold, which is also clearly seen by the quasi-reversible process at less positive potentials, with an oxidation process centred at 0.24 V and its reduction process at 0.20 V. As was discussed in the previous section for gold nanospikes in 1 M NaOH, the quasi-reversibility of this premonolayer oxidation process indicates that the oxidation product is stable at this pH, providing scope for electrocatalysis by an IHOAM type reaction. It should also be noted that the gold electrode shows responses in this region, however the magnitude and peak definition of these processes is much less than at the nanospikes sample. One further reduction process centred at -0.05 V can be observed from the voltammogram, which is attributed to the reduction of recalcitrant oxides which were formed during the forward sweep.[46]

**Figure 3.16:** Cyclic voltammograms of gold nanospikes (red) and a gold substrate (black) in 0.1 M phosphate buffer, recorded at a sweep rate of 50 mV s⁻¹.

The electrochemical behaviour of the gold nanospikes (red) and unmodified gold electrode (black) were then probed in a solution of 1 mM dopamine in 0.1 M PBS (Figure 3.17). The behaviour seen at the different surfaces is marked, with the unmodified gold electrode showing a somewhat sluggish oxidation peak (with a peak potential of 0.29 V) on the forward scan, and a small reduction process on the reverse sweep (peak potential of 0.09 V) related to the reduction of species oxidised
in the forward scan, as is typical of an EC mechanism. The gold nanospikes instead show a much greater degree of quasi-reversibility, with sharper peaks at 0.20 V and 0.15 V for the oxidation and subsequent reduction of dopamine species. This enhanced quasi-reversibility is observed by both a lowered peak-to-peak separation (50 mV as opposed to the 200 mV seen at the unmodified gold), as well as a larger relative current seen in the reduction peak. Of particular interest is the shifted onset potential of the oxidation process, which shifts from a value of 0.14 V at the unmodified gold to a value of 0.09 V at the gold nanospikes. This oxidation peak for dopamine, with its peak potential at 0.20 V, is found at a similar potential to the premonolayer oxidation peak observed in the absence of dopamine, which showed an onset potential of 0.19 V (Figure 13.6). As was discussed for the earlier examples of electrocatalysis at the gold nanospikes, the oxidation of dopamine is also closely related to a premonolayer oxidation event at the underlying gold nanospikes sample.

![Figure 3.17: Cyclic voltammograms of gold nanospikes (red) and an unmodified gold electrode (black) in 1 mM dopamine in 0.1 M phosphate buffer recorded at a sweep rate of 50 mV s⁻¹.](image)

While the IHOAM model of electrocatalysis provides an explanation for the improved electrocatalysis of dopamine, it is also known that nanostructured materials can show altered charge transfer rates to their bulk counterparts. This was studied by electrochemical impedance spectroscopy (EIS), as shown in Figure 3.18 for the gold nanospikes (red) and unmodified gold (black) surfaces for a ferricyanide/ferrocyanide solution in PBS. While a linear region of comparable
gradient is seen across both samples, relating to the diffusion controlled region, the charge transfer resistance, as given by the diameter of the semicircle, is greatly reduced at the gold nanospikes.

![Nyquist plot](image)

**Figure 3.18:** Nyquist plots for gold nanospikes (red) and an unmodified gold electrode (black) obtained in 5 mM Fe(CN)$_{6}^{3-/4-}$ in 0.1 M phosphate buffer, recorded at an amplitude of 5 mV between the frequencies of 0.1 and $10^5$ Hz.

As mentioned previously one of the main challenges in the electrochemical sensing of dopamine is the interference of other electrochemically active species such as ascorbic acid and uric acid. Figure 3.19a shows cyclic voltammograms for a gold electrode in in solutions of 0.1 M phosphate buffer with the addition of either 1 mM dopamine (red) or 1 mM ascorbic acid (black). The peak oxidation potentials for these species were found to differ by only 6 mV, demonstrating that dopamine cannot be selectively sensed in the presence of ascorbic acid using potentiometric methods at this surface. The gold nanospikes (Figure 3.19) however showed different behaviour, with an enhanced peak-to-peak separation (128 mV) between the oxidation of ascorbic acid and dopamine, indicating that a higher degree of selectivity could potentially be achieved between sensing these analytes.
Figure 3.19: Cyclic voltammograms of a gold electrode (a) and gold nanospikes (b) in solutions of 0.1 M phosphate buffer with the addition of either 1 mM ascorbic acid (black) or 1 mM dopamine (red), recorded at a sweep rate of 50 mV s\(^{-1}\).

While better separation between the oxidation of ascorbic acid and dopamine could be achieved by cyclic voltammetry, the behaviour of these materials using differential pulse voltammetry (DPV) was also investigated. This latter technique is commonly employed in electroanalytical applications as it provides a simple and rapid means of reducing the capacitive current present in cyclic voltammetry, and may provide enhanced resolution between different processes, making it better suited to the detection of dopamine at lower concentrations. Figure 3.20 shows the DPV responses of gold nanospikes in a solution containing 1 mM ascorbic acid and dopamine at increasing concentrations from 0 to 90 μM at 10 μM increments. The oxidation of these two processes shows an improved peak-to-peak resolution compared with the CV responses, with the oxidation of ascorbic acid occurring the more negative potential of ca. -0.1 V, compared with the oxidation of dopamine which is found at ca. 0.1 V. As the concentration of dopamine is increased the current magnitude of this latter peak is found to increase in response to the concentration of dopamine present. This response was found to be linear when plotted against the concentration of dopamine (Figure 3.20b), with a correlation coefficient of \( R^2 = 0.998 \) and current magnitude on the order of microamps indicating the validity of sensing dopamine in this manner. The other interesting feature from the DPV results is the response of ascorbic acid, which decreases after the successive additions of dopamine. This may be due to the homogeneous oxidative
catalysis of ascorbic acid by the oxidised dopamine product\cite{69-72} or otherwise by a form of surface fouling localised at the sites where ascorbic acid is adsorbed to the surface.\cite{73} However this process is not observed to interfere with the electroanalysis of dopamine at the gold nanospikes, showing that this surface is a promising electrocatalyst for the detection of dopamine in the presence of interferents.

**Figure 3.20:** (a) Differential pulse voltammograms of gold nanospikes in a solution of 1 mM ascorbic acid in 0.1 M phosphate buffer with the addition of 0-90 μM dopamine in 10 μM increments. Presented in (b) is a plot of the peak current at ca. 0.1 V from (a) against the concentration of dopamine present.

While the DPV results presented in Figure 3.20 show the gold nanospikes to be an interesting material for the detection of dopamine, this system was further extended by the addition of a Nafion layer. Nafion is a well-known material for use as a separator in fuel cells, which carries a negative charge in solution due to the presence of numerous sulfonate groups. This net charge provides a method of screening particular species from the underlying material, where the analyte also carries a negative charge and is therefore electrostatically repelled from the sensing surface.\cite{74} A layer of Nafion was prepared on both the unmodified gold electrode (Figure 3.21a) and the gold nanospikes (Figure 3.21b) by drop casting 10 μL from a solution of Nafion in ethanol (at 0.2 wt.%) on the electrodes and allowing to air dry. The screening of ascorbic acid is clearly evident, with a complete absence of the ascorbic acid oxidation peak (seen at ca. -0.1 V in the absence of Nafion in Figure 3.20a) and a single peak present which increases with the addition of dopamine.
The DPVs recorded at the Nafion coated polycrystalline gold electrode show a much broader oxidation peak and lower current magnitude than the Nafion coated gold nanospikes, which correlates with the reduced electron transfer kinetics observed previously for dopamine oxidation at the polycrystalline gold surface. As was found for the electrooxidation of dopamine at the gold nanospikes in the absence of Nafion, the plot of the peak current against the concentration of dopamine (Figure 3.21c) gives linear relationships for both the Nafion coated polycrystalline gold (black) or gold nanospikes (red). This plot reveals an improved linear relationship at the gold nanospikes ($R^2=0.993$) when compared with the polycrystalline gold surface ($R^2=0.967$), and the limit of detection at a signal to noise ratio of 3 ($3\sigma$) is reduced from 12 μM at the latter surface to 5 μM at the former surface. A clear increase in the sensitivity towards dopamine detection is observed from the gradients of these plots, with the Nafion coated gold nanospikes recording a sensitivity of 0.139 μA μM$^{-1}$, where the Nafion coated polycrystalline gold showed a sensitivity of 0.006 μA μM$^{-1}$.

**Figure 3.21:** Differential pulse voltammograms of a Nafion coated (a) gold electrode and (b) gold nanospikes in 0.1 M phosphate buffer with 1 mM ascorbic acid and 0-100 μM dopamine in 10 μM increments. The peak currents for (a) and (b) are plotted against the concentration of dopamine in (c) for the gold electrode (black) and gold nanospikes (red).
After observing the improved response at the Nafion coated gold nanospikes, this sample was further tested in a more complicated matrix. Shown in Figure 3.22 are DPVs recorded at Nafion coated gold nanospikes in response to 0.05 mM dopamine in 0.1 M PBS (black) and with the addition of 0.2 mM uric acid (red) and further addition of 1 mM ascorbic acid (blue). It can be seen that the oxidation of dopamine is largely unaffected by the presence of these mixtures of common interferents at analytically relevant concentrations, illustrating that the addition of a charged layer such as Nafion to a nanostructured electrode may present a viable option for the electroanalysis of a range of important analytes.

Figure 3.22: Differential pulse voltammograms of Nafion coated gold nanospikes in 0.1 M phosphate buffer with 0.05 mM dopamine (black) and the addition of 0.2 mM uric acid (red) and further addition of 1 mM ascorbic acid (blue).

3.3. Summary

Presented in this chapter is a study on the use of a chemical template to form nanostructured gold surfaces through electrodeposition. This templating method, employing lead acetate, relies on the dynamic physisorption of the lead species to particular planes of the growing electrodeposit, reducing the rate of gold electrodeposition at these sites. The unbound crystal facets, in particular the gold (111) crystal planes, are then available for the reduction of the gold salt, leading to enhanced growth in these crystal planes. This templating method has been shown to result in the growth of gold nanospikes, typically to a length of 500 nm and with
sharp tips of around 10 nm. These structures are free from the incorporation of lead or any capping agents and show promise for application in a variety of areas.

The electrochemical activity of the gold nanospikes was investigated under both acidic and basic conditions, where evidence of substantive premonolayer oxidation processes was observed by both conventional cyclic voltammetry as well as by Fourier transformed ac voltammetry. These premonolayer oxidation processes were observed well within the double layer region, and the correlation of these surface confined processes with the onset of electrocatalytic reactions was seen, in accordance with the IHOAM model of electrocatalysis.

Other possible applications were also explored, including the use of these surfaces in SERS applications and in the electroanalysis of biologically important analytes such as neurotransmitters. This reaction was also found to be coupled to a premonolayer oxidation process and establishes the link between enhancing premonolayer oxidation activity through methods such as the formation of finely nanostructured surfaces and the activity observed under commonly employed electrocatalytic reactions.

3.4. References


Chapter IV

The Electrochemical Formation of Highly Branched Platinum and Platinum-Lead Nanostructures
4.1. Introduction

4.1.1. Electrochemical Formation of Platinum Nanostructures

Owing to the importance of platinum in fields such as catalysis and electrocatalysis, the formation of platinum surfaces has been intensively studied, through methods such as chemical synthesis,[1] electrochemical synthesis,[2-‐3] galvanic replacement[4-­‐5] and evaporation[6] protocols. In particular the formation of platinum nanostructures has attracted attention, with improved catalytic and electrocatalytic activities seen due to features such as the size, shape and crystallographic orientation of the nanomaterials,[7] while at the same time reducing the amount of platinum loading required for these applications.[8]

Of the methods used to fabricate platinum nanostructures the electrodeposition of platinum has featured strongly, especially as the nanostructures are adhered to the underlying support, leading to more reproducible surfaces than drop-cast nanomaterials formed through other methods. As was discussed previously in the case of gold, platinum electrodeposition can be performed in a number of ways depending on the desired nanostructures. The simplest method is to electrodeposit on unmodified electrodes such as glassy carbon,[9-­‐11] highly oriented pyrolytic graphite (HOPG),[12-­‐14] semiconducting materials (including titanium nitride,[15] tungsten monocarbide,[16] indium tin oxide[17] and fluorine-doped tin oxide[2]) or sputtered metal films.[18-­‐19] This is often performed from a deposition bath including a platinum salt and supporting electrolyte, with the electrodeposition performed by the application of a fixed current or potential, by cyclic voltammetry or by pulsed current or potential methods. The various electrodeposition parameters within these methods then controls the size, shape, density and growth mode of the electrodeposited nuclei. For example, while quasi-spherical nanostructures are commonly formed through potentiostatic reduction of a platinum salt,[20-­‐21] by utilising a pulsed potential deposition protocol platinum nanoflowers could be attained.[22]

These electrodeposition protocols have also been extended to surfaces modified with nanostructured supports prior to electrodeposition. One of the more common
supports are carbon nanotubes, either in the form of single (SWNTs) or multi-walled nanotubes (MWNTs). Such nanostructures provide suitable materials for electrodeposition, with the nanotubes acting as conductive, high surface area supports for the electrodeposition of small platinum nanoparticles for use in electroanalytical or fuel cell applications. The preparation of the carbon nanotubes has been reported either on the electrode surface by the use of chemical vapour deposition,[23-24] or by drop-casting from a suspension of preformed, isolated nanotubes.[25] The electrodeposition of platinum on nanotubes has also been reported in the case of a surface modified by carbon nanotubes and TiO₂ nanotubes.[24] Platinum electrodeposition has also been investigated on electrodes modified with a range of polymers, such as polyaniline,[26-27] polyindole,[28] polyyamine,[29] Nafion[30] and Nafion/MWNT[31] surfaces.

The use of physical templates is also reported in the electrodeposition of platinum, often to obtain nanowires. Amongst these templates anodised aluminium oxide (AAO) templates have found popularity, and similarly to porous polycarbonate templates,[32] they can be used to restrict the electrodeposition to within confined channels and therefore result in the electrodeposition of nanowires after the removal of the template.[33-34] However one complication with this method is that while films may be prepared by evaporating a conductive surface on the underside of the AAO template prior to electrodeposition, the modification of an existing surface with nanowires using this method is difficult. Polystyrene and polycarbonate spheres offer other candidates for templated electrodeposition, where a layer (or layers) of these spheres are self assembled on the electrode and restricts electrodeposition to the voids between the spheres.[35-37] Similarly to the AAO templates these spheres may then be removed by chemical dissolution. Physical templating for platinum electrodeposition can also be achieved at surfaces modified with polymers, including polyaniline[38] and Nafion.[39] While these cases are similar to those discussed previously for electrodeposition on modified electrodes, a distinction is made in these instances as the supporting polymer is removed after the electrodeposition step. Lithographic methods can also be used to confine the electrodeposition of platinum to defined regions. This has been reported in the case of both photolithography[40] and electron beam lithography,[41] however
these methods are not commonly reported as a method of templating platinum electrodepositions.

The formation of nanostructured platinum can also be performed using chemical templates. These species are included in the electrodeposition bath and alter the electrodeposition by either adsorbing to particular exposed facets on the growing electrodeposit[42] or by altering the speciation of the platinum salt. Common examples of this kind include the addition of citrate,[43-44] halide or sulphate anions,[42,45] lead acetate,[46] ethylene glycol[47-49] and polyethylene glycol.[46] The use of such additives can also help facilitate electrodeposition on modified surfaces, for example the addition of ammonia resulted in the ligand exchange of PtCl$_6^{2-}$ to Pt(NH$_3$)$_6^{4+}$, which overcame the electrostatic repulsion of the former salt with a Nafion membrane coating the electrode surface.[30] Electrodeposition from eutectic solvents has also been explored recently, with the electrodeposition of platinum nanoflowers achieved by electrodeposition in the presence of choline chloride and urea.[50] While this reaction was noted as being sensitive to the deposition temperature of 80 °C, this method of synthesising nanostructured materials may be an area of future research interest. Another important class of chemical templates used for the electrodeposition of platinum are liquid crystals, which self assemble in solution into channels and restrict the area available for electrodeposition. This templating method has been used to synthesise mesoporous platinum electrodeposits with a regular arrangement of pores.[51-55]

Another species added to modify platinum electrodepositions are lead salts, as illustrated by the formation of platinum black. This was discovered by the inclusion of a number of different heavy metal salts during platinum electrodeposition in order to improve the adherence of platinum to the electrode surface.[56] While many variations on this electrodeposition were investigated including the concentration and speciation of the plating bath as well as the electrodeposition method and parameters, the physical characterisation of the materials with methods such as electron microscopy and X-ray photoelectron spectroscopy has not been widely reported.
The formation of platinum-lead surfaces has since received much attention, beginning with the altered electrocatalytic behaviour of platinum surfaces after modification of the surface by Pb underpotential deposition.\textsuperscript{[57-58]} This has been extended to the study of bulk Pt-Pb materials, using methods such as chemical co-reduction,\textsuperscript{[59]} the electrodeposition of Pb on Pt nanostructured supports\textsuperscript{[60]} or by the co-reduction of Pt and Pb during electrodeposition.\textsuperscript{[61]} These Pt-Pb materials have demonstrated promising electrocatalytic behaviour towards a variety of important electrochemical reactions including methanol oxidation, formic acid oxidation and glucose oxidation.\textsuperscript{[59, 62-64]} This increased activity is often ascribed to the exposed Pb atoms limiting the amount of surface poisoning occurring on the Pt surface, especially the formation of CO\textsubscript{ads}.\textsuperscript{[58]}

\textbf{4.1.2. Research Aims}

Having investigated the shape directing effect of lead acetate on the electrodeposition of gold in Chapter III, attention is now turned to its influence on the electrodeposition of platinum. In particular the promotion of nanostructured growth is desired, both for the activity that it may show across a number of fields as well as providing a method to minimise the amount of platinum loading, as may be required in applications such as fuel cells.

The electrodeposition of platinum and the influence of lead acetate on the deposit will be investigated in this chapter, especially as the electrochemical behaviour of the materials may provide insights into the structure and properties of the nanomaterials. This will involve both conventional dc cyclic voltammetry as well as FT-ac voltammetry, which has not yet been reported at platinum. As active site responses have previously been recorded at platinum surfaces by cyclic voltammetry, the investigation of the materials by FT-ac may provide a clearer picture of the electrochemical behaviour of these active sites. The involvement of these active sites in electrocatalysis through the IHOAM model of electrocatalysis will also be investigated.
4.2. Results and Discussion

4.2.1. Electrochemical Formation of Platinum and Platinum-Lead Nanostructures

The electrodeposition of platinum was investigated from a solution containing 8 mM $K_2PtCl_6$ with 0.1 M HCl on glassy carbon plates. These substrates were chosen in order to provide a reproducible and easy to handle carbon-based electrode to both study the electrodeposition of platinum in the presence of lead acetate and to electrochemically characterise the materials. The electrodeposition of platinum-based nanomaterials on a variety of carbon nanostructures has been reported, including graphene and carbon nanotubes.[31, 65] These nanostructures were used as high surface area supports for the electrodeposition of small platinum nanostructures in order to minimise the surface loading of platinum and increase the mass activity of platinum for electrocatalytic reactions. As the purpose of this study was to investigate the growth and electrochemical behaviour of platinum and platinum-lead nanostructures this work was confined to glassy carbon supports, although this work could easily be extended onto supports such as graphene and carbon nanotubes.

The electrochemical behaviour of the glassy carbon in the electrodeposition solutions is presented in Figure 4.1a. Shown in black is the cyclic voltammogram of a glassy carbon electrode in 8 mM $K_2PtCl_6$ with 0.1 M HCl. The sweep begins at 0.5 V and remains featureless until the onset of $PtCl_6^{2-}$ reduction at ca. 0.27 V. This process presents a broad peak with a peak potential at 0.01 V, after which the current magnitude decreases as the process becomes diffusion limited. A sharp reduction peak can be observed near the lower limit of the scan at -0.18 V which is attributed to the evolution of hydrogen at the electrodeposited platinum nuclei formed during this first scan, which is expected using a background electrolyte of 0.1 M HCl. Upon reversing the scan at -0.2 V no additional peaks can be detected, indicating that the reduction of the platinum salt is not a reversible process.
Figure 4.1: (a) Cyclic voltammograms of a glassy carbon electrode in a solution containing 8 mM K$_2$PtCl$_6$ in 0.1 M HCl with (red) or without (black) the addition of 0.05 mM Pb(CH$_3$COO)$_2$. (b) Cyclic voltammograms of electrodeposited platinum nanostructures in 0.1 M HCl in the absence (black) or presence of 0.5 mM Pb(CH$_3$COO)$_2$ (red). All scan rates were at 50 mV s$^{-1}$.

The electrochemical behaviour of the electrode/electrolyte interface was then studied in the presence of 0.05 mM Pb(CH$_3$COO)$_2$ (Figure 4.1a, Red curve). At higher potentials (between ca. 0.5 V and 0 V) this displayed very similar behaviour to the solution without lead present, with a broad reduction peak observed after an onset potential of ca. 0.27 V, demonstrating that the electrodeposition of platinum in this region is not noticeably altered by the inclusion of lead acetate in the deposition solution. However while a peak potential was observed at 0.01 V in the absence of lead, a small inflection is instead seen at the same potential in the presence of lead acetate, after which a further increase in the current magnitude occurs until reaching a peak potential at ca. -0.03 V. Noticeably the current magnitude below this region is also at increased when lead acetate is present, indicating that the rate of platinum electrodeposition is higher in the presence of lead acetate at potentials lower than ca. 0.03 V.

The electrodeposition of lead was also investigated in the absence of K$_2$PtCl$_6$ (Figure 4.1b). These voltammograms were recorded in a more concentrated solution of lead acetate at nanostructured platinum surfaces (synthesised by electrodepositing at -0.05 V for 600 s on a glassy carbon electrode from a solution of 8 mM K$_2$PtCl$_6$ in 0.1 M HCl) in order to more clearly observe the electrochemical
behaviour of lead acetate in this potential range. While the voltammogram recorded in 0.1 M HCl alone (black curve) was relatively featureless in this region, the addition of 0.5 mM lead acetate (red curve) shows a reduction peak centred at 0.37 V along with an oxidation peak centred at 0.47 V. This quasi-reversible process is assigned to the underpotential deposition (UPD) of lead on the platinum surface,[66] indicating that the UPD of lead on platinum accompanies the electrodeposition of platinum in Figure 4.1a.

Having observed the UPD of lead in this region, the increased rate of electrodeposition at potentials below 0.03 V in the presence of K₂PtCl₆ (Figure 4.1a) is attributed to the reduction of both platinum and lead. It has been widely reported that the galvanic replacement of lead with platinum can be achieved,[67-68] where the difference in the standard reduction potentials of the relevant metal species provides the driving force for the reaction.[59] This in situ replacement of metallic lead with platinum may disrupt the surface of the growing electrodeposit, increasing the surface roughness of the material and allowing for the growth of platinum through both galvanic replacement and direct electrodeposition. This increased rate of platinum reduction is also consistent with the increased magnitude of hydrogen evolution at the lower limit, with a current magnitude at -0.2 V of -122 μA for the sample in the presence of lead as opposed to -72 μA in the absence of lead acetate.

Electrodeposition was then performed from solutions containing 8 mM K₂PtCl₆ and 0.1 M HCl with and without the addition of 0.05 mM Pb(CH₃COO)₂. These electrodepositions were performed at a fixed potential of -0.05 V, as this potential was just below the peak potential for platinum reduction in the presence of lead acetate and significant differences could be observed between the cyclic voltammograms of the two solutions at this potential (Figure 4.1). SEM imaging was performed on these samples after electrodepositing for 600 s (Figure 4.2). As can be seen from Figure 4.2a, the platinum electrodeposited in the absence of lead acetate formed quasi-spherical structures, with an average size of approximately 400 nm. Amongst these nanostructures are a number of smaller particles (approximately 180 nm in diameter) which may have formed through the progressive nucleation of platinum on the glassy carbon surface. While most of the structures are isolated
from each other, it can be seen that several particles are connected which is the result of the particles nucleating close to each other and growing until they merge into larger structures. The inset of Figure 4.2a shows a higher magnification of a platinum nanostructure, where the structure is seen to be quasi-spherical in nature, with the surface consisting of a slightly roughened texture on a number of small pyramid-like protrusions.

**Figure 4.2:** SEM images of samples electrodeposited at -0.05 V for 600 s from a solution of 8 mM K₂PtCl₆ and 0.1 M HCl in the absence (a) or presence (b) of 0.05 mM Pb(CH₃COO)₂.

Upon introduction of lead acetate into the deposition solution the electrodeposited surface changes dramatically (Figure 4.2b). While the growth again occurs at isolated nuclei with a number of connected structures present, these growths are larger than was seen in the absence of lead, with typical sizes of approximately 1 µm. However the largest difference is the morphology of the deposits, which shows dendritic-like growth. This creates a large number of exposed tips on the surface, with these features often appearing below 10 nm. Interestingly these sub-10 nm features lie in a size range which has been reported to be beneficial for electrocatalytic and catalytic applications.[69-70] In order to determine the chemical composition of the materials XPS was then performed. Figure 4.3a shows the spectra recorded in the Pt 4f region for samples deposited under the conditions listed above in the absence (black) or presence (red) of lead acetate. As can be seen the peak positions of these spectra occur at the same binding energies, with binding energies of 71.8 eV and 75.1 eV corresponding to the 4f₇/₂ and 4f₅/₂ orbitals of Pt,
respectively.[71-72] The Pb 4f region was also scanned, as shown in Figure 4.3b. While the sample deposited in the absence of lead acetate (black) shows no peaks, confirming the purity of the sample, the electrodeposited surface grown in the presence of lead (red) shows peaks at 137.4 eV and 142.3 eV, which are attributed to the 4f_{7/2} and 4f_{5/2} orbitals of PbO, respectively.[73] It should be noted that the oxidation of the Pb may have occurred after the removal of the sample from the electrodeposition solution rather than the electrochemical formation of PbO. While these peaks clearly indicate the presence of lead on the surface, a very low intensity was recorded as seen by the low signal-to-noise ratio. Comparison of the peak areas for the Pt 4f and Pb 4f peaks, after compensation for the scattering factors of the different elements, estimates the surface ratio of lead in the electrodeposited material is 2.5 %. This is a very low amount of lead, however it is consistent with the cyclic voltammograms presented in Figure 4.1, where the bulk electrodeposition of platinum occurs alongside the UPD of lead, hence the high amount of platinum seen by XPS. As discussed previously the galvanic replacement of lead with platinum may also influence this low surface concentration of lead, as this replacement reaction is likely to have occurred in the brief time between the end of the electrodeposition and the cleaning of the surface under a stream of Milli-Q water. Confirmation of the concentration of lead was sought by EDX, however any lead present was below the detection limit of the instrument, which is known to be less surface sensitive than XPS.[74]

![Figure 4.3](image)

**Figure 4.3:** XPS spectra for the Pt 4f region (a) and Pb 4f region (b) for nanostructured platinum electrodeposited in the absence (black) or presence (red) of Pb(CH₃COO)₂.
The crystallographic orientation of the platinum and platinum-lead surfaces was probed by XRD (Figure 4.4). The contribution from the underlying glassy carbon substrate, which appears as amorphous humps, was subtracted from the patterns, and the results of the platinum surface (black) and platinum-lead surface (red) were normalised with respect to the intensity of the platinum (111) planes. The presence of lead does not cause any significant differences in these patterns, which was surprising given the noticeably altered morphology of the surfaces. However, these results demonstrate that the morphology and crystallographic orientation of the surface are two distinct properties, and the lead acts to change the shape of the electrodeposit while maintaining its crystallographic orientation, as seen by XRD. Both of these samples display a polycrystalline nature, with a predominant (111) peak but with significant contributions from the (200) and (220) planes as well. The absence of peak shifts by the inclusion of lead in the material is consistent with previous studies on platinum and platinum-lead nanomaterials.[75-76] This was also reported for platinum-lead nanostructures with an estimated 41% loading of lead[59] which is significantly higher than the lead surface coverage determined in this work (2.5%).

![Figure 4.4: XRD patterns for nanostructured platinum samples electrodeposited in the absence (black) or presence (red) of Pb(CH$_3$COO)$_2$.](image)

The growth of the samples was further studied by conducting time dependent electrodeposition (Figure 4.5), with the electrodeposition terminated after 150 s (Figures 4.5a-b), 300 s (Figures 4.5c-d) and 600 s (Figures 4.5e-f) for samples deposited in the absence (Figures 4.5a,c,e) or presence (Figures 4.5b,d,f) of lead.
acetate. For the platinum electrodeposited in the absence of lead a range of particle sizes can be observed after electrodeposition for 150 s (a), with typical particle sizes lying between 80 nm to 260 nm. While there is some degree of heterogeneity to these particle sizes, the majority of particles are approximately 200 nm in diameter. Increasing the electrodeposition time to 300 s results in the growth of these particles, which are generally of a consistent size of approximately 240 nm. The growth of several particles in close proximity can be seen to occur, resulting in the connectivity of these particles. These trends are again observed after electrodepositing for 600 s, where the typical particle size is approximately 410 nm. Importantly the morphology of the deposits is maintained across all times studied, suggesting that similar but smaller structures may be obtained at shorter time points.

This study was also conducted in the presence of lead acetate, and the sample deposited under these conditions for 150 s is presented in Figure 4.5b. Here a typical size of approximately 500 nm is observed, however a greater degree of size variation is seen at this sample than in the absence of lead, with particles as large as 900 nm present. When the electrodeposition is extended to 300 s (Figure 4.5d) this size distribution is again evident, with particles ranging from approximately 80 nm to 500 nm in size, with a typical size of around 400 nm. A greater coverage of particles can also be seen across the sample when compared with the shorter electrodeposition time, which in addition to the range of particle sizes present suggests that the electrodeposition proceeds through a progressive nucleation process, where new nuclei are deposited whilst the existing particles continue to grow. This heterogeneous size distribution is continued at 600 s (Figure 4.5f), with particles as small as 120 nm alongside growths as large as 1.7 µm. At all deposition times larger particles are observed when lead acetate is included in the deposition solution, which is consistent with the increased rate of electrodeposition at -0.05 V.

Also of note is the formation of similar particle morphologies for all deposition times in the presence of lead acetate (Figures 4.5b,d,f). This indicates that while the size and coverage of particles may be controlled by varying the electrodeposition time, the growth directing effect of the lead acetate can be achieved even at
relatively short deposition times, and future work on the formation of similarly branched but smaller structures may be of interest.

Figure 4.5: SEM images of samples electrodeposited at -0.05 V from a solution containing 8 mM K$_2$PtCl$_6$ in 0.1 M HCl in the absence (a,c,e) or presence (b,d,f) of 0.05 mM Pb(CH$_3$COO)$_2$ for 150 s (a-b), 300 s (c-d) and 600 s (e-f).
The effect of the deposition potential was also studied (Figure 4.6), with electrodepositions performed in the absence (Figure 4.6a) or presence (Figure 4.6b) of lead acetate for 150 s at the lower potential of -0.15 V. This potential was chosen as it corresponded to a potential just prior to the evolution of hydrogen at the surface, which was undesirable as hydrogen evolution during electrodeposition may influence the morphology of the electrodeposits (as will be addressed in Chapter V). At this lower potential smaller structures are observed to form, with larger particles of approximately 110 nm in the absence of lead acetate or 390 nm in the presence of lead acetate. Also of note are the greater distribution of particle sizes, with a large number of smaller particles of around 60 nm for Figure 4.6a or 110 nm for Figure 4.6b. However similar structures are obtained at this lower potential to those observed at -0.05 V, with quasi-spherical particles formed in the absence of lead and branched structures in the presence of lead. Electrodeposition at this lower potential therefore provides another method of controlling the particle sizes of the electrodeposited material, while maintaining the shape direction property of the lead acetate.

![Figure 4.6: SEM images showing samples electrodeposited from a solution of 8 mM K$_2$PtCl$_6$ and 0.1 M HCl in the absence (a) or presence (b) of 0.05 mM Pb(CH$_3$COO)$_2$ at a potential of -0.15 V for 150 s.](image)

Whilst glassy carbon provides a facile surface for the growth of the platinum and platinum-lead materials, electrodeposition was also performed on indium tin oxide (ITO) films to investigate if the underlying electrode significantly influenced the morphology of the deposit. Shown in Figure 4.7 are electrodepositions performed
from solutions in the absence (Figure 4.7a,c) or presence of 0.05 mM Pb(CH3COO)$_2$ (Figure 4.7b,d). In the former case platinum can be observed to form quasi-spherical shapes similar to those observed on glassy carbon, however the particles display a more bush-like growth, with some formation of particles on the initial growths visible. The inclusion of lead acetate in the deposition solution causes the growth of isolated dendritic structures, also similar to those observed on glassy carbon substrates (Figure 4.2). It can be seen from Figures 4.7a-b as well as the lower magnification images in Figures 4.7c-d that the electrodeposited materials cover the surface at a relatively high density, and are of similar sizes regardless of the presence of lead acetate. This is attributed to the altered nucleation process at the underlying substrate compared with the glassy carbon substrates studied previously, not only as the materials are different but as the morphology of the underlying ITO substrate consists of a high number of small grains which then make up domains on the surface, whilst the glassy carbon substrates are relatively smooth. These differences in morphology may alter nucleation behaviour of the particles as well as the mobility of electrodeposited adatoms on the surface, favouring a progressive growth mode.

The electrodeposited platinum and platinum-lead samples were also investigated by TEM (Figures 4.7c-d, respectively) after they were removed from the ITO surface by sonication. The quasi-spherical nature of the platinum materials is again observed, with a fine texture visible on the outer section of the particles and the growth of smaller particles on larger particles. The platinum-lead surface was however confirmed to be dendritic in nature, forming a large number of branches which in turn consist of fine tips. The similarity between these materials and the samples electrodeposited on glassy carbon illustrate that this dendritic growth is not the result of the underlying substrate, but is rather the direct influence of lead acetate on the growing electrodeposit. This adds further support to the hypothesis that the underpotential deposition of lead on platinum (Figure 4.1b) increases the formation of branched structures by disrupting the platinum surface during deposition.
Figure 4.7: SEM images of samples electrodeposited on indium tin oxide substrates at -0.05 V for 600 s from a solution of 8 mM $K_2PtCl_6$ in 0.1 M HCl in the absence (a,c) or presence (b,d) of 0.05 mM Pb(CH$_3$COO)$_2$. TEM images of these samples after sonication from the ITO surface are shown in (e) and (f) for samples deposited in the absence or presence of Pb(CH$_3$COO)$_2$, respectively.
4.2.2. Electrochemical Behaviour of the Platinum and Platinum-Lead Nanomaterials

The electrochemical behaviour of the electrodeposited materials was then investigated, with the cyclic voltammograms of platinum electrodeposited in the absence of lead acetate for 150 s (green), 300 s (blue) and 600 s (red) as well as a platinum electrode (black) shown in Figure 4.8a. These scans originate at -0.25 V which is just within the hydrogen evolution region, and upon the forward scan the re-oxidation of hydrogen is observed at ca. -0.22 V. The desorption of hydrogen from the platinum surface can then be seen, with a broad oxidation peak at -0.06 V, after which no processes were observed within the double layer region prior to the onset of the monolayer oxidation formation at ca. 0.73 V. The reverse scan showed the reduction of this monolayer with a peak potential of 0.48 V, after which the adsorption of hydrogen is observed at an onset potential of ca. 0.08 V, with an inflection at -0.06 V and a peak at -0.14 V before the onset of hydrogen evolution at ca. -0.18 V. The electrochemically active surface areas of the electrodeposited materials were calculated from the charge associated with the adsorption of hydrogen in this region. These calculations, based on a value of 210 µC cm\(^{-2}\), indicate that the surface areas of the materials increase from 0.27 cm\(^2\) for deposition at 150 s to 0.58 cm\(^2\) at 300 s and finally 0.71 cm\(^2\) at 600 s.

Figure 4.8: Cyclic voltammograms recorded in 1 M H\(_2\)SO\(_4\) at a platinum electrode (black) and Pt nanostructures electrodeposited at -0.05 V for 150 s (green), 300 s (blue) and 600 s (red) in the absence (a) or presence (b) of 0.05 mM Pb(CH\(_3\)COO)\(_2\), recorded at a sweep rate of 100 mV s\(^{-1}\).
The voltammetric behaviour of the samples electrodeposited in the presence of lead acetate was also investigated, with the samples electrodeposited for 150 s (green), 300 s (blue) and 600 s (red) along with a polycrystalline platinum electrode (black) shown in Figure 4.8b. These results show clear differences from the voltammograms in Figure 4.8a, particularly in the hydrogen region. The oxidation of the hydrogen reduced at the initial potential of -0.25 V can be seen at -0.21 V, with the desorption of hydrogen seen by peaks at -0.12 V and -0.05 V and an inflection at 0.04 V. While the double layer region was found to be absent of peaks for the platinum electrodeposited without lead, in this case a peak can be observed with an onset potential of 0.47 V and a peak potential of 0.59 V. This peak is attributed to the premonolayer oxidation of platinum, showing a shift in onset potential of approximately 260 mV to a lower potential when compared with the onset of the monolayer oxide formation at ca. 0.73 V. On the reverse scan this monolayer oxide is stripped in a broad process with a peak potential of 0.51 V, with the adsorption of hydrogen beginning at 0.11 V and marked by an inflection at 0.02 V and peaks at -0.08 V and -0.16 V prior to the onset of hydrogen evolution at -0.22 V. The adsorption and desorption of hydrogen shows much sharper peaks than the sample electrodeposited without lead acetate, indicating that the surface is more active towards these processes than the relatively sluggish processes occurring in Figure 4.8a. Previous studies have been undertaken at single crystal electrodes in this region, which attribute the peaks at lower potential to the adsorption and desorption of hydrogen from the Pt (110) planes, while the peaks at a higher potential are related to the Pt (100) planes and a broad background current throughout this region was attributed to processes on the Pt (111) surface.\[78] While the determination of the relative proportion of the exposed crystal planes has previously been attempted based on the adsorption of hydrogen, the analysis was complicated by the overlap of peaks from different single crystal electrodes and required additional information in the form of the oxidation of irreversibly adsorbed germanium.\[79] Due to the complications involved in this method and the assumptions which must be made such a determination was not performed on the electrodeposited platinum and platinum-lead nanostructures formed in this work.
The electrochemically active surface area of the platinum-lead samples was also calculated from the adsorption of hydrogen, as discussed previously. The surface area was found to increase from 1.03 cm² after electrodeposition for 150 s to 2.25 cm² at 300 s and finally 3.15 cm² at 600 s. These values are significantly larger than the samples electrodeposited without lead acetate, with the largest surface area for these samples of 0.71 cm² at 600 s. These results are consistent with the SEM images presented in Figure 4.5, with the highly branched platinum-lead sample indicating a greater surface area than the quasi-spherical structures formed in the absence of lead acetate.

The electrochemical behaviour of the electrodeposited platinum samples was also tested using FT-ac voltammetry. While the upper potential limit was maintained at the same value used for the dc voltammetry, the lower limit was changed to a value of 0.2 V. This was chosen as the large amplitude of the applied sinusoidal perturbation (100 mV) caused the lower potential at 0.2 V to briefly step to 0.1 V, which lies very close to the onset of hydrogen adsorption seen by dc voltammetry (onset potential of 0.08 V). Even at this lower limit of 0.2 V a sharp decrease in the current magnitude can be observed at the harmonic responses in Figure 9, which is attributed to the adsorption and desorption of hydrogen from the surface. Unfortunately when this lower limit was reduced the intense response created a ringing effect in the signal which did not allow careful examination of the harmonic responses.
Figure 4.9: FT-ac voltammogram recorded in 1M $H_2SO_4$ for a nanostructured Pt sample electrodeposited at -0.05 V for 600 s from a solution containing 8 mM $H_2PtCl_6$ and 0.1 M $HCl$. Data was recorded at a sweep rate of 40.98 mV s$^{-1}$ with an applied sinusoidal perturbation of 100 mV at a frequency of 20.66 Hz.

The FT-ac voltammogram for platinum electrodeposited in the absence of lead acetate is shown in Figure 4.9, where a similar DC response for potentials above 0.2
V can be seen compared with the dc cyclic voltammetry (Figure 4.8a). As was discussed in Chapter III for the case of gold, this platinum surface also showed a large degree of capacitance, with significant capacitive contributions observed in the first and second harmonic responses. This contribution is lessened in the third harmonic response and is negligible in the fourth harmonic. Aside from the sharp initial decay due to the adsorption of hydrogen on the platinum, as discussed before, peaks can clearly be observed within the double layer region, with two related peaks visible at 0.36 V and 0.44 V, as well as a broad peak with a peak potential of 0.65 V. A minimum value can be observed at approximately 0.79 V, followed by a steady increase in current with a small peak located at ca. 0.93 V. This increased current at potentials higher than 0.79 V is attributed to the onset of the monolayer oxide, which was observed by dc voltammetry at 0.73 V. While a number of peaks can be clearly identified from the fourth harmonic response, these processes are much broader than observed in the case of gold, and the presence of well-defined multiplet peaks cannot be seen. However this result does suggest the presence of premonolayer oxidation well within the double layer region, with an onset potential shifted more than 440 mV lower than the onset of the monolayer oxide formation. Although the morphology of the platinum structures is quasi-spherical, the presence of these active sites is not unexpected as the premonolayer oxidation of platinum has been observed by previous dc cyclic voltammetry studies,[80-82] and the finely textured surface presents a surface where active sites may be located. The FT-ac voltammetry of the platinum-lead surface is presented in Figure 4.10, where capacitive behaviour again dominates the response until the fourth harmonic. Similarly to the electrodeposited platinum surface the adsorption of hydrogen is present at the lower potential limit, decreasing until approximately 0.3 V. Several peaks can be observed within the double layer region, located at 0.41 V and 0.51 V. The current then plateaus until a minor peak at 0.76 V, in the region where the monolayer oxide formation was observed by dc voltammetry. Interestingly further peaks are observed after the onset of this monolayer oxide, with peaks located at 0.99 V, 1.16 V and 1.23 V, which are attributed to hydroxide adsorption processes. Interestingly, while this oxidation is also observed in the dc voltammogram of the platinum electrodeposited in the absence of lead (Figure 4.8a), it does not appear in the FT-ac voltammogram of this sample. A closer study of the behaviour of this
monolayer oxide formation process is required, as this work represents the first study of platinum by FT-ac voltammetry.

**Figure 4.10:** FT-ac voltammogram recorded in 1M H₂SO₄ for a nanostructured Pt sample electrodeposited at -0.05 V for 600 s from a solution containing 8 mM H₂PtCl₆ and 0.1 M HCl with 0.05 mM Pb(CH₃COO)₂. Data was recorded at a sweep rate of 40.98 mV s⁻¹ with an applied sinusoidal perturbation of 100 mV at a frequency of 20.66 Hz.
As the comparison of these FT-ac voltammograms is complicated by the broadness of the peaks, the fourth harmonic responses for the platinum (black) and platinum-lead (red) surfaces are overlayed in Figure 4.11. Here it can be more easily observed that the platinum nanostructures show a greater extent of premonolayer oxidation at lower potentials, with peaks observed at 0.36 V and 0.44 V at a significantly higher magnitude than the peak observed at 0.40 V for the platinum-lead sample. However this latter sample still shows significant premonolayer oxidation activity, with a broad peak at 0.51 V in a region of minimal activity at the platinum sample. For comparison the response recorded at an unmodified glassy carbon surface is also shown (blue), however the magnitude of the response is negligible and demonstrates that the responses obtained at the electrodeposited surfaces are the result of the electrodeposited platinum or platinum-lead, as opposed to the underlying electrode surface.

![Figure 4.11](image)

**Figure 4.11:** Comparison of the fourth harmonic responses obtained from Figure 4.9 and Figure 4.10, with the response for the platinum nanostructures in black and the response for the platinum-lead nanostructures in red, showing the forward (a) and reverse (b) scans. The fourth harmonic responses recorded at an unmodified glassy carbon electrode are shown in blue.

The reverse sweep also shows a number of interesting features, with the platinum-lead sample showing a steady but large increase from approximately 1.1 V until reaching a peak at 0.61 V, before forming a peak at 0.50 V at a similar potential to the peak at 0.51 V which was observed on the forward scan. This peak is also observed on the platinum sample, although the magnitude is not as high as the platinum-lead sample. A further peak is observed at 0.38 V on the platinum sample,
which is at a slightly more positive potential than observed in the forward scan (0.36 V). The broad increase observed on the reverse sweep for both samples is unexpected, possibly suggesting that rearrangement of the surface has occurred as the potential is swept to the upper potential limit of 1.3 V, especially as the sinusoidal perturbation applied to the dc potential ramp increased the effective upper limit of the scan to 1.4 V. While further studies on the FT-ac voltammetry of platinum are required in order to determine the nature of this broad process on the reverse scan, the forward scan in particular provides a clear indication of the active site behaviour exhibited by the platinum and platinum-lead surfaces.

4.2.3. Electrocatalytic and SERS Activity of the electrodeposited platinum and platinum-lead nanomaterials

After investigating the active site behaviour of the electrodeposited nanomaterials in 1 M H₂SO₄, the electrocatalytic oxidation of 1 M methanol in 1 M H₂SO₄ was tested at these surfaces. Shown in Figure 4.12a is the response of a polycrystalline platinum electrode (black) and platinum electrodeposited in the absence of lead for 150 s, 300 s and 600 s. As was discussed in Section 4.2.2, the electrodeposition of platinum for extended times lead to increases in the electrochemically active surface area of the materials, and so the methanol oxidation data has been normalised for the electrochemically active surface area, which allows for comparison between the specific activities of the materials. These scans were initiated at 0 V, where small features relating to the adsorption and desorption of hydrogen from the surfaces are observed. The forward scans then continue until an onset potential for methanol oxidation is observed at approximately 0.47 V, reaching a peak potential at ca. 0.69 V. A decrease in the rate of methanol oxidation is then observed at potentials positive of this peak, as the formation of the monolayer oxide limits the sites available for methanol oxidation. Once this oxide is stripped on the reverse scan a peak appears at ca. 0.53 V, which has been reported as the oxidation of organic species formed in the forward scan including COads.[83] However this process was recently readdressed and it was found that the peak currents in both the forward and reverse scans were related to the oxidation of
The specific activity of the commercially available platinum electrode (black) is almost identical to the activity of the platinum electrodeposited for 150 s, with peak values of 17.8 µA cm\(^{-2}\) and 18.7 µA cm\(^{-2}\), respectively. However, this activity increases rapidly at samples electrodeposited for 300 s and 600 s, recording peak values of 36.3 µA cm\(^{-2}\) and 45.8 µA cm\(^{-2}\), respectively. This increase in electrocatalytic activity may be related to an increase in the density of active sites, with the sample electrodeposited for 600 s showing a relatively broad premonolayer oxidation process at ca. 0.44 V by FT-ac voltammetry (Figure 4.9). This active site response appears at a similar potential to the onset potential of methanol oxidation (0.47 V), confirming earlier findings that the oxidation of methanol on platinum under acidic conditions is mediated by and IHOAM reaction.

**Figure 4.12:** Cyclic voltammograms recorded in 1 M methanol in 1 M H\(_2\)SO\(_4\) at a sweep rate of 50 mV s\(^{-1}\) for a platinum electrode (black) and platinum nanostructures electrodeposited at -0.05 V for 150 s (green), 300 s (blue) and 600 s (red) in the absence (a) or presence (b) of 0.05 mM Pb(CH\(_3\)COO)\(_2\), recorded at a sweep rate of 50 mV s\(^{-1}\).

The electrocatalytic oxidation of methanol was also investigated for the platinum-lead surfaces, as shown in Figure 4.12b. Here a clear difference exists between the specific activity of the commercial platinum electrode (black) and the sample electrodeposited for 150 s (green), increasing from 17.8 µA cm\(^{-2}\) to 41.9 µA cm\(^{-2}\), respectively. Further increases are then seen for longer electrodeposition times, with the 300 s sample showing an activity of 93.7 µA cm\(^{-2}\) and the 600 s sample with a peak activity of 155.4 µA cm\(^{-2}\). This latter value is greater than three times the specific activity of the platinum sample electrodeposited for the same length of time in the absence of lead acetate, showing that the inclusion of lead acetate during the...
electrodeposition creates a more active electrocatalyst for methanol oxidation. While this catalytic process begins at a similar potential (0.49 V) to that found at the platinum surface, a much greater premonolayer oxidation peak was observed by FT-ac voltammetry for the platinum-lead surface in this potential range (Figure 4.11), with a broad peak observed at ca. 0.51 V. While a premonolayer oxidation peak was observed just prior to the onset of methanol oxidation on the electrodeposited platinum surface, it appears that the oxidation of methanol at platinum is more sensitive to the location of the premonolayer oxidation peaks than was found in the earlier study of gold nanostructures (Chapter III). This may be related to the adsorption of methanol being somewhat sluggish at the potential where premonolayer oxidation in this region was observed for the platinum surface, whereas this adsorption may be enhanced at the more positive potential where the active site response is recorded on the platinum-lead surface. Importantly the crystallographic nature and surface chemistry of the materials is closely comparable (as indicated by the XRD patterns in Figure 4.4 and the XPS spectra in Figure 4.3), indicating that these factors do not account for the enhanced electrocatalytic activity towards methanol oxidation. From the evidence presented it appears that the altered morphology of the materials, with the sharp tips and fine features on the platinum-lead surface leads to the formation of a larger number of active sites which oxidise at an appropriate potential to promote the electrocatalytic oxidation of methanol.

While the SERS effect has been reported for platinum surfaces, the magnitude of this enhancement is generally much lower than in the case of copper, silver and gold. This is due to the surface plasmon absorption band for platinum lying outside of the visible region.[85] However, localised enhancement of the electromagnetic field can be promoted by the lightning rod effect, especially in the vicinity of sharp features on the surface.[86-87] Shown in Figure 4.13a is an SEM image recorded at an angle of 45° of the platinum-lead nanomaterial electrodeposited for 600 s at -0.05 V, highlighting the dendritic nature of the surface, which suggests that it may be an appropriate material for use as a SERS substrate. After immobilising Rhodamine B on the surface and removing any loosely adhered dye, the SERS spectrum presented in Figure 4.13b was obtained. While relatively poor peak resolution is observed,
peaks can be observed at values of 1118 cm\(^{-1}\), 1198 cm\(^{-1}\), 1342 cm\(^{-1}\), 1464 cm\(^{-1}\), 1502 cm\(^{-1}\), 1584 cm\(^{-1}\) and 1630 cm\(^{-1}\). Unfortunately, to the best knowledge of the author, these peak positions could not be confirmed in the literature for Rhodamine B on a platinum surface recorded with an excitation wavelength of 785 nm.

![Figure 4.13: SEM images recorded at an angle of 45° and SERS spectra for Rhodamine B immobilised on samples deposited from a solution of 8 mM \(K_2PtCl_6\) with 0.1 M HCl and 0.05 mM \(Pb(CH_3COO)_2\), with the electrodeposition carried out for 600 s at a potential of -0.05 V (a-b) or -0.3 V (c-d).](image)

After finding that the platinum-lead surface showed a moderate degree of SERS enhancement, the electrodeposition procedure was modified in order to increase the density of the nanostructured features on the surface. Platinum-lead materials were then formed by electrodepositing for 600 s at -0.3 V, which is within the hydrogen evolution region at a potential slightly lower than those covered by the cyclic voltammogram in Figure 4.1a. As seen from the SEM image recorded at 45° in Figure 4.13c, this produced similar dendritic structures to those observed in Figure
4.13a, although the deposits were smaller and an increased density of deposits were observed. While the formation of nanostructures with sharp tips is one method of creating SERS active substrates, the formation of nanosized junctions between metallic features is another powerful means of creating SERS hotspots. In this case the higher coverage of deposits on the surface provided the chance for the dendritic branches of the platinum-lead structures to overlay the branches of adjoining structures, increasing the number of hotspots present. The SERS spectrum of Rhodamine B on this material (Figure 4.13d) provides confirmation of this mechanism, with enhanced peak resolution observed in this case and a similar Rhodamine B pattern to that found on the gold nanospikes in Chapter III. The peak positions showed some shifts from the values recorded at the sample in Figure 4.13a, with peaks located at 1118 cm\(^{-1}\), 1198 cm\(^{-1}\), 1356 cm\(^{-1}\), 1468 cm\(^{-1}\), 1504 cm\(^{-1}\), 1594 cm\(^{-1}\), 1646 cm\(^{-1}\). While not consistent across all of these peaks, a sizeable shift of greater than 10 cm\(^{-1}\) is found for the peaks located at 1356 cm\(^{-1}\), 1594 cm\(^{-1}\) and 1646 cm\(^{-1}\) when compared with the spectra recorded at the previous sample. As mentioned previously, further study on the nature of these Raman shifts will be required, with a lack of literature available on the topic and the influence of Pb on the surface creating a further complication. However the clear SERS spectrum presented in Figure 4.13d suggests that these materials may provide promising materials for SERS applications, especially for the study of electrocatalytic or catalytic processes at platinum surfaces.

4.3. Summary

Presented in this chapter is a study on the electrochemical formation of platinum and platinum-lead nanostructures. The electrodeposited materials varied from quasi-spherical particles to highly branched dendritic structures when lead acetate was included in the electrodeposition solution as a growth direction agent. Unlike in the previous chapter where lead acetate influenced the growth of gold by adsorbing weakly to particular exposed crystal facets, under the conditions chosen here the underpotential deposition of lead resulted in the reduction of lead onto the growing electrodeposit. This in turn increased the roughness of the electrodeposit and allowed for the further reduction of platinum to occur via electrodeposition on or
galvanic replacement of the lead nuclei. However very low levels of lead remained on the surface after removal from the deposition solution, with a similar crystallographic profile and Pt 4f XPS spectra, indicating that the lead does not result in the formation of an alloyed nanomaterial.

The electrochemical behaviour of the materials was tested using cyclic voltammetry as well as FT-ac voltammetry, with the latter having not been reported previously for platinum. These studies showed the presence of significant premonolayer oxidation responses for both the platinum and platinum-lead nanomaterials. These active site responses were linked to the electrocatalytic oxidation of methanol under acidic conditions, which was found to be related to the magnitude of an active site response found at ca. 0.51 V in the absence of methanol. This study of the underlying premonolayer oxidation events at monometallic and bimetallic platinum surfaces may prove to be interesting for the further study of electrocatalytic reactions at these materials.

In addition the platinum-lead materials were tested for application as SERS substrates. The sharp tips and highly dendritic morphology of the platinum-lead material allowed the identification of the major Rhodamine B peaks, however the peak resolution was greatly enhanced for a platinum-lead surface electrodeposited at a lower potential. This SERS activity demonstrates the multi-functional nature of the platinum-lead surfaces, and shows promise for the use of lead acetate as a chemical growth direction agent in the future electrodeposition of nanostructured materials.

4.4. References


Chapter V

*The Growth of Honeycomb Gold Surfaces Using the Dynamic Hydrogen Bubble Templating Method*

*Sections of this chapter have been published in the following peer-reviewed journals:*


5.1. Introduction

5.1.1. Electrochemical Formation of Highly Branched Gold Nanostructures

As discussed in Chapter III, the electrodeposition of gold nanostructures has received a large number of reports in the literature. This is generally performed by electrodepositing on an unmodified electrode or on a surface modified prior to electrodeposition, with the use of either chemical or physical templates providing greater control over the structure of the electrodeposit. These methods have been used for the synthesis of a range of gold nanostructures, including spheres,[1] rods,[2] prisms,[3] flowers[4] and dendrites, demonstrating the shape control available through electrodeposition.

Amongst the nanostructured growths listed above, the growth of gold dendrites provides a facile method of synthesising highly branched nanostructures. In the case of gold this has been achieved through a number of different routes, including the electrodeposition on a silicon wafer in a two-electrode configuration.[5] This electrodeposition was performed through the application of a strong potential (5-40 V) in a solution of HAuCl₄, resulting in the growth of gold dendrites on the silicon surface. Dendritic gold nanostructures have also been fabricated by the in situ generation of HAuCl₄, where a gold electrode was oxidised in a chloride-containing solution, with the resultant HAuCl₄ migrating to an adjacent ITO electrode where the electrodeposition took place.[6] Chemical templating has also been chosen for the formation of dendrites, with the addition of cysteine to a solution of HAuCl₄ promoting the growth of these structures.[7] This altered growth mechanism involved the adsorption of cysteine on the (100) and (110) crystal planes of the growing electrodeposit, causing the electrodeposition of gold to occur on the exposed (111) planes. The removal of these chemical templating agents on the (100) and (110) planes could then be attained by a reductive desorption step. Electrodeposition on a surface modified by polypyrrole has also been reported for the formation of a range of structures, including pinecone-like and flower-like structures, along with nanosheets and dendritic rods.[8] Similar dendritic growths
have also been observed at unmodified electrodes, where the formation of the
dendrites was achieved by electrodeposition under non-equilibrium conditions.[9-10]

Another method for the synthesis of highly branched gold nanostructures is the
formation of nanoporous gold surfaces. This can be achieved by the synthesis of a
gold alloy by methods such as melting and homogenising the component metals[11]
or by magnetron sputtering,[12] after which the secondary metal is dissolved from
the alloy. By far the most common alloy used in this process is AuAg,[11-18] as the Ag
component may be selectively etched by immersion in HNO₃. It has been found that
this dissolution does not occur through the straightforward removal of the silver
from the matrix, as the more noble gold atoms are able to aggregate at the solid-
electrolyte interface by fast surface diffusion, altering the shape of the final
structure.[14, 19] This surface rearrangement has lead to the dissolution of Ag by a
combination of electrochemical and chemical dissolution in HNO₃, in order to
control the extent of surface rearrangement during the dealloying process.[20] A
number of other alloys have also been utilised to form nanoporous gold surfaces, for
example gold-aluminium[21-22] and gold-zinc alloys.[23-25] In the latter case this
occurred by electrodeposition of zinc on gold electrodes, with an elevated
temperature used to homogenise the alloy and finally the electrochemical
dissolution of the zinc component.

Nanoporous gold surfaces have also been formed through a variety of other
electrochemical methods. This includes the partial anodisation of gold surfaces in
HCl,[26] KCl[27] or oxalic acid solutions,[28] forming a coral-like gold surface. Another
interesting method involves the formation of a gold oxide layer at a highly oxidising
potential, after which the oxide is chemically reduced to metallic gold by immersion
in a solution of either glucose[29-30] or ascorbic acid.[31] These materials showed
similar coral-like structures to those formed through the dealloying method.

The dynamic hydrogen bubble templating method provides another option for
the synthesis of highly branched nanostructured materials. This method involves
the electrodeposition of a metal from an acidic solution under strongly cathodic
conditions, resulting in the formation of a large quantity of hydrogen bubbles at the
electrode surface which act as templates for the metal electrodeposition. While the
pores formed in this process are much larger than the previously discussed nanoporous gold surfaces (with pores on the order of tens of micrometres as opposed to tens of nanometres, respectively), high surface area materials may be synthesised in this manner with highly dendritic growths occurring in the pore walls. Prior to this current work the synthesis of copper surfaces by the hydrogen bubble templating method had been widely reported,[32-37] along with reports of zinc[38] and silver surfaces.[39-40] While the hydrogen bubble templating method had been used to fabricate porous gold[41] and platinum materials,[42] these reports involved the galvanic replacement of porous copper with the more noble metal as opposed to the direct electrodeposition of the monometallic systems. In the case of gold the direct electrodeposition of a honeycomb-like structure had been reported to be unachievable, due to the rapid hydrogen evolution occurring at both the electrodeposited gold and the underlying substrate.[41] While the galvanic replacement approach to obtain porous surfaces allows the dispersion of noble metals with a similar morphology to the underlying porous copper, the direct synthesis of monometallic noble metal surfaces is desirable as it removes the complication of any templating material remaining in the final structure. This is an important factor in the characterisation and application of the materials, as altered behaviour could be related to the bimetallic nature of the surface as opposed to the structure of the desired material.

5.1.2. Research Aims

Having observed from the earlier study on gold nanospikes (Chapter III) that nanostructured gold can display significant premonolayer oxidation behaviour, the aim of this chapter is to extend this work to other structures and see if similar behaviour is seen, and indeed if it can be promoted by other methods of electrodeposition. The dynamic hydrogen bubble templating method appears to be one such method worth investigating, in spite of it being reported that gold cannot be deposited in this manner. The aim of this chapter is to investigate whether gold can in fact be deposited in this way, and owing to the high surface area and interesting nanostructures reported in the literature for other materials formed in this way these materials may make interesting candidates to study the active site
behaviour of gold and by extension result in the formation of active electrocatalytic materials.

5.2. Results and Discussion

5.2.1. Growth of honeycomb surfaces

The electrodeposition of gold whilst using the dynamic hydrogen bubble templating method was investigated by applying a fixed current density to an evaporated gold film in contact with an aqueous solution of KAuBr₄ with H₂SO₄, using similar conditions to those previously reported for the electrodeposition of honeycomb copper surfaces.⁴² Figure 5.1 shows SEM images of a material synthesised on an evaporated gold film in this manner, using a solution of 0.1 M KAuBr₄ and 1.5 M H₂SO₄ with an applied current density of 2 A cm⁻² for 30 s. The porous nature of the surface is immediately visible and forms a relatively homogeneous coverage (Figure 5.1a). From the magnified image in Figure 5.1b it can be seen that the pores are relatively large and display a heterogeneous size distribution, typically ranging from 20-50 μm. These pores are created by the physical templating effect of the hydrogen bubbles as they are formed and released from the surface, creating a similar structure to that previously reported for materials such as copper and silver.⁴³,⁴⁰ It should also be noted that since this current work was published⁴³ a similar honeycomb-like gold surface was fabricated by Cherevko and co-workers.⁴⁴
Figure 5.1: SEM images of honeycomb gold deposited at 2 A cm\(^{-2}\) for 30 s from a solution of 0.1 M KAuBr\(_4\) and 1.5 M H\(_2\)SO\(_4\).

While the formation of a highly porous gold surface is of interest in applications such as catalysis and electrocatalysis where facile mass transport and high surface areas are beneficial, the nanostructuring of the material is also critical to the behaviour of the material in these applications. A magnified image of the pore walls is shown in Figure 5.2, where it can be observed that the growth of the gold occurs in the form of long, branched rods. These rods can grow to 10 \(\mu\)m in length, with nodules which are ca. 230 nm wide and are raised ca. 530 nm from the surface of the rods. It is also important to note that these pore walls also display a degree of porosity, as opposed to being close packed. This can be attributed to the nature of the electrodeposition, which occurs at a potential far from equilibrium. Under these conditions the growth of the nanostructures is thought to occur by the diffusion-limited aggregation (DLA) growth model, where the electrodeposition occurs by the addition of particles at random sites on the surface.\(^{[10, 45]}\) These particles are then able to migrate across the surface until they meet another particle, where they then form a cluster which continues to grow in this manner. Such growth is thought to favour the formation of dendritic structures as observed here,\(^{[46]}\) creating a material which allows ready accessibility for reactants in catalytic and electrocatalytic settings.
Figure 5.2: High magnification SEM image of honeycomb gold deposited at 2 A cm$^{-2}$ for 30 s from a solution of 0.1 M KAuBr$_4$ and 1 M H$_2$SO$_4$.

In order to study the growth of these porous materials a number of deposition parameters were altered. Displayed in Figure 5.3 are images of the honeycomb gold electrodeposited for 5 s (Figure 5.3a-c), 10 s (Figure 5.3d-f) and 30 s (Figure 5.3g-i) at a constant current density of 2 A cm$^{-2}$. While the beginnings of a large number of small pores can be observed in the sample electrodeposited for 5 s, a large number of disconnected sections can be seen, giving clusters of dendritic-like structures on the surface. Increasing this deposition time to 10 s increases the connectivity of the pore walls, with the rod-like structures again evident from the magnified image in Figure 5.3f. The extension of the deposition time to 30 s leads to the formation of the porous material shown in Figures 5.1 and 5.2. In comparison with the materials formed at shorter deposition times it is noted that the pore walls show a higher degree of connectivity, resulting in the formation of well defined pores. These pores are also much larger than those observed at shorter deposition times, although smaller pores are visible below the larger pores in Figure 5.3h. This is in keeping with the proposed model for the dynamic hydrogen bubble templating method, where smaller pores are formed closer to the electrode surface, with larger pores formed further away from the surface due to the coalescence of hydrogen bubbles at longer reaction times. This coalescence leads to the formation of larger hydrogen bubbles and thus the templating of larger pores at the outermost section of the
material,[47] a feature which may aid in mass transport processes during catalytic or electrocatalytic reactions.

Figure 5.3: SEM images of honeycomb gold deposited at 2 A cm⁻² from a solution of 0.1 M KAuBr₄ and 1.5 M H₂SO₄ for deposition times of 5 s (a-c), 10 s (d-f) and 30 s (g-i).

The crystallographic orientations of the honeycomb gold materials deposited for varying times were investigated using XRD. The resulting patterns are presented in Figure 5.4, where the patterns of the samples deposited for 5 s (black), 10 s (red) and 30 s (blue) have been normalised with respect to the intensity of the (111) peaks and offset in order to assist the analysis of the relative peak ratios. While the (111) peak, relating to the lowest energy facet of face-centred cubic gold,[48] is the predominant peak in each pattern, a number of other crystal faces can be observed at appreciable levels including the (220) and (311) planes. The presence of an appreciable amount of growth in these latter planes is indicative of a disrupted
surface with kinks and steps\textsuperscript{[49]} which can often be desirable in catalytic and electrocatalytic applications\textsuperscript{[50-52]} It can be seen from the XRD patterns that as the electrodeposition progresses the intensities of these peaks relative to the (111) peak increase, approaching half the intensity of the latter peak after electrodeposition for 30 s. This increased growth in the higher energy facets is attributed to the vigorous hydrogen evolution occurring at the growing electrodeposit. It has been established that this process can disrupt the surface atoms through hydrogen embrittlement, creating a surface rich in kinks, steps and defects even under milder conditions than employed here.\textsuperscript{[53-56]} In addition, as the electrodeposition of gold takes place far from equilibrium conditions the crystallographic orientation of the deposit is governed by kinetic rather than thermodynamic conditions, which may result in further growth in the higher energy crystal planes. It should be noted that further studies would be required to decouple the effects of the vigorous metal deposition and hydrogen evolution processes on the crystallographic orientation of the materials, however the overall effect is observed as increased growth in the higher energy facets.

\textbf{Figure 5.4:} XRD patterns of honeycomb gold deposited at 2 A cm\textsuperscript{-2} from a solution of 0.1 M K\textsubscript{Au}Br\textsubscript{4} and 1.5 M H\textsubscript{2}SO\textsubscript{4} for deposition times of 5 s (black), 10 s (red) and 30 s (blue).

The influence of the applied current density during the electrodeposition was also investigated. This was varied between 1-3 A cm\textsuperscript{-2}, which provided a sufficient driving force for the vigorous evolution of hydrogen and gold electrodeposition processes. The structures formed were investigated by SEM, with the results
presented in Figure 5.5. The sample deposited at 1 A cm\(^{-2}\) shows signs of the hydrogen bubble templating effect (Figure 5.5a-b), however these pore walls have not developed into a honeycomb-like structure under these conditions. These poorly formed pores are relatively large, with sizes of between 12-25 µm which may have resulted from the hydrogen evolution and its subsequent coalescence into larger hydrogen bubbles occurring preferentially in these regions. Importantly, however, the nanostructure of the material shows similarity to the dendritic and rod-like structures found at materials with more completely formed pores. This may be an important feature in applications where an overall porous structure is less important than the nanostructuring of the surface, as may be encountered in SERS or electrocatalytic applications involving slowly diffusing species.

Increasing the applied current density to 2 A cm\(^{-2}\) (Figure 5.5d-f) resulted in a more well-defined porous structure, with the pore walls showing a greater degree of connectivity than the 1 A cm\(^{-2}\) sample. The size of the pores can also be seen to decrease at this higher current density, ranging from approximately 8-17 µm. This is likely to be due to the increased rate of hydrogen evolution, which does not appear to allow enough time for the hydrogen bubbles to coalesce into the larger bubbles formed in the previous sample. Extending the applied current density to 3 A cm\(^{-2}\) (Figure 5.5g-i) followed this trend, with well-defined pores being visible across the surface with diameters of approximately 7-14 µm. The magnified image of this material (Figure 5.5i) reveals similar nanostructuring to the 2 A cm\(^{-2}\) sample, with long rods evident which display a high degree of branching. These rods can be seen to grow to lengths of 9 µm or more, creating a highly porous extended network of gold nanostructures.
Figure 5.5: SEM images of honeycomb gold deposited for 10 s from a solution containing 0.1 M KAuBr₄ and 1.5 M H₂SO₄ at current densities of 1 A cm⁻² (a-c), 2 A cm⁻² (d-f) or 3 A cm⁻² (g-i).

The crystallography of the honeycomb gold deposited at the different current densities is presented in Figure 5.6. It can be seen that the sample deposited at the lowest current density of 1 A cm⁻² shows the highest degree of growth in the (111) plane. However this sample still shows a high degree of growth in the higher energy facets, as can be seen by comparison with the XRD pattern of the gold nanospikes (Chapter III, Figure 3.8). This is likely to be due to the faster rate of electrodeposition as well as the activation of the material through the hydrogen evolution process, which introduces further disruptions to the surface in the form of kinks, steps and defects. Electrodepositions were also performed at a higher applied current density, as shown by the red and blue patterns in Figure 5.6 for applied
current densities of 2 A cm$^{-2}$ and 3 A cm$^{-2}$, respectively. These results show that the growth of the higher energy facets is promoted by electrodepositing at a higher applied current density, which is attributed to the increased surface disruption caused by the vigorous hydrogen evolution process and the electrodeposition of gold under such non-equilibrium conditions.

![XRD patterns of honeycomb gold deposited for 10 s from a solution containing 0.1 M KAuBr$_4$ and 1.5 M H$_2$SO$_4$ at current densities of 1 A cm$^{-2}$ (black), 2 A cm$^{-2}$ (red) or 3 A cm$^{-2}$ (blue).](image)

**Figure 5.6:** XRD patterns of honeycomb gold deposited for 10 s from a solution containing 0.1 M KAuBr$_4$ and 1.5 M H$_2$SO$_4$ at current densities of 1 A cm$^{-2}$ (black), 2 A cm$^{-2}$ (red) or 3 A cm$^{-2}$ (blue).

Another variable which can be altered in the electrochemical formation of honeycomb gold surfaces using the dynamic hydrogen bubble templating method is the composition of the deposition bath, including the choice and concentration of gold salt. Shown in Figure 5.7 are SEM images for a honeycomb gold surface electrodeposited from a solution of 0.1 M HAuCl$_4$ in 1.5 M H$_2$SO$_4$. The use of the acidic HAuCl$_4$ salt will lead to a slight change in the pH of the deposition solution, however this effect is negligible under the strongly acidic conditions used in this method (approx. pH 0.1). Figure 5.7 demonstrates that the overall honeycomb-like structure is retained when HAuCl$_4$ is chosen as the gold source, although higher magnification imaging of the surface (Figure 5.7c) reveals that the nanostructure of this sample differs from that of the sample formed from KAuBr$_4$ (Figure 5.3i). The latter sample reveals the growth of a high number of long rods which show small nodules along their length, while the former sample shows a promoted growth of branches from the backbones of the rods. This is attributed to the different
adsorption strengths of Cl⁻ or Br⁻ anions on the growing electrodeposit, especially as the localised concentration of these species at the surface will be high owing to the rapid liberation of either Cl⁻ or Br⁻ from the reduction of the HAuCl₄ or KAuBr₄ salts, respectively. The use of anions is known to affect the shape of nanostructures in both the chemical[57-60] or electrochemical[61-62] synthesis of nanostructures, and it has been reported that Br⁻ is able to adsorb more strongly to the gold surface than Cl⁻.[63] In this instance, while the growth of the nodules on the rods shows a high sensitivity to the choice of gold salt, the length of the gold rods is not significantly altered. This may be the result of very rapid growth occurring along the length of the rods, while the slower growth kinetics perpendicular to the rods are more susceptible to the shape directing effect of these anions.

![Figure 5.7: SEM images of honeycomb gold deposited at 2 A cm⁻² for 30 s from a solution containing 0.1 M HAuCl₄ and 1.5 M H₂SO₄.](image)

The XRD patterns of the samples deposited using the different gold salts are presented in Figure 5.8. Interestingly the sample deposited in the presence of HAuCl₄ (red) does not show a significantly different crystallographic structure to the sample deposited in the presence of KAuBr₄ (black). Given the significant differences in the shapes of the nanostructures this was somewhat unexpected, however this may indicate that the branch-like growths in the samples deposited using HAuCl₄ grow with a similar crystallographic orientation to that of the rod-like backbones. Alternatively the XRD patterns may be dominated by the response from the rods, with the coverage of the secondary nodules too low to significantly alter the XRD patterns.
Figure 5.8: XRD patterns of honeycomb gold deposited at 2 A cm$^{-2}$ for 30 s from a solution containing 1.5 M H$_2$SO$_4$ and 0.1 M KAuBr$_4$ (black) or 0.1 M HAuCl$_4$ (red).

In addition to the choice of metallic salt used, the concentration of this salt in the deposition bath was also investigated. Shown in Figure 5.9 are images of honeycomb gold deposited from a solution of 0.1 M (a-c) or 0.4 M (d-f) KAuBr$_4$ in 1.5 M H$_2$SO$_4$. While the underlying pores of the sample deposited at the higher gold concentration (Figure 5.9e) appear similar to those deposited at the lower gold concentration (Figure 5.9b), the overall honeycomb effect in the former case is altered by the overgrowth of sections of the surface. Indeed this can also result in the formation of very large clusters of gold on the surface, such as the large cluster (180 µm in diameter) seen in Figure 5.9d. The increased KAuBr$_4$ concentration also alters the nanostructure of the deposit, with much larger rod-like growth found to occur (Figure 5.9f). Such overgrowth of the surface, at both the macroscale and the nanoscale, are the result of a greater availability of KAuBr$_4$ at the electrode surface during the electrodeposition. As this reaction takes place under controlled current conditions, the greater availability of the gold salt at the electrode surface will lead to an increase in the amount of gold electrodeposition, which explains the overgrowth of the surface formed from 0.4 M KAuBr$_4$. While such dispersity in the overall morphology may not always be advantageous, the ability to tune the size of the nanostructured components in this manner may be useful to tailor the materials for particular applications.
Figure 5.9: SEM images of honeycomb gold deposited at 2 A cm$^{-2}$ for 30 s from a solution containing 1.5 M H$_2$SO$_4$ and 0.1 M (a-c) or 0.4 M (d-f) KAuBr$_4$.

As can be seen from the XRD patterns in Figure 5.10, the concentration of gold in the deposition solution displays a pronounced effect on the crystallographic orientation of the deposited material. The sample deposited from a solution containing 0.4 M KAuBr$_4$ (red) shows a greater level of growth in the (200), (220) and (311) crystal planes than the sample deposited from the 0.1 M KAuBr$_4$ solution (black) under otherwise comparable conditions. This enhanced growth in the higher index facets may be the result of an increased rate of gold deposition at the higher KAuBr$_4$ concentration, which is consistent with the SEM images presented in Figure 5.9. As the rates of electrodeposition and formation of hydrogen are under kinetic control, an increased amount of KAuBr$_4$ at the electrode/electrolyte interface results in an enhanced rate of electrodeposition. This in turn leads to the formation of a surface showing greater growth of higher index facets, rather than the more thermodynamically favoured lower index facets.
As has been seen from the above section, the electrochemical formation of honeycomb-like gold surfaces has been demonstrated for the first time. The growth of these surfaces may readily be tuned to produce surfaces of a desired overall morphology and crystallographic orientation, with nanostructured growths of different sizes and degrees of branching being achievable. In particular, the surfaces formed using this versatile technique show nanostructures with interesting shape, size and crystallographic orientation which may be useful in a number of applications, as will be explored in the following sections.

5.2.2. Active Site Behaviour of Honeycomb Gold Materials

In order to investigate the electrochemical behaviour of the honeycomb-like gold materials, cyclic voltammetry was performed in 1 M H₂SO₄ (Figure 5.11). The scan was started at -0.25 V, avoiding the hydrogen evolution region, before scanning forward through the double layer region and observing the onset of the monolayer oxide formation at ca. 1.21 V. This monolayer oxide was then stripped in the reverse scan with this process centred at 0.89 V. The large charges involved in forming and reducing this monolayer oxide indicate that the materials possess very high electrochemically active surface areas, in agreement with the SEM imaging presented previously. These electrochemically active surface areas were calculated from the charge required to reduce this oxide, assuming a value of 400 μC cm⁻²,[64-65] which gave values of 0.25 cm² for the unmodified gold film, 6.58 cm² for the 5 s
sample (green), 13.20 cm² for the 10 s sample (blue) and 42.13 cm² for the 30 s sample (red). This latter surface in particular shows a much greater electrochemically active surface area compared with the unmodified evaporated gold film, with an increase of 170 times, illustrating the large surface area available on this highly porous material.

In addition to the greatly enhanced surface areas at the electrodeposited surfaces, a broad redox feature can be seen well within the double layer region at potentials below 0.5 V (Figure 5.11a). Upon closer inspection of this region (Figure 5.11b) a large number of redox processes can be seen to occur within this region, with the effect most visible from the sample deposited at 30 s. This creates a broad response at potentials below 0.5 V, with a peak oxidation potential at 0.08 V as well as minor oxidation peaks at 0.36 V and also at potentials as far negative as -0.08 V.

![Figure 5.11: Cyclic voltammograms in 1 M H₂SO₄ for a polycrystalline gold electrode (black) and honeycomb gold deposited at 2 A cm⁻² for 5 s (green), 10 s (blue), and 30 s (red) from a solution containing 0.1 M KAuBr₄ and 1.5 M H₂SO₄, along with an enlargement of the double layer region in Figure (b). The scan rate for all cases is 100 mV s⁻¹.](image)

While Figure 5.11 shows evidence of premonolayer oxidation on the honeycomb gold surfaces by cyclic voltammetry, further confirmation of these processes was obtained by FT-ac voltammetry in 1 M H₂SO₄ (Figure 5.12). Due to the very large surface area of the honeycomb surface, significant capacitance can be observed in the first and second harmonic responses, on the order of milli-Amps. However, this
contribution is noticeably reduced in the third harmonic response and is negligible in the fourth harmonic response. Examination of this latter result shows a large number of peaks present, with the major peaks in the forward sweep at 0.42 V, 0.59 V and 1.12 V. Interestingly these potentials correlate well with the major peaks seen by FT-ac voltammetry in 1 M H₂SO₄ for the gold nanospikes (Chapter III, Figure 3.10), which were located at 0.41 V, 0.58 V and 1.16 V. This suggests that while a range of active sites are thought to exist on these highly nanostructured materials, a number of these active sites are common to both materials, with the magnitude of their response indicative of their surface coverage.

The stability of the oxidation products of these active sites may also be observed from the FT-ac voltammograms. For the processes located at ca. 0.42 V and 0.59 V this stability is not particularly high under acidic conditions, with a large decrease in peak magnitudes seen in the reverse sweep, which was also observed in the case of the gold nanospikes (Chapter III, Figure 3.10). However the peak located at ca. 1.1 V does not display this level of reduced stability, with significant responses preserved in the reverse sweep. As this premonolayer oxidation process occurs at a more positive value than the other processes discussed, this suggests that the active site at ca. 1.1 V exists in a lower energy state than the more reactive sites located at lower potentials, resulting in more stable response.
Figure 5.12: FT-ac voltammogram of a honeycomb gold surface (deposited at 2 A cm\(^{-2}\) for 30 s from a solution containing 0.1 M KAuBr\(_4\) and 1.5 M H\(_2\)SO\(_4\)) recorded in 1 M H\(_2\)SO\(_4\) showing the forward and reverse scans for the dc and first to fourth harmonic responses. Data was recorded at a sweep rate of 63.33 mV s\(^{-1}\) with an applied sinusoidal perturbation of 100 mV at a frequency of 21.1 Hz.
The dc voltammetric behaviour of the honeycomb materials was also investigated in 1 M NaOH (Figure 5.13). After beginning the sweep at -1.0 V a number of premonolayer oxidation events can clearly be seen within the double layer region, with a broad response located between ca. -0.7 V and -0.2 V followed by two smaller peaks prior to the onset of the monolayer oxide formation at 0.18 V. The reverse scan shows the removal of this monolayer oxide at 0.08 V and also the cathodic components of the premonolayer oxides formed in the forward sweep. As was found under acidic conditions, the large charges associated with the monolayer oxide formation and stripping indicates that the materials possess large surface areas which increase with extended deposition time. Closer inspection of the double layer region (Figure 5.13b) shows that the broad feature continues from -0.68 V to -0.21 V, with a small peak present at -0.59 V and an inflection at ca. -0.37 V. A number of more defined oxidation peaks can also be seen at 0.15 V, 0.04 V, -0.17 V and even at potentials as low as -0.82 V. This latter value is 1.0 V lower than the onset potential of the monolayer oxide formation at 0.18 V, again showing the remarkable redox behaviour of active sites and highlighting why the electrochemical behaviour of such species must be regarded separately from bulk electrochemical processes at gold surfaces. These processes can also be observed on the samples electrodeposited for different times, highlighting the effectiveness of the dynamic hydrogen bubbling technique for creating surfaces which are inherently rich in active sites.

![Figure 5.13: Cyclic voltammograms in 1 M NaOH for a polycrystalline gold electrode (black) and honeycomb gold deposited at 2 A cm⁻² for 5 s (green), 10 s (blue), and 30 s (red) from a solution containing 0.1 M KAuBr₄ and 1.5 M H₂SO₄, with an enlargement of the double layer region shown in Figure (b). The scan rate for all cases is 50 mV s⁻¹.](image-url)
The honeycomb gold surface was also examined by FT-ac voltammetry in 1 M NaOH (Figure 5.14). While significant capacitance is seen in the first harmonic response, this quickly reduces in the second and subsequent harmonics, producing clear, background subtracted peaks by the fourth harmonic. At this latter harmonic a number of redox processes are again evident within the double layer region, with major peaks present around -0.80 V, -0.20 V and 0.17 V. These processes are located close to features seen by cyclic voltammetry, with a minor peak at -0.82 V and a more prominent peak at -0.17 V, while the onset potential for the monolayer oxide formation begins at ca. 0.18 V. A relatively broad peak at -0.55 V in the FT-ac voltammogram also occurs at potentials where features are seen in the cyclic voltammogram, with the onset of the broad redox peak at -0.68 V followed by a small inflection at -0.59 V. As was seen under acidic conditions, the active site responses in the FT-ac voltammogram do not show a high degree of reversibility in the fourth harmonic response, with the exception of the peak at ca. -0.20 V. This may be related to the upper potential limit chosen for the scan, as the formation and stripping of the monolayer oxide may alter the responses in the double layer region seen in the reverse scan. In spite of the diminished magnitude of these peaks in the reverse scan the FT-ac data reveals the presence of significant premonolayer oxidation occurring on the honeycomb gold surfaces at potentials well below the onset of the monolayer oxide formation.
Figure 5.14: FT-ac voltammogram of a honeycomb gold surface (deposited at 2 A cm$^{-2}$ for 30 s from a solution containing 0.1 M KAuBr$_4$ and 1.5 M H$_2$SO$_4$) recorded in 1 M NaOH showing the forward and reverse scans for the dc and first to fourth harmonic responses. Data was recorded at a sweep rate of 63.33 mV s$^{-1}$ with an applied sinusoidal perturbation of 100 mV at a frequency of 21.1 Hz.
5.2.3. Electrocatalytic and SERS Activity of Honeycomb Gold Surfaces

After investigating the heightened active site responses at the honeycomb gold surfaces the materials were then tested for their activity towards a range of electrocatalytic and SERS applications. Shown in Figure 5.15 is the electrocatalytic activity of a honeycomb gold surface towards the oxidation of H$_2$O$_2$ in H$_2$SO$_4$. This scan shows an onset potential of ca. 0.69 V and reaches a peak potential at 0.91 V. Notably the onset potential of H$_2$O$_2$ oxidation is found at a similar potential to a peak at 0.68 V seen by FT-ac in the absence of H$_2$O$_2$ (Figure 5.12). This provides evidence that the oxidation of H$_2$O$_2$ on gold under acidic conditions can occur via an IHOAM based electrocatalytic reaction, as was previously discussed by Burke et al. from dc cyclic voltammetric studies.$^{[55]}$ As there are multiple premonolayer oxidation responses at lower potentials than this peak, it appears that premonolayer oxidation promoted electrocatalysis is a more subtle process than simply requiring premonolayer oxidation to occur at processes as far negative as possible. Rather, it appears in the case of gold that effective electrocatalysts for a particular reaction requires the adsorption of the reactants to occur at a similar potential to where premonolayer oxidation processes take place. This is in agreement with previous work by Burke et al.$^{[66]}$ who observed that the onset potential for a variety of electrocatalytic reactions on gold surfaces occur at distinct potential ranges. In particular the ranges between approximately 0.60-0.65 V and 0.80-0.90 V (vs Ag/AgCl) were identified for acidic conditions, and in the present case the oxidation of hydrogen peroxide takes place in the latter range. With this in mind, FT-ac voltammetry of a variety of surfaces may be performed not only to examine the location and magnitude of the premonolayer oxidation processes but also to identify electrocatalytic reactions which may be particularly effective at that surface.
Figure 5.15: Cyclic voltammogram of 20 mM H$_2$O$_2$ in 1 M H$_2$SO$_4$ at a honeycomb gold surface, recorded at a scan rate of 20 mV s$^{-1}$.

The electrocatalytic activity of the honeycomb gold was also studied under alkaline conditions, with the oxidation of ethanol in NaOH (Figure 5.16). This reaction shows an onset potential of ca. -0.27 V before a peak potential is reached at 0.37 V, after which the formation of the monolayer oxide decreases the activity of the surface towards further oxidation of ethanol. On the reverse scan this oxide layer is stripped at 0.16 V, after which the oxidation of ethanol recommences on the newly available bare gold surface. As was discussed above for the case of H$_2$O$_2$ oxidation in H$_2$SO$_4$, ethanol oxidation in NaOH represents another case of an IHOAM driven electrocatalytic reaction, with the onset potential at -0.27 V being closely situated to an active site response at -0.26 V, after which two other peaks in this region at -0.20 V and -0.14 V are seen (Figure 5.14). These active site responses can be seen to promote the oxidation of ethanol at the surface, and as these processes were found to be stable in both the forward and reverse scans of the FT-ac study in 1 M NaOH this suggests that the honeycomb gold may be a suitable surface for the electrocatalytic oxidation of ethanol.
Figure 5.16: Cyclic voltammogram of 1 M ethanol in 1 M NaOH for a honeycomb gold sample, recorded at 50 mV s\(^{-1}\).

The electrocatalytic oxidation of glucose under alkaline conditions was also examined, as shown in Figure 5.17 at honeycomb gold surfaces deposited for 5 s (green), 10 s (blue) and 30 s (red), along with an evaporated gold film (black). This reaction is known to proceed through the oxidation of glucose to gluconolactate,\(^{67-68}\) which may then undergo further oxidation.\(^{69-70}\) The oxidation of glucose can be seen in Figure 5.17a, with an onset potential at ca. \(-0.78\) V and increasing to a peak potential at ca. \(-0.60\) V. Significantly the onset of this reaction occurs at a potential where a high degree of premonolayer oxidation behaviour was observed by FT-ac voltammetry, with a major peak located at \(-0.80\) V (Figure 5.14). The onset of the second oxidation process at ca. \(-0.50\) V shows similar behaviour, with a broad peak centred at \(-0.54\) V visible from the FT-ac voltammetry. An extended scan was then performed for glucose oxidation at the honeycomb gold sample deposited for 30 s and the results are shown in Figure 5.17b. It can be seen that each of the onset potentials in the forward scan are closely linked to the oxidation of active sites, with the onset potentials for the oxidation of glucose and its by products occurring at \(-0.78\) V, \(-0.50\) V, \(-0.21\) V, \(0.24\) V and \(0.36\) V, while active site responses are seen at \(-0.80\) V, \(-0.54\) V, \(-0.20\) V, \(0.25\) V and a broad response at \(0.38\) V. These results suggest that the oxidation of glucose across this wide potential is largely driven by premonolayer oxidation processes occurring at the underlying gold surface. This provides further evidence that the study of active sites on gold nanomaterials can be
critical to understanding the electrochemical behaviour of nanostructured gold surfaces.

**Figure 5.17:** Cyclic voltammograms of 20 mM glucose in 1 M NaOH showing the initial oxidation processes (a) and an extended scan showing the subsequent oxidation processes for a control gold electrode (black) and honeycomb gold deposited at 2 A cm$^{-2}$ for 5 s (green), 10 s, (blue) and 30 s (red). The scan rates in all cases were 50 mV s$^{-1}$.

The electrochemical reduction of oxygen was also studied at the honeycomb gold surface under acidic and alkaline conditions, with the former reaction shown in Figure 5.18a. This voltammogram remains featureless from the start of the scan at -0.4 V until the onset of oxygen reduction at ca. 0.22 V, with a further increase in reduction at ca. -0.02 V. This scan then continues until reaching a peak potential at -0.14 V, after which the magnitude of the reduction is decreased as the process becomes diffusion limited. A slight decrease can be seen after ca. -0.3 V which is attributed to the evolution of hydrogen, and upon switching the potential at -0.35 V no further peaks can be seen in the reverse scan. Comparison with the FT-ac voltammetry in 1 M H$_2$SO$_4$ reveals the presence of peaks within this potential region, with a broad peak located at 0.25 V in the fourth harmonic response for the reverse sweep (Figure 5.12). This data indicates that the reduction of the premonolayer oxide is coupled to the reduction of oxygen, with the chemical oxidation of the active sites coupling to the reduction of oxygen, and the electrochemical reduction of these sites to their metallic state (Au*) allowing for further reaction to take place. This is in agreement with work by Burke and co-
workers who investigated the reduction of oxygen in acidic conditions at gold electrodes by cyclic voltammetry, attributing the electrocatalytic reaction to be an IHOAM process.\[66, 71\]

The electrocatalytic reduction of oxygen in alkaline conditions is shown in Figure 5.18b. This scan begins at 0.1 V and is featureless until the onset of oxygen reduction at ca. 0 V, following which a small plateau can be observed at -0.12 V, with a further increase in current at ca. -0.16 V. This increase continues until reaching a maximum value at -0.28 V before the process becomes diffusion limited. As was observed under acidic conditions the onset potential of oxygen reduction can be seen to occur at potentials where active site responses are seen by FT-ac voltammetry (Figure 5.14), with a broad peak around 0 V and a large peak at -0.15 V seen in the fourth harmonic of the reverse scan. This IHOAM type behaviour under alkaline conditions was also reported by Burke and co-workers,\[66, 71\] showing that the electrocatalytic reduction of oxygen at a range of different gold surfaces is mediated by the presence of active sites.

**Figure 5.18:** Cyclic voltammograms of O₂ saturated solutions of 1 M H₂SO₄ (a) and 1 M NaOH (b) at honeycomb gold, recorded at a scan rate of 20 mV s⁻¹.

In addition to the investigation of the electrocatalytic activity of the honeycomb gold surfaces, these materials were also tested as possible materials for surface enhanced Raman spectroscopy (SERS). As was seen in Chapter III for the gold nanospikes, nanostructured gold surfaces can provide viable materials for this
application, especially where sharp tips or nanosized junctions are present and result in an enhancement of the local electromagnetic field.[72-73] Figure 5.19 shows the response of an evaporated gold film (black) and honeycomb gold surface (red) after the immobilisation of Rhodamine B and subsequent washing of any loosely adhered dye. While the evaporated gold film does not result in any SERS peaks, clear peaks related to Rhodamine B can be observed at the honeycomb gold surface. However it can be seen that the peak positions are noticeably shifted from those recorded at gold nanospikes (Chapter III, Figure 3.15), with the major peaks located at 1188, 1268, 1348, 1496, 1516 and 1636 cm\(^{-1}\) for the honeycomb gold, while the gold nanospikes showed peaks at 1198, 1280, 1358, 1508, 1528 and 1646 cm\(^{-1}\), which are closer to values reported in the literature.[74-75] This requires further studies to determine the cause of this peak shift, however it is postulated that a charge transfer mechanism may be involved through the adsorption of Rhodamine B at the active sites on the honeycomb gold.

![Figure 5.19: SERS spectra recorded for Rhodamine B immobilised on an evaporated gold film (black) and honeycomb gold (red) electrodeposited for 30 s at 2 A cm\(^{-2}\) from a solution of 0.1 M KAuBr\(_4\) and 1.5 M H\(_2\)SO\(_4\).](image)

The SERS enhancement factor was also calculated for this material, using Equation 1, where the coverage of Rhodamine B molecules on the honeycomb gold surface (\(N_{\text{Surf}}\)) was estimated from the area occupied per Rhodamine B molecule and the electrochemically active surface area of the material, \(N_{\text{Vol}}\) is the estimated number of Rhodamine B molecules in the scattering volume of the control sample.
and $I_{\text{SERS}}$ and $I_R$ are the recorded intensities for the honeycomb gold and control sample, respectively.\cite{76} The evaporated gold surface with adsorbed Rhodamine B could not be used as a control for this calculation as no peaks were recorded, and instead a Raman spectrum of Rhodamine B powder was taken and the estimated number of Rhodamine B molecules was estimated to give $N_{\text{Vol}}$. This resulted in an enhancement factor of approximately $10^3$, which is in keeping with SERS enhancement factors of other gold systems.\cite{77}

$$Enhancement\ factor = \frac{I_{\text{SERS}}/N_{\text{Surf}}}{I_R/N_{\text{Vol}}},$$

(1)

While this enhancement factor is significantly lower than other reported SERS enhancement factors for gold nanostructures, which can be as high as $10^9-10^{10}$,\cite{78} such large enhancement factors are often found at localised hot spots located in the junctions between gold nanomaterials.\cite{79-80} However, the current experiment represents an averaged intensity across the interaction volume of the laser. In addition the calculation of SERS enhancement factors is also somewhat open to interpretation and relies on a number of estimations, especially in the case of surface bound systems such as the one under investigation here.\cite{76,81} These can result in sizeable variations in the enhancement factors, which may also explain the relatively conservative enhancement factor reported for the honeycomb gold surface. In spite of the value of this enhancement, the honeycomb gold surface is capable of producing clear, intense and well-resolved SERS spectra with very little sample preparation, and as no capping agents are employed in the synthesis the influence of these possible interfering species is not seen, as may be found at chemically capped nanoparticle-based SERS surfaces. This demonstrates the multi-functional nature of the honeycomb gold materials, showing promising electrocatalytic properties as well as activity as SERS substrates.

5.3. Summary

Presented in this chapter is the first report of the electrodeposition of a high surface area gold material using the dynamic hydrogen bubble templating technique. This was achieved in spite of a report to the contrary, which stated that
honeycomb gold could not be synthesised in this manner. The fabrication of these materials was studied and a range of parameters affecting the electrodeposition were investigated, showing that the porosity of the surface, the type of nanostructured branching and the degree of high energy crystal facets present could all be controlled in a facile manner.

These materials were found to readily undergo premonolayer oxidation, as evidenced by both cyclic voltammetry and FT-ac voltage. This high level of electrochemical activity, seen by both the current magnitude and the low potentials at which the surfaces oxidised, is thought to be enhanced by the vigorous electrodeposition procedure which involved hydrogen embrittlement, resulting in a surface rich in active sites. A high degree of correlation between these underlying redox processes and the electrocatalytic activity of the surfaces was established for reactions including the oxidation of \( \text{H}_2\text{O}_2 \) and reduction of \( \text{O}_2 \) in acidic conditions, as well as the oxidation of ethanol and glucose and the reduction of \( \text{O}_2 \) in \( \text{NaOH} \). The activity of the materials towards SERS was also established, demonstrating the multi-functional nature of the honeycomb gold surfaces.

5.4. References


Chapter VI

*Active Site Mediated Spontaneous Decoration of Noble Metal Surfaces*

Sections of this chapter have been published in the following peer-reviewed journal:

6.1. Introduction

6.1.1. The Importance of Bimetallic Materials in Electrochemical Applications

As discussed in Chapters III and IV, the formation and electrochemical behaviour of nanostructured monometallic surfaces is of keen interest, especially as this knowledge can shed light on new ways to control the growth of nanostructured surfaces and better prepare materials which are active towards applications such as catalysis and electrocatalysis. While there is a strong research focus on such monometallic systems, bimetallic surfaces are also generating much interest, especially in the fields of catalysis and electrocatalysis. This is due to a number of reasons, including an increased activity towards particular reactions and an increased selectivity of forming particular products over others, both of which are essential features for catalysis. Another important feature is a high tolerance towards poisoning. For example, although many platinum group metals show a high degree of activity towards catalytic and electrocatalytic reactions of interest, the reaction pathway for a number of small molecule oxidation reactions on these monometallic systems can often proceed through the formation of CO\text{ads}. This species is known to interact strongly with the metal surfaces, and often leads to a decrease in the activity of the catalyst during the reaction. The introduction of a second metal component in such cases has been found to decrease the amount of poisoning, as a result of changes in the electronic structure of the surface or as the result of an altered geometric arrangement of the surface atoms which are better suited to particular reactions. In addition to these alterations in the rates of particular reactions, bimetallic surfaces may also show improved stability over their monometallic counterparts, extending the lifetime of the catalyst. By understanding the fundamental processes behind these reactions bimetallic nanostructured materials can be synthesised which show application in real world settings, such as Au/Pt for formic acid electrooxidation and Pt/Ru for methanol oxidation.
6.1.2. The Fabrication of Bimetallic Nanostructured Materials

There are a variety of strategies currently in place for the synthesis of bimetallic nanostructured materials, based on both physical and chemical methods. Examples of physical methods include the use of ion implantation and molecular beams on target surfaces. However there are a much greater variety of chemical synthetic routes to form bimetallic nanostructured materials. This includes the simultaneous reduction of metal complexes which can be achieved by the addition of a suitable reductant, thermal decomposition or reduction through radiolytic, sonochemical, photochemical, biological or microwave methods, illustrating the versatility of this approach. The chemical synthetic route has also been extended to the formation of a variety of core-shell type materials, where a nanoparticulate core is formed by the reduction of a metallic salt, followed by a separate reduction step to deposit the secondary metal in the form of a thin shell on the seed nanoparticle. While many of these methods are capable of creating very elegant structures, there are a number of issues in using these free nanoparticles in heterogeneous catalytic and sensing applications, such as the agglomeration of nanoparticles and the often poor adherence of the nanostructures to the underlying surface, reducing their longevity for these applications. Such issues provides scope for the investigation of other methods which address these practical issues.

Another method of fabricating bimetallic nanostructures which is gaining in popularity is galvanic replacement, in which a metallic template material is placed in a solution of an appropriate metal salt, resulting in the replacement of the initial metal with the second metal. This phenomenon is based on the spontaneous oxidation of a less noble metal surface when in contact with a more noble metal salt, where the driving force for the reaction is the difference in the standard redox potentials of the metal species involved. Examples of such a reaction include the immersion of iron nanocubes in a gold or palladium salt leading to the replacement of iron, as the oxidation of the iron nanocubes occurs at a significantly lower potential (Fe²⁺/Fe at -0.440 V vs SHE) than the gold (AuBr₄⁻/Au at 0.854 V vs SHE) or palladium (Pd²⁺/Pd at 0.915 V vs SHE) couples. This difference in the standard reduction potential can thus couple the oxidation of the surface metal with the
reduction of the metallic salt, and may therefore be used to form a range of bimetallic surfaces.[24-27]

Many studies have already been done in the field of galvanic replacement, and quite sophisticated bimetallic materials may be synthesised in this manner. By controlling the time, temperature, concentrations of metallic salt and the choice of solvent including aqueous, organic or ionic liquid based systems the extent of reaction and the final structure of the bimetallic surface may be altered.[28-32] Another feature of galvanic replacement is that the porosity of the surface may be increased when compared to the monometallic system.[33] This can occur for a number of reasons, for example as the two metals may have appreciably different sizes or as the result of stoichiometric effects,[22] where the oxidation of three divalent atoms can lead to the reduction of two trivalent atoms, resulting in a localised pitting of the surface.

While galvanic replacement is a very useful method for the creation of bimetallic nanostructures one of its major limitations is that it is only applicable when there is an appropriate difference in the redox potentials of the two metal species. This results in the ready replacement of the more reactive metals such as iron, copper and nickel, however for the more noble metals such as the platinum group metals there are fewer elements which are able to couple in their galvanic replacement. This is perhaps most evident in the case of gold, where the oxidation potential of bulk gold is too high to undergo galvanic replacement in this method. One strategy to overcome this issue is the chemical or electrochemical deposition of an intermediate metal on these more noble surfaces which can then undergo galvanic replacement, in a method known as surface limited redox replacement.[34] This method has been used to prepare a variety of surfaces,[35-37] although if the galvanic replacement step is not completed there will be trace amounts of the intermediate metal present which may affect the electrochemical behaviour of the resulting surface.[38]
6.1.3. Spontaneous Decoration

While the thermodynamics involved in galvanic replacement occlude the replacement of a more noble metal surface by a less noble metal species, there are reports in the literature of the spontaneous decoration of such systems, dating back to the 1950s.[39] These reports include the decoration of cesium, osmium,[40-42] palladium,[43-44] ruthenium[40, 45-46] and silver[47] on platinum, as well as osmium,[48-49] platinum,[50] ruthenium[49, 51] and silver[52] on gold. While these reports note the presence of a second metal, care must be taken between reports of the spontaneous adsorption of a metal species and the spontaneous reduction of these species. For instance, reports on the decoration of gold with platinum found that the platinum was actually adsorbed to the surface as complex ions, as opposed existing as an elemental or metallic oxide form.[53-54] This represents a fundamental difference in these systems, as an adsorbed ionic species displays markedly different behaviour to a reduced metal not only in terms of stability but also activity towards catalytic and electrocatalytic reactions, hence these systems should be treated separately. In spite of the relatively early appearance of these spontaneous decoration reports, the mechanism by which the metal reduction occurs remains unclear, especially in the case of the decoration of a more noble metal with a less noble metal where galvanic replacement is not able to occur.[55] Possible mechanisms in these cases include the adsorption of hydrous oxide species or complex ions to the surface,[55] with the reduction of these species either occurring by a later electrochemical treatment[56-57] or by the partial oxidation of the surface.[58] Other reports attribute the metal reduction to be related to the specific adsorption of anionic species such as chloride,[59-60] and as can be determined from the various explanations of the spontaneous decoration process on metal surfaces there is still uncertainty in the literature over the most appropriate explanation.

6.1.4. Research Aims

The aim of this chapter is to further investigate the spontaneous decoration process, and in particular to examine whether the spontaneous decoration of gold with a number of precious metals is feasible, especially as it could show application
across a wide range of areas and especially towards improving electrocatalytic processes. Gold makes an interesting material for this study, not only as it is a weakly chemisorbing material but also as its high oxidation potential should theoretically forbid spontaneous decoration processes.

In addition to determining whether it is possible to spontaneously decorate gold surfaces there are several other research questions to be answered, such as what the driving force for this reaction is and whether the active site behaviour discussed in previous chapters is in any way connected. This knowledge would help to build a picture of which metals can spontaneously decorate a gold surface, and may be extended to other metal surfaces, leading to the formation of a range of materials showing electrocatalytic activity amongst other applications.

### 6.2. Results and Discussion

#### 6.2.1. Decoration of Honeycomb Gold

In order to study the spontaneous decoration process, gold provided an appropriate option as a support material. It is known that due to its high oxidation potential gold cannot be galvanically replaced with other metals, excluding the possibility that any decoration observed was as the result of this process. As discussed previously the redox couple of the substrate / metal salt must be less positive than the redox couple of the replacing metal species in order for the reaction to occur. However, in light of the significant premonolayer oxidation responses observed for nanostructured gold surfaces such as the gold nanospikes (Chapter III) and the honeycomb gold surfaces (Chapter V) it was observed that these surfaces may be capable of driving the spontaneous decoration of other metals.

As a proof of concept of whether nanostructured gold surfaces could drive spontaneous decoration processes the honeycomb gold surfaces were studied first. As seen from the cyclic voltammetry studies (Chapter V, Figures 5.11 and 5.13) and particularly from the FT-ac studies (Chapter V, Figures 5.12 and 5.14) not only were
there many premonolayer oxidation processes, but these occurred at potentials far less positive than the bulk monolayer oxide formation at approximately 0.5 V. While there appear to be a range of different active sites which oxidise at different potentials, it is particularly those active sites which oxidise at lower potentials that would provide the greatest driving force for spontaneous decoration to occur, and so the honeycomb gold surface was the first chosen.

Presented in Figure 6.1 are the XPS results of the Ag 3d scan on both an unmodified honeycomb gold surface (black) and a honeycomb gold surface immersed in 1 mM AgNO$_3$ for five minutes at open circuit potential and then thoroughly washed. As can be seen there was no detectable silver present on the honeycomb gold, however clear peaks were present upon immersion in AgNO$_3$. These peaks, present at 368.6 eV and 374.6 eV, relate to the 3d$_{5/2}$ and 3d$_{3/2}$ peaks of metallic silver, respectively,[61-62] indicating that Ag$^+$ ions from solution have been reduced onto the honeycomb gold surface through the immersion procedure. While it is well known that silver ions may be reduced in a number of ways including the presence of chemical reducing agents or by photoreduction, both of these stimuli were excluded from the decoration process and therefore the electron transfer process which resulted in this metallic silver cannot be ascribed to these common factors. Importantly from the XPS data there is no indication of Ag$^+$ species on the surface, as would be expected in the case of a simple physisorption to the surface. This absence of ionic Ag species suggests that the cleaning procedure employed after decorating the samples is adequate for the removal of any reactants, and is important in the subsequent physical and electrochemical characterisation of the materials.
The morphology of the silver decorated honeycomb gold was then investigated using SEM. While the overall dendritic and rod-like structures of the porous gold are preserved (compare with Chapter V, Figure 5.2) it can be seen from the representative SEM images presented in Figure 6.2 that there are a large number of nanoparticles present on the surface. These nanoparticles range in size from approximately 10 nm to 30 nm and show a relatively even coverage across the surface, and as the bare honeycomb gold shows a relatively smooth texture compared to these samples these nanoparticles may be attributed to the metallic silver seen by XPS (Figure 6.1). The small size of these nanoparticles, in combination with their even distribution across the surface suggests that these materials may display interesting catalytic and electrocatalytic properties.

Interestingly these silver nanostructures show growth away from the dendritic honeycomb gold backbones, as may readily be seen from the SEM image in Figure 6.2b. This is significant as it indicates that the silver reduction process is a surface confined process rather than a solution-based process where the nanoparticles are formed in solution and then adhere to the surface. This finding is in keeping with the hypothesis that it is the facile oxidation of active sites present on the gold surface which provides the electrons required to reduce the silver. The spontaneous decoration of silver on gold nanoparticles has since been reported in the literature, providing supporting evidence for the silver decoration observed in this work.
However it was noted that the presence of capping agents in this report may be involved in the reduction of silver.[63]

**Figure 6.2:** High resolution SEM images showing honeycomb gold decorated with silver.

SEM imaging at lower magnification (Figure 6.3) indicated that although a relatively large amount of silver decoration occurred on the dendritic pore walls the overall morphology of the honeycomb gold structure was preserved. This preservation of the large surface area of the honeycomb-like structure and its mechanical adherence to the underlying substrate points to the relevance of this decoration process to a wider range of catalytic and electrocatalytic applications, especially in light of the relatively high loading of small silver nanoparticles.

**Figure 6.3:** Low magnification SEM image of a porous gold surface after decoration with silver.
The electrochemical behaviour of these decorated materials was investigated in 1 M NaOH (Figure 6.4), which was chosen so that the electrochemical dissolution of silver which occurs readily in acidic solutions was avoided. The comparison of the voltammograms recorded at the silver-decorated honeycomb gold (red) and unmodified honeycomb gold materials presents some interesting behaviour. For instance, while the oxidation of gold seen at ca. 0.3 V can also be observed for the silver-decorated case, the magnitude of this peak is reduced. In combination with the added oxidation peak at 0.52 V for the silver-decorated sample this indicates that the silver decoration has not formed a monolayer coverage across the gold surface. The subsequent reduction of these oxides formed in the forward sweep also shows differences between the samples, with the peak potential shifting to less positive values in the case of the silver decorated surface.

Another interesting point from these voltammograms is that the hydrogen evolution reaction occurs at a more negative potential in the case of the silver-decorated surface (-1.20 V) compared to the honeycomb gold surface (-1.13 V). Although this reaction is not widely studied in alkaline solutions, it provides further evidence of the presence of silver on the surface, which is known to be a poorer electrocatalyst for the hydrogen evolution reaction.

The expanded region of the voltammograms in Figure 6.4b also reveals evidence of the involvement of active sites in the spontaneous decoration process. As was studied in Chapter V, the broad peaks observed for the CV of the honeycomb gold in base (between ca. -0.6 V to -0.15 V) are related to the presence of active sites seen by FT-ac voltammetry (Chapter V, Figure 5.14). In Figure 6.4b these broad peaks are not observable after decoration with silver. This reduction in the active site behaviour of the honeycomb gold is therefore supportive of the hypothesis that the driving force for this reduction process is the result of the facile oxidation of gold active sites.
In order to determine whether this spontaneous decoration process was unique to the case of silver on gold or whether it showed a wider application, the decoration procedure was repeated for the case of palladium. Figure 6.5 shows the XPS spectra for the Pd 3d region of honeycomb gold (black) and honeycomb gold immersed in 1 mM Pd(NO$_3$)$_2$ (red). Both of these scans show a large broad peak at 336.3 eV, although this is attributed to the Au 4d$_{5/2}$ peak. The sample immersed in Pd(NO$_3$)$_2$ reveals two additional peaks at 338.2 eV and 343.6 eV which are attributed to the 3d$_{5/2}$ and 3d$_{3/2}$ peaks of PdO$_2$, respectively,$^{[64-65]}$ where the formation of this oxide is likely to result from the handling of the sample in air. As was the case for silver decoration, ionic palladium species could not be observed, and XPS scans for N which would indicate the presence of Pd(NO$_3$)$_2$ were featureless.
Figure 6.5: XPS spectra of the Pd 3d region for honeycomb gold with (red) and without (black) palladium decoration.

Similarly to the silver decoration case, SEM imaging revealed the formation of palladium nanoparticles following the decoration process. While a high degree of decoration is again seen, with nanoparticles ranging in size between approximately 5-20 nm, this surface coverage is less than the case of silver, which is to be expected as this reduction is a two-electron process as opposed to the one-electron reduction of silver. It is also noted that the spontaneous decoration of palladium occurs predominately at the tips and edges of the honeycomb gold structures. While it is possible that the location of nanoparticle formation and the oxidation of the active site(s) that are responsible may be separate, owing to the ready conduction which can take place across the gold nanostructures and the possible mobility of adatoms across the surface,[66-67] the edges and tips of the gold surface are thought to contain a higher extent of surface roughness and therefore active sites.[68] As such the location of palladium nanoparticles along the tips and edges may not be used as direct evidence of the location of active sites but appear to indicate regions with a higher active site population. As can be seen the active sites which are required for spontaneous decoration are favoured at finely nanostructured materials, and as these active sites are also known to be responsible for the electrocatalytic activity of monometallic systems the importance of creating materials with these finely nanostructured domains is highlighted.
Figure 6.6: High resolution SEM images showing honeycomb gold decorated with palladium.

The voltammetry of the palladium decorated honeycomb gold in 1 M H₂SO₄ is presented in Figure 6.7. This shows many similarities to the voltammetry of the honeycomb gold surface (Chapter V, Figure 5.11) particularly in the monolayer oxide formation and reduction processes. As in the case of silver decoration the voltammetry of the palladium decorated surface shows reduced gold premonolayer oxidation features as the result of the formation of the palladium nanoparticles. The presence of palladium on the decorated surface is also seen by the formation and reduction of palladium oxide at ca. 0.5 V along with the characteristic adsorption and desorption of hydrogen (between 0.22 V to -0.17 V) prior to hydrogen evolution, confirming the presence of palladium.[69]

Figure 6.7: Cyclic voltammograms of palladium decorated honeycomb gold recorded at 50 mV s⁻¹ in 1 M H₂SO₄.
Having investigated the spontaneous decoration process of honeycomb gold with silver and palladium, which can be attributed to the presence of active sites across the gold surface, the spontaneous decoration with nickel was then investigated. Nickel was chosen due to its low standard reduction potential, which is significantly less positive than that of silver or palladium. From the FT-ac studies of honeycomb gold in H₂SO₄ active site responses were observed at potentials as low as -0.1 V (Chapter V, Figure 5.12), where hydrogen evolution occurs at more negative potentials and masks the FT-ac voltammogram. However, it is unlikely that gold surfaces are able to oxidise at such low potentials. As such nickel is able to act as a control for the spontaneous decoration process, as its reduction potential is expected to be too low to be able to couple to the oxidation of gold active sites and thus spontaneously decorate a gold surface.

![XPS spectra of the Ni 3d region for honeycomb gold with (red) and without (black) immersion in a 1 mM solution of Ni(NO₃)₂.](image)

**Figure 6.8:** XPS spectra of the Ni 3d region for honeycomb gold with (red) and without (black) immersion in a 1 mM solution of Ni(NO₃)₂.

The XPS spectra for honeycomb gold (black) and honeycomb gold immersed in Ni(NO₃)₂ are presented in Figure 6.8. It is immediately apparent that neither nickel adsorption or decoration takes place. This was also confirmed by SEM observations of the nickel immersed honeycomb gold surface (Figure 6.9), where nanoparticle formation is not observed across the dendritic and rod-like honeycomb gold surface.
Figure 6.9: High resolution SEM images showing honeycomb gold immersed in Ni(NO$_3$)$_2$.

These findings provide further supporting evidence that the spontaneous decoration process is indeed driven by the oxidation of active sites present on the gold nanomaterials. It also gives insight into the range of metals which may spontaneously decorate a gold surface, for which the reduction potential of the metallic salts must be higher than the premonolayer oxidation potential of the active sites present on the gold surfaces.

One such metal which could theoretically decorate a gold surface is platinum, and bimetallic Au/Pt materials may show promising electrocatalytic behaviour in terms of activity and avoiding the poisoning effects commonly seen at monometallic platinum materials. Figure 6.10 shows the XPS spectra of the Pt 4f region for honeycomb gold (black) and honeycomb gold immersed in K$_2$PtCl$_4$, where the peaks at 73.0 eV and 76.4 eV are attributed to the 4f$_{7/2}$ and 4f$_{5/2}$ energy levels of oxidised platinum species such as Pt(OH)$_2$.\textsuperscript{[70]} While these peaks demonstrate the presence of oxidised platinum on the honeycomb gold surface, the peaks are of weak intensity and suggest a low surface coverage of platinum. This coverage was estimated to be 2.5 % on the basis of a comparison between the peak areas for platinum and gold, having taken the different elemental scattering factors into account. Since the publication of this work\textsuperscript{[71]} the spontaneous decoration of platinum on gold has also been reported,\textsuperscript{[72]} where the gold surface was subjected to an intensive cathodic
polarisation treatment prior to decoration. This independent finding adds further support for the active site mediated spontaneous decoration of platinum on gold observed here.

Figure 6.10: XPS spectra of the Pt 4f region for honeycomb gold with (red) and without (black) platinum decoration.

SEM imaging was performed on this platinum decorated material, however nanoparticle decoration could not be observed. Unlike the nickel system, the XPS results of the platinum system show that decoration has taken place, although less material has deposited than in the silver or palladium systems. It is therefore likely that the platinum has deposited either in the form of nanoparticles too fine to be observed by SEM or that the decoration occurred in the form of a submonolayer coverage.

Figure 6.11: High resolution SEM images showing honeycomb gold decorated with platinum.
Cyclic voltammetry studies of the platinum decorated honeycomb gold (Figure 6.12) again show a material whose response is dominated by the electrochemical behaviour of gold in H\textsubscript{2}SO\textsubscript{4}, seen by the formation and reduction of the monolayer oxide. In spite of the platinum coverage as determined by XPS, cyclic voltammetry provides additional support for the presence of platinum on the honeycomb gold. As with the silver and palladium cases less gold premonolayer oxidation behaviour is observed, and the reduction of platinum oxides formed in the forward sweep is seen at 0.32 V. Platinum electrochemical behaviour is also apparent in the hydrogen adsorption/desorption region followed by hydrogen evolution at ca. -0.15 V. Interestingly the typical butterfly-like peaks for the adsorption/desorption of hydrogen from platinum are not observed. This has been observed in the literature for platinum distributed very sparsely on gold,\textsuperscript{73} however further investigation would be required to assign the platinum response in the present case to a coating of fine nanoparticles as opposed to a thin overlayer.

**Figure 6.12:** Cyclic voltammograms of platinum decorated honeycomb gold recorded at 50 mV s\textsuperscript{-1} in 1 M H\textsubscript{2}SO\textsubscript{4}.

Given the observed decoration of platinum and its relevance in many catalytic and electrocatalytic reactions the platinum decorated honeycomb gold surfaces were then tested in a number of electrocatalytic reactions. As seen in Figure 6.14 the spontaneous decoration of platinum on a honeycomb gold surface led to a remarkable increase in electrocatalytic activity towards hydrogen evolution. This increased electrocatalytic activity was seen through both the shift in onset potential, with the platinum decorated surface shifting ca. 100 mV towards more positive
potentials, as well as an increase in the current magnitude at -0.4 V of approximately seventeen times. Although platinum is known to possess a higher electrocatalytic activity towards this reaction than gold,\textsuperscript{[74]} the magnitude of this result is surprising due to the low surface coverage of platinum (approx. 2.5\%) across the honeycomb gold surface.

\textbf{Figure 6.13:} Linear sweep voltammograms in 1 M H$_2$SO$_4$ for a honeycomb gold (black) and a platinum decorated honeycomb gold (red) sample recorded at a sweep rate of 5 mV s$^{-1}$.

In addition to the electrocatalytic evolution of hydrogen in H$_2$SO$_4$ the effect of platinum decoration was also tested towards the oxidation of ethanol in NaOH. As can be seen from Figure 6.14a the oxidation of ethanol at a polycrystalline gold electrode (black curve) begins at ca. -0.25 V, whereas the oxidation at a polycrystalline platinum electrode (blue curve) begins at a substantially less positive potential of ca. -0.60 V. These scans both increase to a peak current value at which point the formation of the monolayer oxides decreases the activity of the materials, which is then stripped on the reverse scan. Also of note from these polycrystalline electrodes is the degree of oxidation which occurs on the reverse sweep. Such oxidation processes often occur as a result of the incomplete oxidation of species in the forward sweep and has often been used to indicate that the material is susceptible to poisoning, measured as the ratio of the peak current passed in the forward and reverse scans (I$_F$/I$_B$). Sun \textit{et al.} recently published work questioning this method, and while this is not a quantitative measure it may still be useful to provide qualitative evidence about how readily the electrode can be
poisoned.\textsuperscript{[75]} As can be seen from Figure 6.14a the ratio of $I_F/I_B$ is much lower in the case of polycrystalline platinum ($I_F/I_B = 1.36$) than polycrystalline gold electrodes ($I_F/I_B = 4.46$), suggesting that the gold electrode is less susceptible to poisoning than platinum electrodes.

\textbf{Figure 6.14:} Cyclic voltammograms showing the electrocatalytic oxidation of ethanol from a solution containing $1 \text{ M}$ ethanol in $1 \text{ M}$ NaOH recorded at $50 \text{ mV s}^{-1}$. The voltammograms for polycrystalline platinum (blue) and gold (black) electrodes are shown in Figure (a), and in Figure (b) the honeycomb gold (black) and platinum-decorated honeycomb gold (red) are presented. Figure (c) shows a chronoamperometry experiment for ethanol oxidation held at $0.18 \text{ V}$ for $300 \text{ s}$.

The effect of decorating the honeycomb gold with platinum towards the oxidation of ethanol was also investigated (Figure 6.14b). Large differences were seen in the activity of the honeycomb gold (black) and the platinum decorated honeycomb gold (red), with the latter sample showing a shift in onset potential of ca. $300 \text{ mV}$
towards less positive potential compared with the former. The magnitude of the reaction is also striking, with the platinum decorated honeycomb gold recording a peak current value of 35.0 mA compared with the honeycomb gold peak current of 15.4 mA. This increase in current magnitude is unexpected as the polycrystalline platinum electrode showed a shifted onset potential but comparable current magnitude to the polycrystalline gold electrode (Figure 6.14a), indicating the presence of bulk platinum does not account for the increased current magnitude seen for the platinum decorated honeycomb gold. This significant increase in activity is also unexpected as the decorated surface only shows a relatively small coverage of platinum.

While the activity of the honeycomb gold was clearly enhanced by the spontaneous decoration of platinum, interesting results were also found for the effect of decoration on the poisoning of the surfaces. In agreement with results presented in Chapter V, polycrystalline gold does not show a high level of poisoning ($I_F/I_B = 4.46$) during the electrooxidation of ethanol under basic conditions (Figure 6.14a), and this propensity to poison is even less in the case of honeycomb gold ($I_F/I_B = 7.50$). The platinum decorated honeycomb gold demonstrated a degree of poisoning ($I_F/I_B = 2.35$) than the former sample, however increased poisoning tolerance was displayed compared to the polycrystalline platinum electrode ($I_F/I_B = 1.36$). Further studies on this system are required in order to determine the exact cause of the decreased level of poisoning and the increased electrocatalytic activity seen at these materials, which may be related to the size and morphology of the platinum deposits (e.g. fine nanoparticles or a submonolayer coverage) or the crystallography of the platinum deposits.

The activity and poisoning of the honeycomb gold and platinum decorated honeycomb gold was further investigated using chronoamperometry (Figure 6.14c). By applying a potential of 0.18 V (the peak oxidation potential for the platinum decorated sample) for 300 s it was seen that the steady state response of both the honeycomb gold and the platinum decorated honeycomb gold is preserved over the timescale of the reaction. This stability and resistance to poisoning, in combination
with their activity, demonstrates their applicability for electrocatalytic applications, especially for fuel cell related applications.

Owing to the enhanced electrocatalysis seen at the decorated samples as well as the range of materials which can readily be created in this manner the spontaneous decoration of honeycomb materials with their enhanced active site behaviour provides numerous opportunities for the creation of surfaces not only for electrocatalysis but also for other applications where bimetallic surfaces are desirable.

### 6.2.2. Decoration of Evaporated Gold Films

Having investigated the spontaneous decoration of electrodeposited honeycomb gold films attention turned from electrodeposited materials to see whether this phenomenon occurred in other gold systems. The evaporated gold films employed previously as substrates for electrodeposition and also as control samples for electrocatalytic processes were chosen for this purpose. The formation of metallic films by evaporation is a common process in a variety of applications, such as the fabrication of semiconductor components, various lithographic processes and in the formation of electrode materials, so the modification of these materials by spontaneous decoration may be of interest in these fields.

To confirm whether these evaporated films would provide suitable materials for spontaneous decoration their electrochemical behaviour in acidic and basic solutions was tested. While the relevant voltammograms have been presented in Chapter III (CV in 1 M H₂SO₄ presented in Figure 3.9 and CV in 1 M NaOH given in Figure 3.11), the presence of premonolayer oxidation events was hard to detect by cyclic voltammetry as compared to the enhanced response seen at electrodeposited materials. FT-ac voltammetry was then employed to study these evaporated films, and the FT-ac voltammogram of evaporated gold in 1 M H₂SO₄ is presented in Figure 6.15.
Figure 6.15: FT-ac voltammogram of an evaporated gold film in 1M H₂SO₄ showing the forward and reverse scans for the DC and first to fourth harmonic responses. Data was recorded at a sweep rate of 63.33 mV s⁻¹ with an applied sinusoidal perturbation of 100 mV at a frequency of 21.1 Hz.
As can be seen from the dc response in Figure 6.15a-b typical electrochemical behaviour for gold in H\textsubscript{2}SO\textsubscript{4} is displayed, showing no obvious redox processes in the double layer region. While the capacitive contributions are still quite large in the first and second harmonic responses (Figure 6.15c-f), as confirmed by the non-zero current passed at the beginning of the scans, these contributions are significantly reduced at the fourth harmonic response (Figure 6.15i-j). Here a very small peak is present at 0.79 V, suggesting the presence of a low coverage of active sites on the evaporated gold film whose oxidation product is of low stability in H\textsubscript{2}SO\textsubscript{4}, which was seen for the electrodeposited gold nanomaterials in Chapters III and V.

The FT-ac voltammetry was then repeated in 1 M NaOH, as the [Au\textsubscript{2}(OH\textsubscript{9})\textsuperscript{3-}] species, which are thought to be the product of premonolayer oxidation at the active sites, are more stable in an alkaline solution.\textsuperscript{[76]} While the main features of the DC response (Figure 6.16a-b) are the formation of the monolayer oxide and its subsequent reduction, several peaks can also be seen within the double layer region, with an oxidation peak at ca. -0.14 V and reduction peaks at -0.48 V and -0.84 V visible, unlike the H\textsubscript{2}SO\textsubscript{4} case where redox processes were not observed. Again the capacitive contribution in the first harmonic response (Figure 6.16c-d) was noticeable, and by the fourth harmonic response this contribution diminished revealing the behaviour of Faradaic processes at the evaporated gold films.

Although the magnitude of these responses is lower than for the electrodeposited gold nanostructures discussed earlier, these premonolayer oxidation processes are clearly present on the surface. Of particular note are the potentials at which these processes occur, with the largest premonolayer oxidation seen at -0.90 V. As discussed previously for the honeycomb gold materials, the range of premonolayer oxidation responses seen by FT-ac is thought to relate to the presence of a variety of active sites which show different redox behaviour as a result of their different activities. The presence of these more reactive active sites, which will oxidise at less positive potentials, is significant in the case of spontaneous decoration as it will create a larger driving force for the spontaneous decoration. These FT-ac results therefore confirm that the spontaneous decoration of evaporated gold films is a feasible reaction.
Figure 6.16: FT-ac voltammogram of an evaporated gold film in 1M NaOH showing the forward and reverse scans for the DC and first to fourth harmonic responses. Data was recorded at a sweep rate of 63.33 mV s\(^{-1}\) with an applied sinusoidal perturbation of 100 mV at a frequency of 21.1 Hz.
The gold films were then tested for spontaneous decoration by immersion in a 1 mM AgNO$_3$ solution for five minutes, as had been the case for the honeycomb gold materials. Silver was chosen as the main system for this study as the decoration of honeycomb gold with silver had shown the highest surface coverage and resulted in the ready identification of nanoparticles on the gold surface. The XPS spectra for the Ag 3d region of an evaporated gold film and a silver decorated gold film are presented in Figure 6.17. It can be seen that no silver is detectable for the evaporated gold film, indicating the purity of the samples prior to decoration. Two peaks were observed for the silver decorated sample at ca. 368.6 eV and 374.6 eV which are attributed to the 3d$_{5/2}$ and 3d$_{3/2}$ shells of metallic silver, respectively.\textsuperscript{[61-62]} As was the case for the honeycomb gold, this decoration did not result in the detection of ionic species on the surface, showing that the silver present on the surface is in the metallic form and that any unreacted species are removed in the washing step.

![XPS spectra showing the Ag 3d region for an evaporated gold film (black) and a silver-decorated gold film (red).](image)

**Figure 6.17:** XPS spectra showing the Ag 3d region for an evaporated gold film (black) and a silver-decorated gold film (red).

ICP-MS was also performed on the 1 mM AgNO$_3$ solution after the decoration of a gold film in order to examine if gold was oxidised into the solution through the spontaneous decoration of silver, however no gold species could be detected. This suggests that the silver decoration is coupled to the premonolayer formation of surface oxides rather than the dissolution of the active sites.
Having confirmed the presence of elemental silver as a result of the spontaneous decoration of the evaporated films, the morphology of the deposit was investigated by electron microscopy. Figure 6.18 shows the SEM images of an evaporated gold film (Figure 6.18a) and a silver decorated gold film (Figure 6.18b). Comparison of these images reveals that the underlying gold substrate has similar grain size and structure (ca. 40-50 nm), however there are no detectable nanoparticles in the case of the silver decorated sample. This finding was unexpected and is in contrast with the results found for the honeycomb gold case, where a large number of nanoparticles were found to decorate both the tips and flatter regions of the surface. The XPS results of the silver decorated gold film clearly show the presence of silver, suggesting that the lack of observable nanoparticles may be due to the deposited silver being present as either nanoparticles smaller than the working resolution of the SEM (approx. 10 nm) or as a submonolayer coverage.

![Figure 6.18: SEM images of evaporated gold surfaces before (a) and after (b) silver-decoration.](image)

In order to gain a better insight on the morphology of the silver decorated films TEM studies were conducted. While TEM offers enhanced resolution as compared to SEM and can provide valuable structural information on nanosized objects its application in electrochemical studies is often limited by its requirements for sample preparation. As TEM is based on the transmission of electrons through a sample, as opposed to the emission of secondary electrons from the surface of a
sample in SEM, samples must allow enough electrons to transmit through to the detector. This often requires a very thin sample, which may include either drop cast nanoparticles on a support grid or a very thin film sample. In the present case it was determined that the preparation of the evaporated films for TEM would be complicated and the integrity of the structure could not be guaranteed, so it was decided not to analyse these films by TEM. An alternative was found in the form of a commercially available gold TEM grid. These grids are formed by the evaporation of gold on a carbon support grid, forming a gold mesh, on which a single crystal gold film is formed. Care was taken to avoid gold-coated copper grids as any decoration may be due to a galvanic replacement reaction with copper through defects in the gold film. While the commercially available gold TEM grids are generally used for image and diffraction pattern calibration purposes, they provide a suitable material to further investigate the spontaneous decoration of silver on gold films.

Due to the prohibitive cost of the gold TEM grids their electrochemical behaviour was not investigated, which would require separate samples so that the surface was not disrupted by reordering during the electrochemical testing. This grid was then subjected to the same decoration procedure used previously, washed thoroughly and allowed to air dry. The presence of silver on this material was confirmed by EDX performed on the TEM (Figure 6.19b), where a small but distinct peak was seen at 2.96 keV relating to the Ag L shell. XPS analysis was also performed and revealed the presence of metallic silver, with the 3d5/2 and 3d3/2 peaks found at 368.08 eV and 374.08 eV (Figure 6.19b), further confirming the decoration of silver on the gold TEM grid.
TEM imaging was performed and representative images are shown in Figure 6.20. Although the gold film was nominally a single crystal surface with a (100) orientation many defects were present on the surface such as raised steps, visible in Figure 6.20a. It is the presence of such defects and active sites which appear to be responsible for the spontaneous decoration of the gold TEM grid.

While nanoparticle decoration was not observed across this sample, the presence of silver has been shown by the EDX and XPS analyses. EDX mapping (Figure 6.20b) was then performed on the region shown in Figure 6.20a by mapping the AgL peak across the surface (blue), which showed the highest intensity and best resolution of the silver peaks. This mapping revealed a relatively even, although somewhat sparse, coverage of silver across this region. Although EDX mapping was also performed at higher magnification a balance between recording enough counts from the AgL peak against the drift which was experienced at this magnification precluded a high level of confidence in these results. This issue was avoided by performing high resolution imaging in regions where higher silver coverage was seen, and a typical result is shown in Figure 6.20b. Although the EDX mapping revealed the presence of silver in these regions no nanoparticle formation could be observed, indicating that the silver existed in a submonolayer coverage across the surface. It should be noted that this finding does not directly relate to the evaporated films studied in this chapter, however the propensity for silver to form a

Figure 6.19: EDX (a) and XPS (b) analysis of the silver-decorated gold TEM grid.
submonolayer coverage on gold has been noted before\cite{78-79} and is consistent with the XPS and SEM results presented here.

\textbf{Figure 6.20:} TEM imaging of a silver-decorated gold TEM grid showing (a) a low magnification image, (b) EDX map of the region in image (a) with silver appearing blue. The inset of image (a) was taken at high resolution in the region indicated.

The voltametric behaviour of the decorated evaporated films was investigated in 1 M NaOH (Figure 6.21). While the active site behaviour of the evaporated gold is not seen by CV, the adsorption of OH\textsuperscript{-} at ca. -0.1 V is seen for both the evaporated gold and the silver decorated evaporated gold. As with the honeycomb gold case the decoration of evaporated gold with silver led to altered electrochemical behaviour in NaOH, with changes seen in the monolayer oxidation at the upper potentials and more noticeably as a shift of approximately 60 mV in the reduction peak to more negative potentials due to the reduction of silver oxide formed on the forward sweep. While the charge required to reduce such oxides may be used to determine the electrochemically active surface area of electrode surfaces,\cite{80} the overlap of the contributions from the reduction of the gold oxide and silver oxide limits the use of such calculations in this instance. However it should be noted that the magnitude of the reduction peaks for the gold film and the silver decorated gold film are comparable, suggesting that the surface area of the film has not been considerably altered as a function of the decoration process.
Figure 6.21: Cyclic voltammograms in 1 M NaOH for an evaporated gold film (black) and a silver-decorated gold film (red) recorded at a scan rate of 50 mV s\(^{-1}\).

The voltammetry of these materials was also probed in 1 M H\(_2\)SO\(_4\) (Figure 6.22), where silver stripping becomes feasible at moderate potentials. The appearance of additional anodic processes are readily observable, and as seen in the enlarged section in Figure 6.22b this consists of a defined peak at ca. 0.89 V and a wave-like peak to less positive potentials, which begins at an onset potential of ca. 0.68 V. Such oxidation has previously been reported for surfaces modified with silver nanoparticles, although there is some controversy over whether this effect was the result of the particle size of the nanoparticles or whether it was an effect brought about by the ensemble of nanoparticles.\(^{81-83}\)

Aside from this noticeable stripping process the voltammograms are remarkably similar. The similarities in the reduction peaks at ca. 0.93 V, which occur after the stripping of silver from the surface, indicate that the electrochemically active surface area of the gold film is not significantly altered by the decoration process.
The presence of active sites on metallic surfaces was recently reported by Scholz and co-workers, where they elegantly demonstrated that Fenton’s reagent was capable of removing these roughened surface features. This was seen by not only a decrease in the roughness and surface area of the electrodes but also a reduced electrocatalytic activity towards reactions such as oxygen reduction. The authors also probed the nature of the active sites by examining the effect that Fenton’s reagent treatment had upon both inner and outer sphere reactions on the electrodes, which differ in how strongly the electroactive species must adsorb on the surface in order for a redox reaction to take place. This was probed using the hydrogen evolution reaction and the benzoquinone/hydroquinone couple to examine inner sphere reactions (where strong adsorption is required), and a Ru$^{3+/2+}$ hexamine couple in the case of an outer sphere reaction (where the adsorption required for reaction is negligible). These studies showed that outer sphere reactions are insensitive to the presence of active sites, whereas the removal of active sites through the action of Fenton’s reagent has a significant impact on the behaviour of inner sphere reactions.

Similar reactions were also performed in this work to test the nature of the active sites of the gold and decorated gold films. The behaviour of the gold films and decorated gold films towards an outer sphere reaction was tested using
ferrocenemethanol in KNO$_3$ (Figure 6.23a). As can be seen, the oxidation of the Fe$^{2+}$ to Fe$^{3+}$ on the forward scan and its subsequent reduction back to Fe$^{2+}$ is practically identical for both the evaporated gold film (black) and the silver decorated gold film (red). This outer sphere reaction, which is insensitive to the presence of silver or gold shows very similar behaviour to that reported by Scholz and co-workers for gold films exposed to Fenton’s reagent,$^{[85]}$ confirming that when active sites are removed from the surface by chemical polishing or by spontaneous decoration that no significant differences are seen for electrocatalytic processes based on weakly adsorbing species.

Figure 6.23: Cyclic voltammograms in 1 mM ferrocenemethanol in 0.1 M KNO$_3$ (a) for an evaporated gold film (black) and silver-decorated gold film (red) recorded at a scan rate of 100 mV s$^{-1}$. Linear sweep voltammograms in 1 M H$_2$SO$_4$ (b) for an evaporated gold film (black), a silver-decorated gold film (red) and an evaporated silver film (blue) recorded at a scan rate of 5 mV s$^{-1}$.

The electrochemical behaviour of the films was also investigated towards the hydrogen evolution reaction in H$_2$SO$_4$, which proceeds via an inner sphere reaction.$^{[86]}$ Gold is known to be a more active electrocatalyst for the HER than silver, which is reflected in the LSV in Figure 6.23b. Here the evaporated gold film (black) showed the highest activity compared with the silver decorated gold film (red) and the evaporated silver film (blue). As has been noted with the earlier electrocatalytic testing of decorated materials there are significant differences in the electrochemical behaviour of the gold materials and their decorated counterparts. In this case the decoration with silver led to an 85% decrease in the current
magnitude at -0.5 V, although only approximately 12 % of the surface was covered with silver, suggesting that the active sites which were oxidised to drive the spontaneous decoration are largely responsible for the electrocatalytic activity of the evaporated gold film in this instance. It should be noted that the silver decorated film still shows higher activity compared to the evaporated silver film, indicating that the regions of the gold surface not decorated with silver are also active towards HER, however the electrocatalytic activity of the evaporated gold in this instance appears to be dominated by the behaviour at active sites.

While the decoration of gold with silver was shown to shut down the electrocatalytic activity of the HER, this should not be taken as an indication that this material is a generally poor electrocatalyst. This is because the electrocatalytic activity of a material is highly correlated to the reaction of interest as the result of a contribution of numerous factors, based on how the reactants adsorb, react and desorb from the surface.\textsuperscript{[87-88]} This is strongly influenced by the composition, size, shape, crystallographic orientation and porosity of the material, and therefore different materials are better suited to particular electrocatalytic reactions than others.\textsuperscript{[89-93]} The decorated materials were therefore investigated as possible oxygen reduction electrocatalytic materials. This reaction is of particular interest, not only as it is often used as a model electrocatalytic reaction but as it is of interest applications such as fuel cells and lithium-air batteries, where the sluggish reduction of oxygen can often be a limiting factor in the former case.\textsuperscript{[94]}

Figure 6.24a shows the reduction of oxygen from a solution of O\textsubscript{2} saturated 1 M H\textsubscript{2}SO\textsubscript{4}. This reaction is particularly sluggish for an evaporated gold film (black), where a well-defined reduction peak could not be observed prior to the evolution of H\textsubscript{2} at ca. -0.4 V. The spontaneous decoration of silver (red) resulted in a dramatic increase in oxygen reduction, with a clear peak visible at -0.25 V and an onset potential shifted by ca. 170 mV towards more positive potentials than the gold film. It is interesting to note that Scholz reported that the removal of active sites decreased the electrocatalytic activity of the polycrystalline gold electrodes towards oxygen reduction in acidic conditions, seen as a shift to more negative potentials. However in this case, even though the active sites are being used in the spontaneous
decoration procedure, the resulting bimetallic surface shows an improved electrocatalytic activity towards oxygen reduction. This improvement is not thought to be the direct result of the different electronic structure of the gold and silver decorated gold films as XPS results do not show significant shifts in the binding energy of the Au 4f peaks.

**Figure 6.24:** Cyclic voltammograms in O\textsubscript{2} saturated 1 M H\textsubscript{2}SO\textsubscript{4} (a) and 1 M NaOH (b) for an evaporated gold film (black) and a silver-decorated gold film (red), recorded at a scan rate of 50 mV s\textsuperscript{-1}.

The electrocatalytic activity of the materials was also tested in O\textsubscript{2} saturated 1 M NaOH (Figure 6.24b). As was observed under acidic conditions the evaporated gold film shows sluggish behaviour, with a broad reduction peak centred at -0.53 V. Interestingly this reduction was found to be quasi-reversible, with an anodic component found at 0.065 V. This quasi-reversibility has not received much attention in the literature, to the best knowledge of the author. In order to confirm this result rotating ring-disk studies were completed in O\textsubscript{2} saturated 1 M NaOH (Figure 6.25). The results for the gold disk with platinum ring are plotted in black, with O\textsubscript{2} reduction occurring at similar potentials to the evaporated gold film under hydrostatic conditions. The platinum ring electrode was held at 0.3 V in order to oxidise any peroxide that was formed at the disk, and although the response is small on the scale presented the presence of peroxide can be observed by the oxidative current detected at the ring. It is therefore suggested that the quasi-reversibility of the evaporated gold films is due to the two electron reduction of O\textsubscript{2} to peroxide.
which is re-oxidised to $\text{O}_2$ on the reverse scan. It should be noted from the ratio of the magnitudes of the ring current versus the disk current at -0.8 V ($|I_A|/|I_C| = 7\%$) that it is likely that oxygen reduction does not proceed exclusively through either the two electron or four electron reduction mechanisms, and may instead involve both of these processes at different surface sites.

Figure 6.25: Rotating ring disk electrode studies showing a gold disk (black) and a silver-decorated gold disk (red) electrode in an $\text{O}_2$-saturated 1 M NaOH solution. The platinum ring electrode was held at 0.3 V (vs Ag/AgCl) in order to detect peroxide formation on the disk. The electrode rotation rate was 2000 RPM and the sweep rate was 10 mV s$^{-1}$.

As was seen under acidic conditions, the decoration of gold films with silver lead to markedly different electrocatalytic responses towards the reduction of $\text{O}_2$ in 1 M NaOH. This material displayed a higher degree of reversibility than the evaporated gold film, with well-defined peaks at -0.33 V and -0.06 V. Significant shifts in the peak potentials are seen compared with the evaporated gold film, with a 200 mV shift towards more positive potentials for the cathodic process and a 125 mV shift towards less positive potentials for the anodic process. This increased degree of reversibility suggests that the two electron reduction of $\text{O}_2$ is promoted at the silver decorated film, as had been found for the evaporated gold film. RRDE studies were repeated in $\text{O}_2$ saturated 1 M NaOH using a silver decorated gold disk with a platinum ring electrode (red curve in Figure 6.25), with the applied potential at the ring electrode held at 0.3 V. The response from the decorated electrode towards the RRDE experiment shows the reduction of $\text{O}_2$ beginning at a similar potential to the
silver decorated evaporated gold film, with a higher current magnitude than the gold disk electrode in agreement with the case of the evaporated films. The oxidation at the ring is more appreciable for the silver decorated gold disk than it was in the case of the gold disk, and its connection to the reduction of $O_2$ at the disk electrode is seen from its onset potential beginning at the onset potential of $O_2$ reduction at the disk. The magnitude of hydrogen peroxide formed in this case is higher for the decorated electrode, which was also reflected in the ratio between the magnitudes of the oxidation current to the reduction current ($|I_A|/|I_C|= 21 \%$) and indicated a greater extent of the two-electron reduction of $O_2$. The direct assignment of this promoted electrocatalytic process is difficult, especially as there is disagreement in the literature over the exact mechanisms of $O_2$ reduction for both gold and silver surfaces. For example there is debate over whether the two- or four-electron reduction pathways are promoted at nanostructured silver surfaces with nanoparticles of different size and crystallography orientation. Since the exact nature of the silver deposit in this instance is unclear these effects cannot be decoupled using the data currently available. In addition there is uncertainty over the mechanism of oxygen reduction at gold surfaces, and so for a complicated surface such as the silver decorated evaporated gold films more work is required before the mechanism for the promoted electrocatalytic activity can be assigned.

### 6.2.3. Extension of Spontaneous Decoration to Other Materials

In addition to the studies presented above, the spontaneous decoration process was also investigated for other materials presented in this thesis, although a full study of these materials is beyond the scope of the current work. For instance, gold nanospikes were tested in the same procedure as outlined previously, and it was found that bimetallic surfaces could be formed with silver, as demonstrated from the XPS results in Figure 6.26b.
Figure 6.26: SEM image (a) and XPS spectrum (b) of silver decorated gold nanospikes.

The morphology of the silver decorated gold nanospikes was also investigated using SEM (Figure 6.26a), however these images resemble typical SEMs for gold nanospikes (Chapter III, Figure 3.2) with no obvious nanoparticle decoration. These SEM results were surprising in light of the prior work on the decoration of honeycomb gold and evaporated gold films, where decoration in the form of nanoparticles was more evident in the case of the nanostructured honeycomb gold and submonolayer coverages were found for evaporated films. Having observed these results it was expected that the nanostructured gold spikes with their higher proportion of exposed active sites compared to evaporated gold films would display a greater number of nanoparticles as the result of spontaneous decoration. More work is required in order to make a definite assignment for these differences, however it is expected the crystallographic structure of the outer most layer of the gold surface plays an important role in directing the morphology of the decoration. This could be the result of factors such as the propensity of particular metals to sit upon different geometric arrangements of surface atoms (such as on atop or three-fold sites),[97] as well as by altering the surface mobility of the foreign adatoms on the gold surfaces.

The spontaneous decoration of platinum nanostructures was also investigated, having observed the active site behaviour of the platinum nanostructures in Chapter IV. The silver decoration of the platinum nanostructures electrodeposited in the
absence of lead was explored, and shown in Figure 6.27 are an SEM image and XPS spectrum of the Ag 3d region. While the morphology of the deposit is not significantly different from those observed without decoration (Chapter IV, Figure 4.2), the decoration of silver is evident from the XPS analysis. As was discussed in the case of gold this decoration is due to the oxidation of active sites on these platinum nanostructures. This demonstrates that the spontaneous decoration process is not restricted to gold but may also take place on a variety of other metals where active site behaviour is displayed.

Figure 6.27: SEM image (a) and XPS spectrum showing the Ag 3d region for silver decorated platinum nanostructures deposited from a solution of 8 mM H₂PtCl₆ in 0.1 M HCl for 600 s at -0.05 V on a glassy carbon surface.

The silver decoration of the platinum-lead nanomaterials was also investigated. As can be observed from the SEM image of this material in Figure 6.28a the decoration of silver does not lead to the formation of nanoparticles on the surface, however the XPS results in Figure 6.28b clearly indicates the presence of silver on the surface. This decoration is to be expected, due not only to the oxidation of the exposed active sites (as demonstrated in Figure 6.26) but also to the ready galvanic replacement of the exposed lead on this nanomaterial. The ability to decorate a range of surfaces including platinum and platinum-lead may show interest in the future development of bimetallic and trimetallic nanostructured materials, especially in light of the facile and fast decoration process which can occur by simple immersion of the material at open circuit potential.
Figure 6.28: SEM image (a) and XPS spectrum showing the Ag 3d region for silver decorated platinum-lead nanostructures deposited from a solution of 8 mM \(\text{H}_2\text{PtCl}_6\) with 0.05 mM \(\text{Pb(CH}_3\text{COO})_2\) in 0.1 M HCl for 600 s at -0.05 V on a glassy carbon surface.

6.3. Summary

After focusing on the electrochemical formation of nanostructured materials and studying their active site behaviour in earlier chapters, the possibility of utilising these active sites for the formation of bimetallic surfaces was presented in this chapter. While very little has been reported on such systems previously, and even less for the decoration of gold surfaces, this work identified that metals such as gold and platinum can undergo a spontaneous decoration reaction when immersed in a solution of an appropriate metal salt. This work focused on the decoration of gold, which as the most noble element was not considered to be a suitable candidate for spontaneous decoration from a thermodynamic standpoint.

Importantly, it was found that the facile oxidation of active sites, as studied previously, was responsible for the spontaneous decoration. The coupling of this oxidation process to the reduction of the metal salt provides an explanation of the driving force for this reaction, which has not been reported previously to the author’s knowledge. This provides a key insight into the mechanism of spontaneous decoration and allows further research to be rationally designed into different systems where this reaction may take place. As the spontaneous decoration process is driven by the active sites present on these surfaces it also helps us to gain a better
insight into the coverage and behaviour of these surface sites, an important factor in the design and understanding of electrocatalytic materials.

While such studies have proved to be interesting from a fundamental point of view, the work also shows interest from an applied viewpoint. The fabrication of nanomaterials and bimetallic systems is an area of keen research interest, however a common problem can exist in the form of trying to find simpler methods which require less time, money or effort to create, isolate and implement such materials. The spontaneous decoration process has shown to be a particularly facile method, not reliant on any external stimuli to begin the process, and is not hindered by line of site issues as may be encountered in nanofabrication methods such as sputtering or lithographic processes. For materials where nanoparticles are formed by spontaneous decoration, the size range of these particles is of interest from a catalytic and electrocatalytic nature. This is reflected in the electrocatalytic experiments investigated, where the decoration of only a small percentage of the surface lead to significant increases in the electrocatalytic activity of the materials towards a variety of technologically important reactions such as used in fuel cell and lithium-air battery applications.

6.4. References


Chapter VII

Conclusions and Future Work
7.1. Summary of Key Findings

The electrochemical formation of a range of novel nanostructured materials has been reported in this work, including the synthesis of gold nanospikes, platinum-lead dendritic nanostructures and porous gold surfaces. These methods involve chemical templating during electrodeposition, either in the form of lead acetate or hydrogen bubbles generated in situ. In the former case, lead acetate was found to template the growth of gold nanospikes through preferential adsorption on the growing electrodeposit, while in the electrodeposition of platinum the underpotential deposition of lead both roughened the surface of the platinum electrodeposit and provided sites for galvanic replacement to occur. In the case of the porous gold surfaces, the dynamic hydrogen bubble templating method was applied to the electrodeposition of gold for the first time, in spite of a previous report that this could not be achieved. All the materials studied were found to possess a high degree of nanostructuring, and apart from the incorporation of a small amount of Pb in the platinum-lead nanostructures (2.5 %), the gold nanospikes, porous gold and quasi-spherical platinum nanostructures did not show the incorporation of the templating species.

The electrochemical behaviour of these nanomaterials was investigated using both conventional dc cyclic voltammetry as well as FT-ac voltammetry. While typical electrochemical behaviour relating to the formation and reduction of monolayer oxides was seen, the appearance of premonolayer oxidation processes was observed within the double layer region of all materials studied. These premonolayer oxidation responses indicate the oxidation of active sites on the materials, which are thought to exist as low lattice coordinated atoms or clusters of atoms on the surface that are prone to oxidation at lower potentials than observed for the bulk surface. The study of the materials with FT-ac also revealed a number of other premonolayer oxidation processes which had been masked by the capacitive current seen by dc cyclic voltammetry. These results highlight the large shifts in oxidation potentials from that of the bulk surface, and show a high degree of
correlation with the onset potentials for a range of important electrocatalytic reactions. This provides further evidence that these reactions are governed by the incipient hydrous oxide adatom mediator (IHOAM) model of electrocatalysis, where the electrocatalytic reaction is enhanced by the surface confined redox behaviour of an active site/metallic hydrous oxide species.

Having observed the extent of premonolayer oxidation which occurred at the nanostructured materials, the possibility of spontaneously reducing a number of metallic salts at the nanostructured surfaces was then investigated. The decoration of honeycomb gold, gold nanospikes and even evaporated gold films was observed by simply immersing the materials in solutions of either K$_2$PtCl$_4$, Pd(NO$_3$)$_2$ or AgNO$_3$ at open circuit potential followed by thorough washing to remove any loosely adhered species. The reduction of these metal salts to their elemental states was attributed to the facile premonolayer oxidation of the nanostructured materials, with the coupling of these reactions providing a suitable driving force for the decoration process. The decoration of both platinum and platinum-lead nanostructures with silver was also observed, and while galvanic replacement of lead with silver may occur in the latter case the decoration of the former surface provides evidence that the premonolayer oxidation of platinum active sites can also be used to drive the spontaneous decoration of the surfaces. This method provides a means to study the coverage and reactivity of active sites, and was also shown to be a facile means of creating bimetallic surfaces which display altered electrocatalytic activity compared with their monometallic systems.

### 7.2. Future Work

The work presented in this thesis provides much scope for future work in this area. Ideally, this will involve the rational design of metallic nanostructures through templated electrodeposition which display optimal activity and stability towards fields such as electrocatalysis, electroanalysis and SERS applications. In order to work towards this goal, future work can be classified under the electrodeposition of nanostructured metals, the fundamental behaviour of active sites and the spontaneous decoration of metallic surfaces.
In the field of electrodeposition, further work stemming from this project includes studying the effect of lead acetate on the electrodeposition of a number of other technologically important metals, such as silver and palladium. While the ability to direct the growth of these metals is likely to be different on a case-by-case basis, depending on factors such as the UPD behaviour of Pb on these metals, the formation of nanostructured materials may be possible. These monometallic or bimetallic surfaces may provide interesting materials for anti-microbial, catalytic, electrocatalytic or SERS applications, and lead to similar investigations on the active site behaviour of these metals in a nanostructured form. Further to this, the electrodeposition of gold and platinum in the presence of other heavy metal salts may be explored, including bismuth, tin and germanium. In a similar manner to varying the electrodeposited metal, altering the heavy metal salt may provide further insights on the interaction between the growing electrodeposit and the introduced metal salt.

The study of active sites on gold, platinum and a number of other metals also represents an area of further research. One of the major aims of such work is to identify the structure and physical properties of the active sites. This is a challenging aim due to the relatively low coverage of active sites and their apparent heterogeneous nature, as they appear to exist on polycrystalline surfaces in a number of different forms and may possess a degree of mobility on the surface. Additionally, determining the chemical nature of the oxidised active sites under a range of different conditions is a further goal in this area. Several strategies to reach this aim include studying the premonolayer oxidation process in situ via synchrotron radiation, as well as studying mass changes on the surface of nanostructured materials such as porous gold by electrochemical QCM. Theoretical modelling of the oxidation of an atomically roughened surface may provide complementary results to the FT-ac studies shown here, demonstrating the large shifts in oxidation potential observed experimentally at nanostructured electrodes. However, directly correlating modelling data with the experimental results is not possible at the present time as the exact structure of the active sites on the polycrystalline surfaces has not yet been established. Another interesting experiment would be to investigate the electrochemical behaviour of single crystal
electrodes with FT-ac voltammetry. As defects are thought to be present on all surfaces this may provide a means to identify the level of disorder on these single crystal surfaces, as well as providing confirmation of the Faradaic behaviour of the basal planes on these electrodes after the capacitive contribution is removed.

The spontaneous decoration on metallic surfaces provides another exciting route for further research. This includes the study of other substrate/metallic salt combinations, particularly for substrates where active site behaviour has previously been reported. This study could also be extended to include spontaneous decoration in the presence of multiple metallic salts and may lead to the formation of a range of trimetallic materials. The decoration of other nanomaterials can also be explored, including free nanoparticles and nanorods. While the presence of capping agents may alter this decoration process, their removal prior to decoration may provide not only a simple method of decorating these ubiquitous nanomaterials but may also be used to study the spontaneous decoration process at the defined crystal facets present on these materials.

Other work on the spontaneous decoration process includes gaining an understanding of why the decoration occurs as nanoparticles in some cases and as a submonolayer coverage in others. The coverage of active sites and also the crystallography of the surface may play an important role in this process, as the extent of charge propagation may influence the formation of these morphologies. Another area of study is to investigate whether spontaneous decoration can influence the determination of electrochemically active surface areas using metallic salts. While this has previously been performed by measuring the charge associated with the underpotential deposition of the metallic salt, if spontaneous decoration occurs under open circuit potential conditions then this may affect the accuracy of the surface area determination. Such findings may lead to improved techniques to characterise metallic surfaces. Spontaneous decoration may also play an important role in the shape directing behaviour of species such as Ag\(^+\) during the chemical or electrochemical synthesis of metallic nanomaterials. This mechanism may involve the spontaneous decoration of metallic silver at an active site on the growing nanomaterial, which could then be included in the nanostructure or depending on the composition of the solution could undergo galvanic replacement. Such
knowledge may aid in both the understanding of how these templates behave as well as allowing the rational selection of templates for future nanomaterial syntheses.
Appendix

Research Outcomes

Peer-Reviewed Journal Papers


Peer-reviewed Journal Papers Under Preparation or Submission


Journal Cover Page

– Analyst, 2011, 136

Peer-reviewed Conference Paper

Relevant Awards and Scholarships

- Endeavour Postdoctoral Research Fellowship (2013), to be undertaken with Prof. Richard Compton at the University of Oxford.


- Deputy Vice Chancellor’s (Research and Innovation) Postgraduate Research Student International Conference Fund (2012).

- Professor CNR Rao Postgraduate Research Excellence Award in Materials Science (2010), which included the opportunity to work with Prof. Rao at the Jawaharlal Nehru Centre for Advanced Scientific Research (JNCASR) in Bangalore, India.

- Australian Postgraduate Research Award (2009-2012).