Sonication Enabled Liquid Marble Frameworks: Synthesis, Characterizations and Applications

A thesis submitted in fulfilment of the requirements for the degree of Doctor of Philosophy

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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 the thesis is the result of work which has been carried out since the official commencement date of the approved research program; any editorial work, paid or unpaid, carried out by a third party is acknowledged; and, ethics procedures and guidelines have been followed.

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Abstract

Liquid marbles are liquid droplets coated with hydrophobic powders. The properties of the liquid core, the incorporated micro- and nano-coating materials and the core/coating interfaces offer new opportunities for creating novel units for sensing, liquid manipulations, microfluidics and micro-reactors. Conventional liquid marbles are usually in millimeter scales, which considerably limit the interfacial properties because of the low surface-to-volume ratio as a result of the large core dimensions.

In this PhD research, the author develops ‘liquid marble frameworks’ which are made of micro- to nano-sized liquid marbles using sonication. It is shown that the size, the surface chemical/physical compositions and the order of coating of the developed liquid marbles can be tuned. To obtain various functionalities, the PhD candidate develops liquid marble frameworks made of micro- to nano-sized coated spheres using different types of liquid cores and coatings. The synthesized frameworks provide enhanced performance for heavy metal ion sensing, photocatalysis, hydrogen gas sensing and surface enhanced Raman scattering (SERS). The PhD project is conducted in four distinct stages that each results in novel outcomes.

In the first stage, liquid metal/metal oxide (LM/MO) frameworks are developed by sonicating liquid metal galinstan. The candidate characterizes the developed frameworks, and finds that their surface morphology and chemical composition are functions of the sonication duration. The LM/MO framework, made with sonication duration of 20 min show photocatalytic efficiency of \(~47\ %\ h^{-1}\). This efficiency is much higher than the efficiency of films made of pure tungsten oxide (WO$_3$) nanoparticles, which is used as a benchmark. The enhancement is ascribed to the excellent visible light absorption properties of LM/MO frameworks and the unique LM/MO interfaces that facilitate charge separation and suppression of electron–hole recombination. Afterwards, WO$_3$ nanoparticles are incorporated to LM/MO frameworks to obtain high sensitivity towards low concentrations of heavy metal ions. The sensitivity towards Pb$^{2+}$ as low as 100 ppb is obtained, which is about 80 times improvement compared to bulk liquid marbles. The detection limit is lower than the hazardous
thresholds of heavy metal ions for humans. The author associates the improvement of sensitivity to the high surface–to–volume ratio of LM/MO frameworks providing a large dipole surface for efficiently attracting ions.

In the second stage, the candidate synthesizes gallium oxide (Ga$_2$O$_3$) using a solvothermal method. The synthesized Ga$_2$O$_3$ are incorporated to the LM/MO frameworks to realize enhanced photocatalytic systems. The surface stoichiometry of these systems can be tuned by changing the loading of incorporated Ga$_2$O$_3$ nanoparticles. With 1 wt% loading of incorporated Ga$_2$O$_3$, the photocatalytic efficiency of the systems is $\sim 100 \% \, h^{-1}$, which is much higher than the efficiency of either LM/MO frameworks or pure Ga$_2$O$_3$. This is attributed to the possible formation of pseudo–ohmic contacts between liquid metal core and Ga$_2$O$_3$ nanoparticles, which reduce the free carrier injection barrier to Ga$_2$O$_3$.

In the third stage, WO$_3$ nanoparticles are incorporated to liquid metal (LM) frameworks in order to form liquid metal/tungsten oxide (LM/TO) hydrogen (H$_2$) gas sensors. The results of characterization shows that the incorporated WO$_3$ nanoparticles are partially reduced when incorporated to the surface of liquid metal cores. The optimum operating temperature for the LM/TO sensor is found to be 200 ºC. At this temperature, the response time of the LM/TO sensor towards 1% H$_2$ at is 90 s, which is approximately 2.5 times faster than H$_2$ gas sensors based solely on WO$_3$ nanoparticles. This can be attributed to the formation of oxygen vacancies in substoichiometric WO$_{3-x}$ and the presence of catalytically active gallium in the liquid core, which facilitate the H$_2$ redox reaction. The LM/TO H$_2$ gas sensors also show excellent reproducibility when exposed to increasing concentrations of H$_2$ gas.

In the final stage, silver (Ag) nanoparticle/oleic acid liquid marble frameworks are developed by encapsulating Ag nanoparticles to micro–sized oleic acid liquid spheres, which is achieved via sonication. Optimum order of Ag nanoparticle coating can be obtained when the frameworks are sonicated for 60 min. The SERS responses of frameworks towards an organic thiolate are measured. The frameworks with sonication of 60 min show the strongest response. Efficient solar energy absorption of the frameworks is also demonstrated. Results show that frameworks with sonication of
60 min experience the largest temperature rise (11.8 °C) after being illuminated under a simulated solar source for 30 min, which is also associated to SERS.

In summary, the author believes that the outcomes of this PhD research create new knowledge in the fields of liquid metals, liquid marbles, catalysis, sensing and SERS. The author also believes that the investigations show new opportunities for using liquid marble frameworks in future applications.
List of Figures

Figure 1.1 Schematic illustration of selected liquid core and coatings for the formation of liquid marbles of this PhD research. ................................................................................................................................. 2

Figure 2.1 (a) The SEM image of an assembly of LM/MO spherical structures after sonication for 20 min and drop casted on a substrate. (b) The magnified image of the dotted area. .............................. 24

Figure 2.2 (a) A top view SEM image of an assembly of LM/MO spherical structures after 20 min sonication. (b) The plot of average diameters of spheres within spherical structures after different sonication durations. SEM images of spheres after sonication for (c) 2, (d) 5, (e) 10 and (f) 20 min and their corresponding magnified images (g–j). ................................................................................................................................. 25

Figure 2.3 SEM images of LM/MO spherical structures after sonication for 60 min in different magnifications. ................................................................................................................................. 26

Figure 2.4 SEM images of LM/MO frameworks (a) before and (b) after dipping into DI water for a prolonged .............................................................................................................................................. 26

Figure 2.5 SEM images of LM/MO spherical structures after sonication for (a) 5 and (b) 20 min, respectively. Their corresponding EDX mappings of (c–d) gallium element and (e–f) oxygen element. All images are in the same magnification and the scale bars represent a distance of 500 nm. ............. 28

Figure 2.6 SEM images of LM/MO spherical structures after the sonication for (a) 5 and (b) 20 min, respectively. Their corresponding EDX mappings of (a–b) gallium element, (c–d) indium element and (e–f) tin element. All images are in the same magnification and the scale bars represent a distance of 500 nm. .............................................................................................................................................. 28

Figure 2.7 The XPS spectra of Ga 3d, In 3d, Sn 3d and O 1s for LM/MO spherical structures after sonication for 5 min: (a), (c), (e), (g); and 60 min: (b), (d), (f), (h). ................................................................................. 30

Figure 2.8 The XPS spectra of Ga 3d films made of LM/MO spherical structures, which are formed after the sonication for 5 min: (a), (b), (c), (d); and 60 min: (e), (f), (g), (h). Spectra of Ga 3d are collected at 20 different etching layers from the surface as the reference. Layer 1: (a) and (e); Layer 5: (b) and (f); Layer 10: (c) and (g); Layer 20: (d) and (h). ..................................................................................................................... 31

Figure 2.9 The intensity of oxygen signal at different etching layers. ................................................................................................................................. 32
Figure 2.10 Schematic images of LM/MO spherical structures during sonication. Grey shapes, red circles and red ovals stand for galinstan spheres, oxide layers and nanoplatelets, respectively. 

Figure 2.11 XRD spectra of LM/MO spherical structures after sonication for (a) 20 min and (b) 60 min.

Figure 2.12 SEM images of LM/MO spherical structures. (a) Surface oxide layer cracks and forms nanoplatelets; (b) Residual oxide nanoplatelets and (c) Magnified image.

Figure 2.13 SEM images of an assembly of micro- and nano-sized liquid metal marbles formed by coating WO₃ nanoparticles onto LM/MO spherical structures prepared after 20 min of sonication.

Figure 2.14 Raman spectra of (a) micro-sized liquid metal marbles; (b) LM/MO spherical structures; (c) WO₃ nanoparticles.

Figure 2.15 UV–Vis absorption spectra of the LM/MO spherical structures obtained after different sonication duration: (a) 5, (b) 10, (c) 20 and (d) 60 min.

Figure 2.16 UV–Vis absorption spectra of the suspended LM/MO sphere containing solutions obtained after 20 min of sonication with and without WO₃ nanoparticles.

Figure 2.17 UV–Vis absorption spectra of the same suspended LM/MO sphere containing solution prepared after 20 min of sonication (Measurement 1), 24 h (Measurement 2) and 48 h (Measurement 3).

Figure 2.18 Cross sectional SEM images of assembled LM/MO framework in different magnifications.

Figure 2.19 Differential pulse stripping voltammograms for different concentrations of Pb²⁺ using (a) micro- to nano-sized LM/MO frameworks incorporating WO₃ nanoparticles (b) micro- to nano-sized LM/MO frameworks.

Figure 2.20 Differential pulse stripping voltammograms for increasing concentrations of Pb²⁺ recorded at micro- and nano-sized liquid metal marbles along with the background response (dotted line). Inset i shows the stripping peak current values versus different concentrations of Pb²⁺. Inset ii shows the comparison of a hanging galinstan droplet electrode (marked as “H”) and a micro- and nano-sized liquid metal marbles (marked as “M”) for DPVs recorded for the reduction of Pb²⁺ to Pb⁰ under same testing conditions.
Figure 2.21 Four consecutive cycles of differential pulse stripping voltammograms for the same LM/MO framework incorporating WO$_3$ in the presence of 500 ppb of Pb$^{2+}$.................................43

Figure 2.22 Differential pulse stripping voltammograms for different concentrations of Cd$^{2+}$, Pb$^{2+}$ and Cu$^{2+}$ recorded using the LM/MO framework incorporating WO$_3$ nanoparticles along with the background response (dotted line).................................................................44

Figure 2.23 Photocatalytic properties of LM/MO frameworks, WO$_3$ nanoparticles and micro-and nano-sized liquid metal marbles. (a) Degradation of 10 µM CR in the presence of LM/MO frameworks prepared after different sonication durations. WO$_3$ nanoparticles with the same mass serve as the benchmark. (b) Degradation of 10 µM CR in the presence of micro-sized liquid metal marbles containing WO$_3$ nanoparticles which are in different weight percentages..........................46

Figure 2.24 Photocatalytic properties in four consecutive cycles using the same LM/MO framework. .................................................................................................................................47

Figure 3.1 (a) A bulk galinstan droplet kept in DI water. (b) Suspension of micro- to nano-sized liquid metal marble spheres. SEM images of (c) top view of LM/MO frameworks with incorporated Ga$_2$O$_3$ nanoparticles (1 wt%), (d) LM/MO frameworks without incorporated Ga$_2$O$_3$ nanoparticles, inset shows native oxide nanoplatelets, scale bar of the inset is 500 nm. (e) TEM image of solvothermally synthesized Ga$_2$O$_3$ nanoparticles, and (f) TEM diffraction patterns of Ga$_2$O$_3$ nanoparticles.................................................................56

Figure 3.2 XRD spectrum of solvothermally synthesized Ga$_2$O$_3$ nanoparticles........................................57

Figure 3.3 SEM images of surface morphology of micro-sized galinstan spheres with different loadings of Ga$_2$O$_3$: (a) 0 wt%, (b) 0.2 wt%, (c) 1 wt% and (d) 2 wt%..................................................58

Figure 3.4 SEM images of LM/MO frameworks with different loadings of Ga$_2$O$_3$ nanoparticles: (a) 0 wt%, (b) 0.2 wt%, (c) 1 wt% and (d) 2 wt%.................................................................58

Figure 3.5 The XPS spectra of Ga 3d of LM/MO frameworks with different loadings of Ga$_2$O$_3$ nanoparticles: (a) 0 wt%, (b) 0.2 wt%, (c) 1 wt% and (d) 2 wt%. (e) The XPS spectrum of Ga 3d of solvothermally synthesized Ga$_2$O$_3$ nanoparticles. (f) UV–Vis absorption spectra.................................60

Figure 3.6 UV–Vis (a) reflectance and (b) transmission spectra of LM/MO framework with 1 wt% Ga$_2$O$_3$ nanoparticles.................................................................61
Figure 3.7 (a) Degradation of 10 µM CR in the presence of Ga$_2$O$_3$ nanoparticles, LM/ MO frameworks and LM/MO frameworks incorporated with different loadings of Ga$_2$O$_3$ nanoparticles. (b) Degradation of 10 µM CR in the presence of one sample of LM/MO frameworks with 1 wt% incorporated Ga$_2$O$_3$ in four consecutive cycles. The difference of decomposition rates among four consecutive cycles is less than 2%.

Figure 3.8 Degradation of 10 µM CR in the presence of LM/MO frameworks and LM/MO frameworks with incorporated different loadings of Ga$_2$O$_3$ nanoparticles.

Figure 3.9 Degradation of 10 µM CR in the presence of Ga$_2$O$_3$ nanoparticles, LM/MO frameworks with incorporated 1 wt% Ga$_2$O$_3$ and aluminium particles with incorporated 1 wt% Ga$_2$O$_3$ nanoparticles.

Figure 3.10 (a) Mott–Schottky plots of LM/MO frameworks and Ga$_2$O$_3$ nanoparticles measured in Na$_2$SO$_4$ solution (0.3 M, pH 7.0). (b) XPS valence band spectra of LM/MO frameworks and Ga$_2$O$_3$ nanoparticles. (c) Band structure diagram of the combined system.

Figure 3.11 Linear sweep voltammogram of LM/MO framework with incorporated 1 wt% Ga$_2$O$_3$ nanoparticles.

Figure 3.12 Cyclic voltammogram of LM/MO framework with incorporated 1 wt% Ga$_2$O$_3$ nanoparticles.

Figure 3.13 XPS valence band spectra of Ga$_2$O$_3$ nanoparticles, LM/MO frameworks and LM/MO frameworks with different loading of Ga$_2$O$_3$ nanoparticles.

Figure 4.1 Schematic illustration of the synthesis procedure: (a) Adding bulk galinstan to DI water, (b) adding WO$_3$ nanoparticles to the LM frameworks, (c) obtaining the LM/TO suspensions.

Figure 4.2 Schematic diagram of (a) gas sensor, and (b) gas sensing measurement system.

Figure 4.3 SEM images of LM/TO gas sensing film made of micro– and nano–sized LM frameworks with incorporated WO$_3$ nanoparticles. The sonication duration was 20 min.

Figure 4.4 The plot of average diameters of galinstan spheres after different sonication durations.

Figure 4.5 XRD spectrum of the LM/TO sensors.
Figure 4.6 XPS spectra of (a) Ga 3d of LM/MO frameworks, (b) W 4f of original WO₃ nanoparticles, (c) Ga 3d of LM frameworks with WO₃ coating and (d) W 4f of LM frameworks with WO₃ coating.

Figure 4.7 (a) The dynamic response of the LM/TO sensor towards 1% H₂ gas at different temperatures. (b) The dynamic responses of the LM/TO sensor and original WO₃ nanoparticles at 200 °C.

Figure 4.8 (a) The dynamic response of LM/TO sensor measured with increasing concentrations of H₂ gas at 200 °C and (b) response time and recovery time with respect to H₂ gas concentration at 200 °C.

Figure 5.1 Schematic illustrating the synthesis of Ag nanoparticles/oleic acid liquid marbles. (a) Adding oleic acid into a glass vial filled with DI water, (b) adding Ag nanoparticles into the vial, (c) positioning the glass vial in a sonication bath for a desired time, and (d) obtaining the micro–sized Ag nanoparticles/oleic acid liquid marble suspension.

Figure 5.2 Optical image of (a) micro–sized Ag nanoparticles/oleic acid liquid marbles after 60 min sonication, and (b) magnified image. (c) TEM image and (d) TEM diffraction pattern of Ag nanoparticles.

Figure 5.3 Optical images of Ag nanoparticles/oleic acid liquid marbles after sonication for (a) 20, (b) 40, (c) 60, and (d) 80 min. Scale bar = 200 µm. (e) The plot of average diameters of oleic acid spheres coated with Ag nanoparticles at four different sonication times.

Figure 5.4 (a) UV–vis absorption spectra of micro–sized Ag nanoparticles/oleic acid liquid marbles after different sonication times, and Ag nanoparticles powder. (b) SAXS spectra of Ag nanoparticles/oleic acid liquid marbles after four different sonication times. Inset shows the magnified region of interest.

Figure 5.5 Raman spectra of 0.5 mg PTT on Ag nanoparticles/oleic acid liquid marbles after 20, 40, 60 and 80 min of sonication. The Raman spectra of 0.5 mg of PTT on Au substrate and in oleic acid are presented as control measurements. The Raman spectrum of Ag nanoparticles/oleic acid liquid marbles after 60 min of sonication is also measured. The spectra were shifted vertically for clarity.
Raman peaks (1004 cm\(^{-1}\)) intensity of 0.5 mg of PTT on liquid marbles after four different sonication times, and on gold substrate. ................................................................. 91

Figure 5.6 (a) Raman spectra of different loadings of PTT on Ag nanoparticles/oleic acid liquid marbles after at 60 min of sonication. The spectra were shifted vertically for clarity. (b) Raman peaks (1004 cm\(^{-1}\)) intensity of different loadings of PTT on liquid marbles after 60 min of sonication. Raman peak (1004 cm\(^{-1}\)) intensity of 0.4 mg of PTT on Au substrate is also presented, shown as a yellow dashed line ................................................................. 93

Figure 5.7 (a) Raman spectra of 0.5 mg PTT on Ag nanoparticles/oleic acid liquid marbles after 60 min of sonication. The incubation time is varied. (b) Raman peak (1004 cm\(^{-1}\)) intensity of 0.5 mg of PTT on liquid marbles with various incubation durations on a gold substrate ........................................ 94

Figure 5.8 Thermal images of Ag nanoparticles/oleic acid liquid marbles after four different sonication times and pure oleic acid under illumination for 30 min. Room temperature is 24 °C. ...... 95

Figure 5.9 ESEM images of Ag nanoparticles/oleic acid liquid marbles after 60 min of sonication... 96
List of Tables

Table 3.1 The composition of LM/MO frameworks incorporated with different amounts of Ga$_2$O$_3$ nanoparticles. ................................................................. 54

Table 3.2 Raw data of repeatability of photocatalysis. ......................................................... 62
# Table of Content

Acknowledgement ........................................................................................................... i

Abstract ......................................................................................................................... iii

List of Figures ................................................................................................................ vi

List of Tables .................................................................................................................. xii

Table of Content ........................................................................................................... xiii

Chapter 1 Introduction and Literature Review ............................................................... 1

1.1 Motivation ............................................................................................................... 1

1.2 Objectives ............................................................................................................. 5

1.2.1 Investigation of Liquid Metal/Metal Oxide Frameworks ............................ 5

1.2.2 Investigation of Liquid Metal/Metal Oxide Frameworks with Incorporated Ga₂O₃ for Photocatalysis ................................................................. 7

1.2.3 Investigation of Liquid Metal/Metal Oxide Frameworks Functionalised with WO₃ Nanoparticles for Hydrogen Gas Sensing ................................................. 8

1.2.4 Investigation of Silver Nanoparticle/Oleic Acid Liquid Marbles for SERS Enhancement .............................................................................................................. 8

1.3 Thesis Organization ............................................................................................. 9

1.4 References ........................................................................................................... 11

Chapter 2 Liquid Metal/Metal Oxide Frameworks ......................................................... 20

2.1 Introduction ....................................................................................................... 20

2.2 Experimental Details ....................................................................................... 21

2.3 Results and Discussion .................................................................................... 24

2.4 Conclusion ...................................................................................................... 48

2.5 References ..................................................................................................... 49

Chapter 3 Liquid metal/metal oxide frameworks with incorporated Ga₂O₃ for photocatalysis .............. 52

3.1 Introduction ..................................................................................................... 52

3.2 Experimental Details ..................................................................................... 53

3.3 Results and Discussion .................................................................................... 55

3.4 Conclusion ...................................................................................................... 68

3.5 References ..................................................................................................... 69

Chapter 4 Liquid Metal/Metal Oxide Frameworks Functionalised with WO₃ Nanoparticles for Hydrogen Gas Sensing ........................................................................... 70

4.1 Introduction ..................................................................................................... 70

4.2 Experimental Details ..................................................................................... 71

4.3 Results and Discussion .................................................................................... 74
| 4.4  | Conclusion                                                                 | 80   |
| 4.5  | References                                                                 | 82   |

Chapter 5 Sonication synthesis of micro–sized silver nanoparticle/oleic acid liquid marbles: a novel SERS sensing platform ................................................................. 84

| 5.1  | Introduction                                                               | 84   |
| 5.2  | Experimental Details                                                      | 85   |
| 5.3  | Results and Discussion                                                    | 87   |
| 5.4  | Conclusion                                                                | 97   |
| 5.5  | References                                                                | 98   |

Chapter 6 Conclusions and Future Work ........................................................................ 99

| 6.1  | Conclusions                                                               | 99   |
| 6.2  | Publications                                                              | 104  |
| 6.3  | Recommendations for future works                                          | 106  |
Chapter 1

Introduction and Literature Review

1.1 Motivation

The term “liquid marbles” was first introduced in 2001 by Pascale Aussillous and David Quéré.[1] Liquid marbles are liquid droplets encapsulated by micro– or nano–sized hydrophobic particles.[1, 2] The encapsulated liquid is separated from the outside media, which is either air or liquid, resulting in the formation of a non–adhesive entity. This unique structure provides the potential for liquid marbles to be used for a variety of applications such as sensing,[3, 4] liquid manipulations and microfluidics,[5, 6] and establishment of micro–reactors.[5]

Manually developed liquid marbles are usually in millimeter scale. Such liquid marbles have low surface–to–volume ratio because most of the liquid core is redundant. Therefore, in applications that require high surface–to–volume ratio, such as catalysis and sensing,[3] performance of macroscopic liquid marbles is strongly limited. Additionally, efficient surface enhanced Raman scattering (SERS) is rarely obtained on conventional liquid marbles because the phenomenon mainly relies on small size entities.

In this PhD research, the candidate identifies the aforementioned research gap regarding liquid marbles. He searches for appropriate methods to reduce the size of liquid marbles and hence increases the surface–to–volume ratio. He identifies that one of the most facile approaches to obtain micro– to nano–sized liquid marbles is sonication. During the process, acoustic cavitation breaks down bulk
liquid with large size to small entities. Additionally, co–sonication of liquid and micro/nanoparticles facilitates the formation of surface coating by these micro/nanostructures. During the process, these particles come into intimate contacts with the broken down liquid core to establish physical or chemical bonds, hence the coating. The liquid marbles suspensions produced by sonication can then be drop casted or printed on substrates to form thin films. The thin films consist of micro– to nano– sized liquid marbles that are in the proximity of each other and are highly porous, which provides the needs for sensing and catalysis.

As such, the PhD candidate becomes involved in the development of platforms called “liquid marble frameworks” using sonication. The project investigates the functionalities of these frameworks with and without incorporated coating materials. Depending on the choice of materials for liquid core and coating, liquid marble frameworks can offer a variety of capabilities as the schematic presented in Figure 1–1.

![Schematic Illustration](image)

**Figure 1.1** Schematic illustration of selected liquid core and coatings for the formation of liquid marbles of this PhD research.

Liquid core can be made of liquid metals. Liquid metals belong to the family of low–melting–point materials that maintain a liquid state at near room temperature. For years, mercury was the most used
liquid metal; however, mercury’s high toxicity has resulted in its gradual phasing out for many applications. Nowadays, gallium–based alloys, such as eutectic gallium–indium (EGaIn) and galinstan, are increasingly being used as replacements of mercury in different applications due to their relatively lower toxicity.\(^{7, 8}\) Additionally, gallium based liquid metal alloys produce lower vapor pressures in comparison to mercury, and higher electrical and thermal conductivity. In the presence of air, a thin layer of oxide (mainly made of gallium oxide) is formed on the surface of galinstan. This is another point of difference between these liquid metal alloys and mercury that stabilized their structure which provide opportunities for creating advanced systems in microfluidics,\(^{9-11}\) electronics,\(^{12-14}\) self–healing devices,\(^{15, 16}\) and optics.\(^{17, 18}\)

Oil is another suitable candidate for liquid core that is investigated by the PhD candidate. Most recently, it has been demonstrated that a liquid–liquid interface, especially oil–water interface, can facilitate the accumulation of silver (Ag), platinum (Pt) and gold (Au) nanoparticles at the interface.\(^{19-22}\) The established systems are capable of probing oil–soluble molecules, by taking advantage of their plasmonic properties. The idea of using such functional interfaces is attractive. However, the potential of these liquid–liquid interfaces is limited by their surface area. Enhancing the surface area of such interfaces, by micro– and nano–structuring processes, can increase the chances of interactions between the marbles and dissolved chemical species, resulting in augmented performances in applications such as catalysis,\(^{23, 24}\) energy storage/generation\(^{11, 25}\) and sensing.\(^{3, 26}\)

The other step is to choose the right functional coating for the frameworks. Functional metal oxides, such as Gallium oxide (Ga\(_2\)O\(_3\)) and tungsten oxide (WO\(_3\)), have been widely studied and utilized. Hence they seem to be viable candidates for coating. Ga\(_2\)O\(_3\) is a wide bandgap metal oxide which has the advantage of providing photogenerated charges with high oxidizing potentials. Because its valence band edge is found to be located at −7.75 eV vs. vacuum.\(^{27}\) However, photocatalytic applications of Ga\(_2\)O\(_3\) are considerably limited on the grounds that it fails to generate sufficient electron–hole pairs upon illumination by solar light, as it has a wide band gap reported to be \(~4.8\) eV.\(^{27}\) Different approaches have been reported to form a metal/Ga\(_2\)O\(_3\) system in order to enhance its photocatalytic performance. One of the most popular methods is to use noble metal nanoparticles to increase visible
light absorption, by taking advantage of the surface plasmon resonance effect,\cite{28} which has yet to be fully understood. Another approach is to dope metal ions into Ga$_2$O$_3$, but this inevitably prejudices the advantage of a highly negative conduction band edge.\cite{29,30}

WO$_3$ has been widely investigated as a resistance based hydrogen (H$_2$) sensor because of its excellent electrochromic and gasochromic properties.\cite{31-34} The sensing mechanism is based on its conductivity being varied when H$_2$ breaks down into H$^+$ ions and electrons on the surface of this material that spill over and intercalate into the oxide.\cite{35} This intercalation process increases the free charge carrier concentration which in turn augments the conductivity of the material allowing for a detectable sensing response.\cite{36} During the process water is also generated and evaporates at the surface at the elevated temperatures typically employed for these gas sensors.\cite{35} For recovery in air, oxygen molecules are adsorbed on the surface of the reduced tungsten oxide and oxidize it, then extract electrons from the conduction band thereby increasing the resistance of the material.\cite{36} To improve the sensitivity and reduce the response/recovery time, catalysts such as Pt and palladium (Pd) have been utilized on the surface of sensing materials,\cite{37-39} as these catalysts are capable of splitting H$_2$ molecules more efficiently than the native oxide. Therefore, the reaction rate and sensitivity of such gas sensors are improved compared to pure WO$_3$. The PhD candidate believes that liquid marbles developed using functional metal oxides are likely to provide similar functionalities to the frameworks and as such Ga$_2$O$_3$ and WO$_3$ are used for coating liquid metals. Catalytic nanoparticles such as Pt and Au cannot be used with liquid metals as they rapidly amalgam with them. So liquid metal based frameworks are only investigated with functional oxide of choice.

Metal particles have been used as coating materials to form liquid marbles with organic or aqueous based cores.\cite{40} They are thermally and electrically conductive and can show catalytic properties.\cite{41} They are also capable of generating surface plasmons for SERS applications.\cite{42} SERS is a process in which Raman signals of molecules are enhanced by augmented local electromagnetic fields at nano-sized tips and boundaries of a material.\cite{43} It is generally suggested that the excited surface plasmon resonances (SPRs), which are collective electron excitations, can significantly enhance the local electromagnetic field.\cite{44} In particular, it is known that noble metal nanoparticle assemblies and
complex structures are capable of producing strong SPRs at visible wavelengths. Relevant observations have led to considerable research on the development of Ag, Pt and Au nanostructures, consisting of nanoparticles, nanoshells, nanorods and nano-dendrites. As such, the PhD candidate chose to use the Ag nanoparticles in conjunction with oil based liquid core to develop sensitive and SERS capable frameworks in this research.

According to the aforementioned justifications and motivations, the objectives of this PhD work are presented in the following sections.

1.2 Objectives

1.2.1 Investigation of Liquid Metal/Metal Oxide Frameworks

“Solid state metal”/“metal oxide” (SM/MO) micro- and nanostructures have attracted great interest for their unique physiochemical properties, which are achieved in combination but are not exhibited by the individual metal and metal oxides counterparts. These interesting properties originate from the functionalities of both metals and metal oxides as well as the interfaces between them, providing systems which enable the manipulation of charge, light, and mechanical vibrations as well as many other functionalities.

A variety of solid metals have been used in forming SM/MO structures. It has been shown that these structures facilitate charge separation, assist in light absorption and scattering as well as in providing a template for generating strong SPR. They have also been used for a variety of sensing applications including chemical and biochemical sensors.

In principle, solid metals can be replaced by liquid metals to form “liquid metal”/“metal oxides” (LM/MO) structures. Interestingly, despite their immense potentials, LM/MO structures have rarely been reported. Furthermore, none of these works take advantage of the nature of the incorporated liquid metals. In addition to the well-known benefits that solid metals can offer, liquid metals add
extra dimensions to the structures, which originate from their soft and liquid nature. This brings flexibility, the possibility of amalgamation with other metals and their recoverability, mobility and high conformation to the system.

The possibility of coating relatively large liquid metal droplets of galinstan using metal oxide nanoparticles has been previously shown.[10, 25, 76] By doing this, liquid metal marbles with extraordinary physical and chemical properties were created. Investigations associated these properties to the interfaces between liquid metal and metal oxide nanoparticles in combination with the flexibility of the marbles, thereby providing extra degrees of freedom in order to manipulate their functionalities on demand. As discussed before, the properties of large liquid metal marbles are strongly surface dependent and the bulk of the droplet is mostly redundant. For using the bulk of liquid metals, it should be divided into the smallest possible stable entities.

In the first step of this PhD research, the candidate will develop a micro- to nano-sized LM/MO frameworks based on liquid metal galinstan via sonication. The physiochemical properties of these frameworks will be characterized. The candidate will demonstrate that the surface morphology and chemical composition can be actively controlled. A hypothesis regarding chemical changes of liquid metal during the process of sonication will be proposed. The PhD candidate will study the photocatalytic performance of LM/MO frameworks. Additionally, WO$_3$ nanoparticles will be incorporated into these frameworks for heavy metal ion sensing.

1.2.2 Investigation of Liquid Metal/Metal Oxide Frameworks with Incorporated Ga$_2$O$_3$ for Photocatalysis

With increasing global concerns regarding environmental remediation, the implementation of solar light driven metal/metal oxide photocatalysts for the decomposition of pollutants has drawn great interest.[77–79] The photocatalytic performance of such systems can be influenced by many factors including the efficiency of electron–hole pair generation and separation,[80–82] as well as the oxidizing...
potentials of the photogenerated charges.\textsuperscript{[83]} The former is relevant to the bandgap and how facile the electron–hole pairs can be separated. The latter is determined by the band position of the metal oxide component.\textsuperscript{[84]} The ideal metal oxides in such a system are those with valence band edges exceeding the $\text{H}_2\text{O}/\text{O}_2$ oxidation potential, and with bandgap energies capable of absorbing the full solar light spectrum.

As previously discussed, Ga$_2$O$_3$ is capable of providing photogenerated charges with high oxidizing potentials for photocatalytic activities. It is also demonstrated that LM/MO frameworks are capable of efficiently utilizing the solar spectrum as well as preserving metallic features that contribute to charge separation upon illumination. In light of this, it is hypothesized that an efficient LM/MO photocatalytic system can be potentially made of such frameworks upon the incorporation of additional Ga$_2$O$_3$.

In the second stage of this PhD research, the candidate will synthesize Ga$_2$O$_3$ nanoparticles using a solvothermal method. These Ga$_2$O$_3$ nanoparticles will be incorporated to the LM/MO frameworks introduced in the previous stage to form hybrid systems. Properties of the hybrid systems will be investigated and controllability will be demonstrated. The LM/MO frameworks with incorporated Ga$_2$O$_3$ nanoparticles will be utilized for photocatalysis. The performance of the hybrid system will be assessed and studied. The PhD candidate will further explore the band structure of the developed hybrid systems.

1.2.3 Investigation of Liquid Metal/Metal Oxide Frameworks Functionalised with WO$_3$ Nanoparticles for Hydrogen Gas Sensing

As mentioned before, WO$_3$ has been recognized as an efficient resistance based H$_2$ sensor. The PhD candidate hypothesizes that an improvement in H$_2$ gas sensitivity can be obtained by coating the gallium alloy based frameworks with WO$_3$. It has been previously shown that binary compounds of WO$_3$ with other metal oxides such as MoO$_3$ and TiO$_2$ can provide improved sensitivity and kinetics
for gas sensing.\textsuperscript{[85, 86]} Also the presence of metals such as gallium, tin and indium may also facilitate catalytic activities.\textsuperscript{[87, 88]} It has to be determined which of these two effects is more dominant in establishing LM/MO frameworks with incorporated WO$_3$ nanoparticles for H$_2$ gas sensing.

In the third stage of this PhD research, the PhD candidate will incorporate WO$_3$ nanoparticles to liquid metal (LM) frameworks to develop liquid metal/tungsten oxide (LM/TO) framework based hydrogen gas sensors. He will characterize the sensors and study the surface chemical compositions of these frameworks. Optimum operating temperature will be found for sensing responses as the key parameters of interest. The sensor responses will be compared to references such as standard WO$_3$ films to explore the origins of the operation of the frameworks. The sensing mechanism of the LM/TO gas sensor will be fully explored.

1.2.4 Investigation of Silver Nanoparticle/Oleic Acid Liquid Marbles for SERS Enhancement

As presented before, oil–water interfaces are great bases for sensing and SERS, and it is possible to facilitate their activities by incorporating Ag, Pt and Au nanoparticles into such interfaces. Because assemblies and complex structures of noble metal nanoparticles are capable of producing strong SPRs at visible wavelengths.

In the fourth stage of this PhD research, the PhD candidate will develop a liquid marble framework made of oleic acid spheres encapsulated by Ag nanoparticles via sonication as a model system to explore his hypothesis. The physical and optical properties of the platform will be characterized. Investigations will be conducted to achieve the optimum coating of Ag nanoparticles. The Ag nanoparticles/oleic acid liquid marble frameworks will be investigated for sensing an organic material (thiolate as a model material). The capacity of the frameworks for increasing solar light absorption and energy conversion into heat will also be investigated. The PhD candidate will carry out a concerted effort to reveal the mechanisms that the frameworks provide for enhanced SERS responses and solar energy absorption.
1.3 Thesis Organization

This thesis consists of six chapters which are presented as follows:

- Chapter 1 is an overview of the PhD candidate’s motivation for performing the research as well as the objectives and the organization of this thesis.

- Chapter 2 presents the development and investigations of LM/MO frameworks. Active control of the diameters of the spheres and the stoichiometry of the structures will be demonstrated. The performance of LM/MO frameworks for photocatalytic activities will be assessed and studied. WO$_3$ nanoparticles will be incorporated into LM/MO frameworks for heavy metal ion sensing.

- Chapter 3 presents the development and investigations of LM/MO frameworks with incorporated Ga$_2$O$_3$ nanoparticles. The photocatalytic activities of the hybrid systems will be demonstrated. A theoretical study of band structure of these systems will also be shown.

- Chapter 4 presents the development and investigations of LM/MO frameworks with incorporated WO$_3$ for H$_2$ gas sensing. Optimum operating temperature will be found. The sensing response of the sensors towards H$_2$ will be measured and studied.

- Chapter 5 presents the development and investigations of Ag nanoparticle/oleic acid liquid marble frameworks. The candidate will fully characterize the system. The SERS performance and thermal absorption of the system will be demonstrated.

- Chapter 6 presents the conclusions of this thesis, the suggestions for possible future work, and the PhD candidate’s achievements during the candidature.
### 1.4 References


Chapter 2

Liquid Metal/Metal Oxide Frameworks

2.1 Introduction

A new platform described as the liquid metal/metal oxide (LM/MO) framework will be introduced in this chapter. The constituent spherical structures of these frameworks will be made of micro– to nano–sized liquid metal spheres and nano–sized metal oxides, combining the advantages of both materials. It will be shown that the diameters of the spheres and the stoichiometry of the structures can be actively controlled via a sonication process. Additionally, it will be demonstrated that the liquid suspension of these spheres offer tuneable plasmon resonances. These spherical structures will be assembled to form LM/MO frameworks which will be capable of demonstrating high sensitivity towards low concentrations of heavy metal ions, and enhanced solar light driven photocatalytic activities.

The PhD candidate will utilize micro– to nano–sized galinstan spheres with coated metal oxide nanoparticles to form the LM/MO spherical structures suspended in aqueous solutions. As per Chapter 1, galinstan (68.5 wt% Ga, 21.5 wt% In, and 10 wt% Sn) is chosen as it poses less health hazards in comparison to liquid metals such as mercury. The density of galinstan is 6440 kg/m³. Its melting point is –19 °C. Its vapor pressure is less than 10⁻⁶ Pa at 500 °C. In the process, the surface metal oxide nanoparticles will be either inherently formed during the synthesis process or coated onto the surface of galinstan spheres. The candidate will fully characterize the LM/MO spherical structures in terms of stoichiometry and optical properties, including the demonstration of plasmon resonances.
To show the functionality of the created material, he will assemble LM/MO spherical structures into LM/MO frameworks and investigate their capabilities as recoverable and reusable photocatalysts. In addition, he will demonstrate a highly sensitive electrochemical sensor for the detection of heavy metal ions.

The content of this chapter was fully reviewed and published in Advanced Functional Materials[1].

2.2 Experimental Details

Chemicals, reagents, and preparation

Galinstan (Geratherm Medical AG, Geschwenda, Germany) was chosen as the source of LM/MO spherical structures and their associated liquid metal marbles. For preparation of LM/MO spherical structures suspensions, 20 μL of bulk galinstan (108.9 mg) was added into 3 mL of DI water. They were kept in a sonication bath (UNISONICS AUSTRALIA, FXP10DH, 240V ac, 5V, 50 Hz) at 25 °C for controlled durations. The samples used for UV–Vis measurements are diluted 8 times, yielding a concentration of ≈0.8 μL mL⁻¹. Tungsten oxide (WO₃) nanopowder (NaBond Technologies Co., Limited, particle size ranges from 20–100 nm) was used for realizing a WO₃ suspension which was prepared by mixing 50 mg WO₃ nanopowder with 100 mL DI water to yield a concentration of 0.5 mg mL⁻¹. Then the WO₃ suspension was kept in a sonication bath for 10 min and then filtered through filter paper (Whatman Grade 1) to prevent agglomeration. The micro– and nano–sized liquid metal marbles were synthesized by adding different concentrations of the WO₃ suspension into the LM/MO spherical structures suspensions and then stirring for 10 min.

Characterization

A FEI Nova NanoSEM was utilized for Scanning electron microscopy (SEM) and Energy–dispersive X–ray spectroscopy (EDX). For X–ray photoelectron spectroscopy (XPS) measurements, a VG–310F instrument using Al non–monochromated X–rays (20 kV, 15 mA) with a hemispherical energy
analyzer was set at a pass energy of 100 eV for the survey spectrum and 20 eV for the peak scans. A Bruker D8 DISCOVER micro-diffractometer was used for X-ray diffraction (XRD). A system incorporating an Ocean Optics QE6500 spectrometer and a 532 nm laser was chosen to perform Raman measurements. A VARIAN 50 Bio UV–Visible spectrophotometer was used for UV–Vis spectroscopy.

*Heavy metal ion sensing*

The micro– and nano–sized liquid metal marbles suspension was synthesized by adding 10% WO₃ suspension into LM/MO spherical structures suspensions, which was obtained after sonication for 20 min. The working electrode for lead ions (Pb²⁺) detection was first prepared by wetting copper tape with liquid galinstan. Then the liquid metal marbles suspension was uniformly deposited onto the substrate and dehydrated on a hotplate at 70 °C for 20 min. All measurements were performed using a CH Instruments (CHI 413A) electrochemical analyzer. The reference electrode was Ag/AgCl (aqueous 3 M KCl) and an inert graphite rod (3 mm diameter, Johnson Matthey Ultra “F” purity grade) was used as the auxiliary electrode. A biasing three–electrode configuration was used for the electrochemical measurements. All chemicals were of analytical grade purity and all aqueous solutions were prepared using Milli–Q water. All electrochemical measurements were commenced after degassing the electrolyte solutions with nitrogen for at least 10 min prior to any measurement. For stripping voltammetry, 0.1 M acetate buffer solutions with a pH of 4.5 were used as the supporting electrolyte, which was prepared by dissolving a sample of ammonium acetate (7.7 g) from Ajax Finechem in Milli–Q water (100 mL). The pH was corrected by adding acetic acid (99.7%, Ajax Finechem) and measured using a microprocessor controlled pH meter (PH 213, HANNA Instruments). Lead ions (Pb²⁺) were incorporated in the supporting electrolyte by dissolving lead (II) acetate 3–hydrate (BDH, AnalaR). Prior to every scan, a preconditioning step (60 s at −0.65 V) was applied. The voltammogram was recorded by applying a positive going scan from −0.65 to 0 V (with a step increment of 5 mV, amplitude of 80 mV, and pulse period of 0.2 s). For the comparison of micro– and nano–sized liquid metal marbles and hanging galinstan drop electrode, the pH value of acetate buffer
solutions was adjusted to 6.0 and 33.33 g of ammonium acetate was dissolved in Milli–Q water for the buffer solution. Then all the parameters for DPV were kept constant.

Photocatalytic activity

LM/MO structures suspensions were prepared after 5, 10, 20, and 60 min sonication. LM/MO spherical structures suspensions were uniformly deposited onto the glass substrate with a rough surface. Then the LM/MO spherical structures were dehydrated on a hotplate at 70 °C for 20 min. The WO₃ only sample was prepared using the same procedure. The deposited LM/MO spherical structures and WO₃ were of the same mass. In realization of micro– and nano–sized liquid metal marbles, the WO₃ suspension was added into the LM/MO spherical structures suspensions which were sonicated for 20 min, yielding weight percentages of 0%, 2%, 5% and 10%. Then these liquid metal marbles were also dehydrated on the glass substrate using same procedure. The substrates with LM/MO frameworks were placed in the CR solution for obtaining the time–concentration charts in order to assess and compare the photocatalytic properties. All samples were put in a quartz vial containing 2 mL of 10 μM CR, which was placed 15 cm away from a simulated solar lamp (Abet Technologies LS–150). The degradation rates of CR were determined by measuring the absorbance of the solutions at λ = 500 nm every 30 min for 120 min.

Inductively coupled plasma mass spectrometry

The concentrations of Ga³⁺, In³⁺, and Sn⁴⁺ ions in the CR solutions before and after photocatalytic activities for 2 h using an inductively coupled plasma mass spectrometer (ICP–MS) (Agilent Technologies HP4500 series 300, Shield Torch ICP–MS). The working solutions are diluted 50× with 2% nitric acid before conducting the measurements.
2.3 Results and Discussion

Micro– to nano–sized liquid metal/metal oxide spherical structures are prepared from bulk galinstan metal (Geratherm Medical AG, Geschwenda, Germany) in the presence of sonication induced forces for different durations. The surface morphology of LM/MO spherical structures is investigated using a scanning electron microscope. From Figure 2.1 (a), it is observed that the bulk galinstan droplet is transformed into micro– to nano–sized spheres after sonication. Figure 2.1 (b) shows that there are a number of spheres with diameters of less than 100 nm.

![Figure 2.1](image_url) (a) The SEM image of an assembly of LM/MO spherical structures after sonication for 20 min and drop casted on a substrate. (b) The magnified image of the dotted area.

Figure 2.2 (a) is an image of an assembly of LM/MO spherical structures after sonication for 20 min. It is found that the dimensions of these spheres are related to the sonication duration. The average size of the spheres is observed to reduce from ≈13 to ≈1 μm with the increase in the sonication duration from 2 to 60 min (Figure 2.2 (b)). As reported by V. Sivan et al., galinstan droplets exposed to aqueous solutions or air are homogenously covered by a thin native oxide layer.\(^2\) The morphology of this thin native oxide layer is also found to be strongly dependent on the sonication duration. Figures 2.2 (c) to (j) show SEM images of LM/MO spherical structures prepared after different sonication durations of 2, 5, 10, and 20 min, respectively. From Figures 2.2 (c) and (g), the surface of the spheres appears smooth with no wrinkles after 2 min sonication, indicating that the native oxide layer has not
been disturbed by the sonication induced forces after such a short duration. However, increasing the sonication duration to 5 min results in a winkled appearance on the surface of the spheres (Figures 2.2 (d) and (h)). This could be caused by an increase in thickness and volume of the initial native oxide layer, which is consistent with previous observation that the volume of metal oxide increases due to the insertion of oxygen into the metal during the oxidation process.\cite{3} With a further increase of sonication duration to 10 min, a dense distribution of nanoplatelets can be observed on the surface of the spheres as shown in Figure 2.2 (e). These nanoplatelets have an average length and width of 200 and 50 nm, respectively (Figure 2.2 (i)). After sonication for 20 min, the dimensions of these nanoplatelets increase, but concomitantly their coverage is sparser (Figures 2.2 (f) and (j)).

**Figure 2.2** (a) A top view SEM image of an assembly of LM/MO spherical structures after 20 min sonication. (b) The plot of average diameters of spheres within spherical structures after different sonication durations. SEM images of spheres after sonication for (c) 2, (d) 5, (e) 10 and (f) 20 min and their corresponding magnified images (g–j).

After 60 min of sonication, the nanoplatelets show the largest average dimensions and most of the spheres are transformed into thicker oxide platelets (Figure 2.3). It is observed that the average
dimensions of nanoplatelets obtained after 60 min sonication are ~1 µm, which is much larger than those obtained after shorter sonication durations.

**Figure 2.3** SEM images of LM/MO spherical structures after sonication for 60 min in different magnifications.

The durability of the LM/MO spherical structures in DI water is investigated and results are shown in Figure 2.4. It is shown that there is no apparent damage can be observed for the structure of LM/MO framework after the experiments. The oxide nanoplateles are still adhered onto the surface of spheres.

**Figure 2.4** SEM images of LM/MO frameworks (a) before and (b) after dipping into DI water for a prolonged

Similar to galisntan, other gallium containing liquid metal alloys such as EGaIn can also be formed into LM/MO spherical structures and frameworks. As also presented in the introduction, the formation of the micro–to nano–spheres of EGaIn has been successfully demonstrated by Hohman et al.\cite{4}
Obviously, such gallium containing liquid alloys are also suitable for similar investigations. Additionally, mercury is tested for the formation of micro– to nano–sized spheres under similar sonication conditions but without much success because the formed spheres are not stable and rapidly merge back into a large droplet after the sonication.

The chemical composition of the observed nanoplatelets is investigated using EDX mapping, as shown in Figure 2.5. For brevity, the candidate only presents the results for the LM/MO spherical structures after sonication for 5 and 20 min. While there is no obvious difference on the distributions of elements Ga, In, and Sn as a function of the sonication duration (Figure 2.6), the oxygen element distribution is found to correlate with the growth of nanoplatelets on the surface of the spheres. It is identified that the oxygen element is uniformly distributed after sonication for 5 min (Figure 2.5 (e)), revealing the existence of a compact but thin native oxide layer on the sphere surface after this short sonication duration. For the case of 20 min sonication, the nanoplatelets on the surface are significantly larger (Figure 2.5 (b)) and their corresponding texture can be observed in the EDX mapping of the oxygen element (Figure 2.5 (f)). The nanoplatelets contain significantly more oxygen than the surrounding area, confirming that they are made of galinstan oxide rather than liquid galinstan metal.
Figure 2.5 SEM images of LM/MO spherical structures after sonication for (a) 5 and (b) 20 min, respectively. Their corresponding EDX mappings of (c–d) gallium element and (e–f) oxygen element. All images are in the same magnification and the scale bars represent a distance of 500 nm.

Figure 2.6 SEM images of LM/MO spherical structures after the sonication for (a) 5 and (b) 20 min, respectively. Their corresponding EDX mappings of (a–b) gallium element, (c–d) indium element and (e–f) tin element. All images are in the same magnification and the scale bars represent a distance of 500 nm.
To further characterize the LM/MO spherical structures and the surface oxide nanoplatelets, the candidate conducts X–ray photoelectron spectroscopy (XPS) measurements on LM/MO spherical structures obtained after 5 and 60 min sonication to show their composition. These two sonication durations are chosen as they represent the important points for the growth of surface oxide nanoplatelets: at 5 min, surface nanoplatelets start to emerge, while the largest dimension platelets are obtained after 60 min of sonication. In XPS spectra of Ga 3d (Figures 2.7 (a) and (b)), the peak at the binding energy of 18.6 eV corresponds to metallic gallium (Ga$^0$), whereas two peaks at 19.7 and 20.7 eV represent the valence states of Ga$^{1+}$ in Ga$_2$O and Ga$^{3+}$ in Ga$_2$O$_3$, respectively. The O 2s peak at 23.9 eV is also found in the Ga 3d photoelectron spectra, which confirms the oxidation of the galinstan spheres.

According to the In 3d XPS spectra shown in Figures 2.7 (c) and (d), the peaks locating at 443.8 and 451.4 eV are ascribed to the metallic indium (In$^0$). Similarly, in the Sn 3d photoelectron spectra (Figures 2.7 (e) and (f)), the peaks which are centered at 484.9 and 493.3 eV correspond to the metallic tin (Sn$^0$). The signals reflecting the In$^{3+}$ and Sn$^{4+}$ states are much less significant compared to their metallic states. This means that the nanoplatelets are mainly composed of gallium oxides with a negligible amount of tin and indium oxide mixtures. Figures 2.7 (g) and (h) show the XPS spectra of O 1s. They can be deconvoluted into two components centered at 531.88 (marked as “L”) and 533.45 eV (marked as “H”), which indicate the existence of both full stoichiometric oxides and oxygen vacancies, respectively. In Figure 2.7 (g), as the area of the “H” peak is comparable to that of the “L” peak, the candidate concludes that there is a significant amount of sub–stoichiometric gallium oxide existing in the nanoplatelets.

Comparing Figures 2.7 (a) and (b), the candidate finds that the signals due to Ga$^0$ and Ga$_2$O significantly decrease after 60 min of sonication, which indicates the promotion of the oxidation of gallium to Ga$_2$O$_3$ by sonication. Interestingly, the signals due to metallic indium and tin are nearly constant when comparing to those after 5 min sonication. Furthermore, the intensity of “H” peaks in the oxygen spectrum presents a remarkable decrease while the intensity of the “L” peak is greatly increased, indicating the recombination of the initial oxygen vacancies during the sonication process.
The candidate believes that sonication facilitates oxidation of the galinstan surface preferentially at gallium rather than indium or tin, which is consistent with previous reports.\cite{7, 9}

![Figure 2.7](image)

**Figure 2.7** The XPS spectra of Ga 3d, In 3d, Sn 3d and O 1s for LM/MO spherical structures after sonication for 5 min: (a), (c), (e), (g); and 60 min: (b), (d), (f), (h).

The stoichiometry of the whole LM/MO spherical structures is also characterized by investigating the stoichiometry of etching layers. Results are shown in Figures 2.8 and 2.9. From Figure 2.8, it is observed that by etching more into the depth of the film, the intensity of Ga\(^{3+}\) decreases and inversely Ga\(^{0}\) increases, confirming that the top layer of the film made of LM/MO spherical structures are more oxidized than the bottom layers. Comparing Figures 2.8 (d) and (h), the candidate finds that after 20 etching layers, the LM/MO spherical structures prepared after 60 min of sonication are more oxidized than those prepared after 5 min of sonication, indicating that a more fully oxide layer is produced as the sonication duration increases. In addition, he finds that the intensity reduces with the increase of the etching layers number (Figure 2.9). It is observed that the deep layer of LM/MO spherical structure prepared after 60 min of sonication contains a stronger oxygen signal than that of structure after 5 min sonication.

The equivalent thickness of each etched layer is ~50 nm therefore the total etching depth for 20 layers is ~1 µm. The average diameter of LM/MO spheres after 5 and 60 min of sonication are ~8 and
~1 µm (Figure 2.1), respectively. As the area of the field during the XPS measurements is 400 µm × 400 µm, the XPS spectra represent the average of the stoichiometry of a large number of spheres in each etching level. During the etching process, the individual spheres at the top of the film are gradually etched and this opens larger and larger void for the beam to access the underneath spheres. As a result, the XPS depth spectra demonstrate the stoichiometry of both etched layers and the surface of underneath spheres, which is inevitable and cannot be absolutely separated. However, the XPS depth profile measurements provide average information as how thick the oxide layers on the spheres can be and to what degree they are oxidized.

Figure 2.8 The XPS spectra of Ga 3d films made of LM/MO spherical structures, which are formed after the sonication for 5 min: (a), (b), (c), (d); and 60 min: (e), (f), (g), (h). Spectra of Ga 3d are collected at 20 different etching layers from the surface as the reference. Layer 1: (a) and (e); Layer 5: (b) and (f); Layer 10: (c) and (g); Layer 20: (d) and (h).
Figure 2.9 The intensity of oxygen signal at different etching layers.

Based on the aforementioned observations, the candidate hypothesizes a four phase morphological transformation process on the surface of a galinstan sphere during the sonication, which is illustrated in Figure 2.10.

![Diagram of morphological transformation](image)

Figure 2.10 Schematic images of LM/MO spherical structures during sonication. Grey shapes, red circles and red ovals stand for galinstan spheres, oxide layers and nanoplatelets, respectively.

In phase (i) after a very short time, a thin native oxide layer is formed on the surface of the galinstan sphere. Upon prolonging the sonication duration, this oxide layer, which in time becomes thicker, is strongly deformed, wrinkled and eventually cracks under the effect of a sonication induced force.
(phase ii). As the oxidation reaction continues, the oxide layer is detached from the surface (phase iii) and forms small planar residues. These residual oxide layers are gradually placed on top of each other and out of registry, which is confirmed in XRD patterns (Figure 2.11), appearing as randomly orientated nanoplatelets (Figure 2.12). In phase (iv), at longer sonication times, the residual oxide nanoplatelets become thicker and are simultaneously detached, which results in larger dimension nanoplatelets but with sparser coverage on the surface of the galinstan sphere. Due to the removal of these nanoplatelets, the underlying galinstan metal is exposed to water and subsequently forms a new surface oxide layer. The newly formed oxide layer is again affected by continuous sonication and becomes thicker. Eventually, this new oxide layer will crack and form nanoplatelets. Therefore, each of these phases is continuously repeated and the galinstan sphere is gradually consumed.

Figure 2.11 XRD spectra of LM/MO spherical structures after sonication for (a) 20 min and (b) 60 min.
As demonstrated in previous work, liquid metal galinstan droplets can be used as a platform for the realization of liquid metal marbles.\textsuperscript{[2]} Here, the candidate demonstrates that LM/MO spherical structures can also be utilized but with significantly smaller dimensions. By mixing galinstan spheres obtained after sonication for 20 min with metal oxide nanoparticles, he forms micro and nano-sized liquid metal marbles with a homogenous dispersion. Figures 2.13 shows the surface morphology of these liquid metal marbles coated by WO\textsubscript{3} nanoparticles together with the nanoplatelet oxides formed during the sonication process which is previously described. The existence of WO\textsubscript{3} is confirmed by Raman spectroscopy as shown in Figure 2.14. Although the candidate only presents the marbles based on the 20 min sonicated LM/MO spherical structures, it is obvious that sonication duration also plays an important role on the dimension of the liquid metal marbles. Moreover, the concentration of nanoparticles in the liquid environment is also an important factor in determining the homogeneity and density of the coating.

\textbf{Figure 2.12} SEM images of LM/MO spherical structures. (a) Surface oxide layer cracks and forms nanoplatelets; (b) Residual oxide nanoplatelets and (c) Magnified image.
Figure 2.13 SEM images of an assembly of micro- and nano-sized liquid metal marbles formed by coating WO$_3$ nanoparticles onto LM/MO spherical structures prepared after 20 min of sonication.

Figure 2.14 Raman spectra of (a) micro-sized liquid metal marbles; (b) LM/MO spherical structures; (c) WO$_3$ nanoparticles.

UV–Visible (UV–Vis) spectroscopy is implemented to assess the optical changes of the spherical suspended structures after certain sonication duration. It is known that some ultra–doped metal oxides are capable of showing plasmon resonances in the visible region and that the substoichiometry is directly associated with the doping levels of these metal oxides.$^{[10, 11]}$ The aforementioned XPS analysis shows that the metal oxide nanoparticles on the surface of liquid metal spheres are strongly substoichiometric, and their substoichiometry can be tuned by changing the duration of the sonication.
Figure 2.15 shows the UV–Vis absorption spectra of LM/MO spherical structures prepared after different sonication durations. The structures which are sonicated for 5, 10, and 20 min show a strong absorption signal in the deep UV region at less than 220 nm. This increased absorption can be ascribed to the surface plasmon resonances (SPRs) of submicron– or nano–sized galinstan spheres.[4]

It is noted that the SPR feature almost vanishes upon increasing the sonication time to 60 min, presumably due to the near complete oxidation of the nano–sized galinstan spheres. Interestingly, a broad absorption peak spanning UV and visible wavelengths could be observed for all LM/MO spherical structures obtained after different sonication durations, which can be attributed to plasmonic responses from the quasi–metallic substoichiometric gallium oxides inherently formed on the surface of the spheres. This is due to the fact that the tin and indium oxide concentrations are much less than the substoichiometric gallium oxide as evidenced by the XPS analysis. The broadness of the plasmonic peaks may be due to the polydispersity in terms of size and shape of the oxide nanostructures as evident in Figure 2.1. More importantly, there is a red–shift in the plasmonic peak as a result of increasing the sonication time. This shift in the plasmonic peak position is possibly due to the fact that more stoichiometric oxide is produced with increasing sonication time which causes a decrease in the oxygen vacancy concentration and hence the decrease in free charge carrier concentration.[12]
Figure 2.15 UV–Vis absorption spectra of the LM/MO spherical structures obtained after different sonication duration: (a) 5, (b) 10, (c) 20 and (d) 60 min.

The UV–Vis spectrum of the LM/MO framework containing WO$_3$ nanoparticles is also measured (Figure 2.16). It is observed that with WO$_3$ nanoparticles the plasmon response at visible wavelength decreases. Additionally, WO$_3$ did not produce any shift in the existing peaks or extra peaks.
Figure 2.16 UV–Vis absorption spectra of the suspended LM/MO sphere containing solutions obtained after 20 min of sonication with and without WO$_3$ nanoparticles.

Additionally, the stability of the plasmonic response of LM/MO spherical structures is investigated. From Figure 2.17, it is observed that the absorption spectrum of the same suspended LM/MO sphere solution only shows a slight decrease in time, which indicates that the plasmonic response is relatively stable.
Figure 2.17 UV–Vis absorption spectra of the same suspended LM/MO sphere containing solution prepared after 20 min of sonication (Measurement 1), 24 h (Measurement 2) and 48 h (Measurement 3).

To show the functionalities of LM/MO spherical structures, they are assembled into LM/MO frameworks. Figure 2.18 shows the cross-sectional SEM images of LM/MO framework assembled from LM/MO spherical structures. It is observed that the framework is made of stacked spherical structures. The thickness is approximately 18 μm.

Figure 2.18 Cross-sectional SEM images of assembled LM/MO framework in different magnifications.
Here the candidate demonstrates two different applications: heavy metal ion sensing and photocatalysis.

Similar to mercury, galinstan can amalgamate with other metals and can accommodate a large concentration of different heavy metal species.\textsuperscript{[13]} It has been previously reported that liquid metal marbles are capable of sensing heavy metal ions with a much higher sensitivity in comparison to their liquid metal droplet counterparts without any coating.\textsuperscript{[2]} This is ascribed to the generation of a localized electric field at the nanoparticle/liquid metal/electrolyte triple phase boundary as well as the large surface area produced by the nanoparticles.\textsuperscript{[2]} Obviously, the LM/MO spherical structures should be able to increase the sensitivity even further as they have an impressive surface to volume ratio, which would greatly improve the effect of the nanoparticles coating, comparing to conventional liquid metal marbles.

A Pb\textsuperscript{2+} heavy metal ion sensing system is used to evaluate the aforementioned hypothesis. In this system, micro– and nano–sized liquid metal marbles are established from coating WO\textsubscript{3} nanoparticles (average \approx 80 nm diameter) onto LM/MO spherical structures prepared after 20 min of sonication. The micro– and nano–sized liquid metal marbles are immobilized on a copper substrate and used as the working electrode, while a graphite rod and Ag/AgCl (in 3 M KCl) are employed as the counter and reference electrodes, respectively. WO\textsubscript{3} nanoparticles are chosen as it has been previously reported that the sensitivity for heavy metal ion detection using WO\textsubscript{3} coated liquid metal marbles is much higher than the sensitivity of uncoated galinstan droplets,\textsuperscript{[2]} which is also evident in Figure 2.19. In Figure 2.19, the sensing properties of LM/MO frameworks with and without WO\textsubscript{3} nanoparticles are compared. The candidate finds that without the addition of WO\textsubscript{3}, sensing responses are not observed, confirming the importance of the incorporation of WO\textsubscript{3} into the LM/MO frameworks. The significant improvement is possibly attributed to WO\textsubscript{3} nanoparticles serving as nano–facilitators to generate intense localized electric fields as discussed in previous work.\textsuperscript{[2]}
Figure 2.19 Differential pulse stripping voltammograms for different concentrations of Pb$^{2+}$ using (a) micro– to nano–sized LM/MO frameworks incorporating WO$_3$ nanoparticles (b) micro– to nano–sized LM/MO frameworks.

Figure 2.20 shows the differential pulse anodic stripping voltammograms as a function of Pb$^{2+}$ concentration in ammonium acetate buffer. In all cases a cathodic potential of −0.65 V is applied for 60 s to preconcentrate metallic lead into the LM/MO electrode. The differential pulse voltammograms (DPV) are then recorded from −0.65 to −0.15 V. The oxidation peak potential for Pb$^0$ stripping is found to be at −0.55 V. The amplitude of this oxidation current peak has a linear response to the Pb$^0$ concentrations (Inset i in Figure 2.20). The Pb$^{2+}$ ions detection limit of the system is found to be 100 ppb. It should be noted that in previous study, by using a hanging galinstan droplet electrode, the reduction of Pb$^{2+}$ to Pb$^0$ has a peak current of −85 μA in response to 21 ppm Pb$^{2+}$. The LM/MO structures based system under identical conditions demonstrates a remarkable 80 times improvement with a current amplitude of −665.8 μA (Inset ii in Figure 2.20). This significant improvement may be ascribed to the dramatic enhancement of the available surface area within the assembled LM/MO frameworks that is capable of accommodating more WO$_3$ nanoparticles which serve as nano–facilitators to generate intense electric fields. Moreover, this in turn creates a larger surface area of the liquid metal to interact with Pb$^{2+}$ ions which increases sensitivity.
Figure 2.20 Differential pulse stripping voltammograms for increasing concentrations of Pb$^{2+}$ recorded at micro– and nano–sized liquid metal marbles along with the background response (dotted line). Inset i shows the stripping peak current values versus different concentrations of Pb$^{2+}$. Inset ii shows the comparison of a hanging galinstan droplet electrode (marked as “H”) and a micro– and nano–sized liquid metal marbles (marked as “M”) for DPVs recorded for the reduction of Pb$^{2+}$ to Pb$^{0}$ under same testing conditions.

The stability of the sensing performance is investigated. From Figure 2.21, it is observed that the reduction peak of 500 ppb Pb$^{2+}$ at −0.55 V is consistent for all measurements, showing the excellent stability of LM/MO frameworks for heavy metal ion sensing applications.
Figure 2.21 Four consecutive cycles of differential pulse stripping voltammograms for the same LM/MO framework incorporating WO$_3$ in the presence of 500 ppb of Pb$^{2+}$.

The capability of simultaneously sensing several heavy metal ions using micro– and nano–sized liquid metal marbles is also shown in Figure 2.22. The reduction potential regions of Cd$^{2+}$, Pb$^{2+}$ and Cu$^{2+}$ are marked, respectively. The candidate finds that there are no consistent sensing responses towards Cd$^{2+}$ and Cu$^{2+}$. In contrast, the LM/MO framework incorporating WO$_3$ nanoparticles is highly selective and responsive to Pb$^{2+}$ ions.
Figure 2.22 Differential pulse stripping voltammograms for different concentrations of Cd\(^{2+}\), Pb\(^{2+}\) and Cu\(^{2+}\) recorded using the LM/MO framework incorporating WO\(_3\) nanoparticles along with the background response (dotted line).

There is no example for direct comparison of the heavy metal ion sensing performance of the LM/MO frameworks with their SM/MO counterparts, as none of the solid metals can efficiently amalgamate heavy metal ions, which is a unique advantage offered by liquid metals.

As another demonstration of the functionality of LM/MO spherical structures, the candidate prepares LM/MO frameworks and investigates their photocatalytic properties. As the frameworks provide metallic/metal oxide interfaces, the photocatalytic activities should be enhanced.\(^{[14, 15]}\)

Congo red (CR) is utilized as the indicative dye to evaluate the photocatalytic performances of the LM/MO frameworks.\(^{[16]}\) A film made of WO\(_3\) nanoparticles, with the same weight as the films made of LM/MO frameworks, is selected as the benchmark because WO\(_3\) is known to be one of the most efficient metal oxide photocatalysts.\(^{[17]}\) Figure 2.23 a depicts the normalized concentration of 10 μM CR in solution during simulated solar light illumination in the presence of LM/MO frameworks prepared under different sonication times and WO\(_3\) nanoparticles only, where C\(_0\) and C denote the concentration of CR at the start of the experiment and after certain irradiation durations, respectively.
It is noted that CR is efficiently decomposed by all four LM/MO frameworks. The highest photodegradation efficiency of 93% is observed for the LM/MO frameworks prepared after 20 min of sonication, showing the fastest photo-degradation kinetics amongst the samples. However, more importantly the frameworks consistently manifest an approximately three time enhancement in the photocatalytic activity in comparison to WO\textsubscript{3} nanoparticles only. This substantial improvement of the LM/MO frameworks is possibly due to the combination of the following:

1. The LM/MO spherical structures are demonstrated to have UV and visible light absorbance as presented in Figure 2.15. This suggests that light within a large region of the UV and visible spectra can be efficiently utilized by the frameworks.

2. The unique structure within the LM/MO frameworks, in which the galinstan oxides serve as the shell while the core remained to be galinstan metal, can be also an important factor to contribute to such an impressive improvement. It is well-known that in metal/metal oxides photocatalytic systems, the presence of the metal acts as an electron sink and suppresses electron–hole recombination and therefore promotes the hole transfer process at the semiconductor–solution interface, where organic species such as CR can be oxidized thereby realizing photocatalytic degradation\textsuperscript{[18]} Similarly, the galinstan core serves as the sink which improves interfacial charge transfer processes and charge separation.

3. Additionally, the presence of substoichiometry gallium oxide may enhance the photocatalytic activity of the system. It is known that the conduction band edges of the surface gallium oxides (which constitutes the majority of the nanoplatelets formed during the sonication process) is more negative compared to that of WO\textsubscript{3}, resulting in a higher decomposition efficiency towards CR due to the easier transfer of valence band electrons into the conduction band which is required for a photocatalytic process\textsuperscript{[19]}

For comparison, the candidate also includes the photocatalytic properties of micro– and nano–sized liquid metal marbles which are obtained by coating different weight percentages of WO\textsubscript{3} nanoparticles onto LM/MO spherical spheres prepared after 20 min of sonication, as shown in Figure
2.23 (b). A pristine LM/MO framework without WO\textsubscript{3} addition (0\%) is shown as a benchmark. Interestingly, the pristine LM/MO framework displays the highest degradation efficiency. The photodegradation ability of the synthesized micro– and nano–sized liquid metal marbles tends to decline upon increasing the loading of WO\textsubscript{3} nanoparticles, indicating that WO\textsubscript{3} compromises the photocatalytic efficiency of the micro– and nano–sized liquid metal marbles, which is expected given the poor performance of WO\textsubscript{3} only (Figure 2.23 (a)). It appears that the intimate contact of liquid galinstan metal and the inherent nanostructured metal oxides facilitates better charge separation than that between liquid metal galinstan and the attached WO\textsubscript{3} nanoparticles.

![Figure 2.23](image_url)

**Figure 2.23** Photocatalytic properties of LM/MO frameworks, WO\textsubscript{3} nanoparticles and micro–and nano–sized liquid metal marbles. (a) Degradation of 10 \(\mu\)M CR in the presence of LM/MO frameworks prepared after different sonication durations. WO\textsubscript{3} nanoparticles with the same mass serve as the benchmark. (b) Degradation of 10 \(\mu\)M CR in the presence of micro–sized liquid metal marbles containing WO\textsubscript{3} nanoparticles which are in different weight percentages.

The photocatalytic kinetics of LM/MO frameworks are comparable with those of systems based on Pt nanoparticles together with WO\textsubscript{3} nanocrystals.\textsuperscript{[20, 21]} As a result, by considering that Pt is a well–known and high performance catalyst, my LM/MO framework is presented as a viable candidate for highly efficient photocatalysis.
The reusability of LM/MO frameworks, which is an important factor for photocatalysts, is also investigated. The photocatalytic efficiency does not show significant loss after four continuous cycles, indicating the excellent recoverability and reusability of LM/MO frameworks (Figure 2.24).

![Figure 2.24](image)

**Figure 2.24** Photocatalytic properties in four consecutive cycles using the same LM/MO framework.

The concentrations of Ga$^{3+}$, In$^{3+}$, and Sn$^{4+}$ ions before and after photocatalytic activities for 2 h in CR solutions are measured. The ion concentrations are within the acceptable range for human health.$^{[22]}$

The candidate measures the concentrations of Ga$^{3+}$, In$^{3+}$ and Sn$^{4+}$ ions in the CR solutions before and after photocatalytic activities for 2 h using an inductively coupled plasma mass spectrometer (ICP–MS). This is conducted to assess the concentrations of the released metal ions from the LM/MO spheres in time. The concentrations of Ga$^{3+}$, In$^{3+}$ and Sn$^{4+}$ are found to be 3932, 625 and 239 ppb, respectively, after the photocatalytic experiments. Such a concentration of Ga$^{3+}$, which is an order of magnitude larger than the other two ions, is still within the acceptable range for human health.$^{[22]}$
2.4 Conclusion

The PhD candidate successfully synthesized micro– to nano–sized LM/MO spherical structures, which were made of core galinstan and metal oxide nanoparticle coatings, from bulk galinstan via sonication, where the duration of the sonication was shown to be a crucial factor in influencing the morphology and stoichiometry of the oxide nanoparticles. He also demonstrated that the stoichiometry and plasmonic properties of these spherical structures in a suspension were a function of the sonication duration. He showed that the visible light plasmon resonances could be actively tuned as a function of the oxygen vacancies in the spherical structures. The developed structures were assembled into LM/MO frameworks. These frameworks were then incorporated into two representative examples of heavy metal ion sensing and photocatalytic systems in order to investigate their functionalities. These spherical structures were used to form micro– and nano–sized liquid metal marbles together with WO$_3$ nanoparticles for establishing a highly sensitive electrochemical sensing platform for heavy metal ions. These marbles were able to sense Pb$^{2+}$ at concentrations as low as 100 ppb, indicating about 80 times improvement in comparison to the sensitivity of their bulk counterpart. This was attributed to the high surface–to–volume ratio of the structures as well as the formation of intense electric fields on the surface of the spheres. Furthermore, he showed that these frameworks were able to provide improvement of about three times over the photocatalytic efficiency of films made of pristine WO$_3$ nanoparticles under similar testing conditions. This was ascribed to their excellent visible light absorption properties and the unique LM/MO interfaces that facilitate charge separation and suppression of electronhole recombination. Good recoverability and reusability of photocatalytic LM/MO frameworks were also depicted by the results recorded during multiple cycles of the photocatalytic procedure. Altogether, the demonstrations provided strong prospects for the LM/MO structures as promising candidates for the development of other high performance devices and systems such as solar cells, photodiodes and biosensors.

In the next chapter, the candidate will present the outcomes of his research on using the LM/MO frameworks for photocatalysis.


2.5 References


Chapter 3

Liquid metal/metal oxide frameworks with incorporated Ga$_2$O$_3$ for photocatalysis

3.1 Introduction

In the work presented in this chapter, solvothermally synthesized gallium oxide (Ga$_2$O$_3$) nanoparticles will be incorporated into liquid metal/metal oxide (LM/MO) frameworks in order to form enhanced photocatalytic systems. The LM/MO frameworks, both with and without incorporated Ga$_2$O$_3$ nanoparticles, will show photocatalytic activity due to a plasmonic effect where performance will be related to the loading of Ga$_2$O$_3$ nanoparticles. Optimum photocatalytic efficiency will be obtained with an amount of incorporation of Ga$_2$O$_3$ nanoparticles. This will be attributed to the sub–bandgap states of LM/MO frameworks, contributing to pseudo–ohmic contacts which will reduce the free carrier injection barrier to Ga$_2$O$_3$.

The PhD candidate will develop a combined system made of LM/ MO frameworks and incorporated Ga$_2$O$_3$. He will investigate the methods for improving its photocatalytic performance by incorporating different loadings of Ga$_2$O$_3$.

The content of this chapter was fully reviewed and published in ACS Applied Materials & Interfaces$^{[1]}$. 
3.2 Experimental Details

Synthesis of Ga$_2$O$_3$ nanoparticles

Ga$_2$O$_3$ nanoparticles were prepared by a solvothermal method reported earlier,[2] and this method was modified slightly for this work. In a typical synthesis procedure, 0.5 g of Ga(NO$_3$)$_3$•xH$_2$O was dissolved in 2 ml of concentrated hydrochloric acid. It was evaporated repeatedly by adding water. To this 4.5 ml of ethylene glycol was added and the pH of the solution was adjusted to 10. A jelly like liquid was obtained and was transferred into a 9 ml autoclave. The autoclave was filled up to 80% with water. The overall water to ethylene glycol ratio was 2:3. The autoclave was kept in an oven at 195 °C for 6 hours and then cooled to room temperature. A white precipitate was obtained and washed with water and ethanol respectively. The solid product was dried in an oven at 80 °C.

Synthesis of LM/MO frameworks suspensions and Ga$_2$O$_3$ nanoparticles suspensions

Galinstan (Geratherm Medical AG, Geschwenda, Germany) was chosen as the source of LM/MO frameworks suspensions. 20 µL of bulk galinstan (108.9 mg) was added into 3 ml of DI water, yielding a concentration of 36.3 mg/ml. They were kept in a sonication bath (UNISONICS AUSTRALIA, FXP10DH, 240V AC, 5V, 50 Hz) at 25 °C for 20 min. 10 mg of Ga$_2$O$_3$ nanoparticles was added into 3 mL of DI water, yielding a suspension with a concentration of 3.33 mg/ml.

Synthesis of photocatalytic samples

For the samples consist of LM/MO frameworks and Ga$_2$O$_3$ nanoparticles, the amount of LM/MO frameworks was fixed and the amount of Ga$_2$O$_3$ nanoparticles was varied. 3.3 µl, 16.3 µl and 32.6 µl of Ga$_2$O$_3$ nanoparticle suspensions were added into 150 µl (~5.45 mg) of LM/MO frameworks suspensions and they were co-sonicated for 5 min, yielding different weight percentages of 0.2%, 1% and 2% (wt%), respectively. 150 µl of LM/MO frameworks suspensions and 1.64 ml (~5.45 mg) of Ga$_2$O$_3$ nanoparticle suspensions were chosen as comparisons. Each working electrode was made by drop-casting the sample solution onto a Fluorine–doped Tin Oxide (FTO) glass substrate (1cm × 2cm) and dehydrated at 70 °C for 20 min.
Table 3.1 The composition of LM/MO frameworks incorporated with different amounts of Ga$_2$O$_3$ nanoparticles.

<table>
<thead>
<tr>
<th>Ga$_2$O$_3$</th>
<th>5.45 mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>LM/MO</td>
<td>5.45 mg</td>
</tr>
<tr>
<td>0.2 wt% Ga$_2$O$_3$</td>
<td>5.45 mg (LM/MO) + 11 μg (Ga$_2$O$_3$)</td>
</tr>
<tr>
<td>1 wt% Ga$_2$O$_3$</td>
<td>5.45 mg (LM/MO) + 54 μg (Ga$_2$O$_3$)</td>
</tr>
<tr>
<td>2 wt% Ga$_2$O$_3$</td>
<td>5.45 mg (LM/MO) + 109 μg (Ga$_2$O$_3$)</td>
</tr>
</tbody>
</table>

Photocatalytic activity

The samples were placed in the Congo red (CR) solution for obtaining the time–concentration charts in order to assess and compare the photocatalytic properties. All samples were put in a quartz vial containing 2 ml of 10 μM CR, which was placed 15 cm away from a simulated solar lamp (Abet Technologies LS–150). The duration of a whole photocatalytic procedure was 120 min. During the procedure, the absorbance of CR solution at 500 nm was measured every 30 min in order to determine the photodegradation rate. 500 nm was chosen as a reference. The repeated photocatalysis experiments were carried out with Congo red solution for every cycle. Each cycle lasted 120 min (only responses from 0 to 60 min were shown).

Mott–Schottky measurements

Based on a three–electrode configuration, Mott–Schottky experiments were performed using a CH Instruments (CHI 413A) electrochemical analyzer. 0.3 M sodium sulfate solution with a pH of 7.0 was chosen as the electrolyte. Substrates with deposited LMMO frameworks and Ga$_2$O$_3$ nanoparticles were used as working electrodes. The reference electrode was Ag/AgCl (aqueous 3 M KCl) and a platinum electrode was used as the auxiliary electrode.

Characterization

The candidate utilized a FEI Nova NanoSEM and a HRTEM (JEOL 2100F) for Scanning electron microscopy (SEM) and Transmission electron microscopy (TEM), respectively. A Bruker D8
DISCOVER micro-diffractometer was used for X-ray diffraction (XRD). For X-ray photoelectron spectroscopy (XPS) measurements, a VG–310F instrument using Al non-monochromated X-rays (20 kV, 15 mA) with a hemispherical energy analyser was set at a pass energy of 100 eV for the survey spectrum and 20 eV for the peak scans. A VARIAN 50 Bio UV–Visible spectrophotometer was used for UV–Vis spectroscopy.

3.3 Results and Discussion

The suspension of micro– to nano–sized liquid metal marble spheres is prepared by sonicating bulk galinstan in DI water (Figures 3.1 (a) and (b)). A thin film of LM/MO frameworks is prepared by drop casting. The Ga$_2$O$_3$ nanoparticles are synthesized using a solvothermal process$^{[2]}$. Different amounts of Ga$_2$O$_3$ nanoparticles are incorporated onto these galinstan spheres, via cosonication, in order to realize a variation of loading ratios. SEM images of LM/MO frameworks with and without an incorporated Ga$_2$O$_3$ nanoparticle coating can be seen in Figures 3.1 (c) and (d), respectively. The inset of Figure 3.1 (d) shows that before incorporating Ga$_2$O$_3$ nanoparticles the LM/MO frameworks consist of micro– to nano–sized galinstan spheres with native sub–stoichiometric oxides that originate through the sonication process. Figure 3.1 (e) shows the transmission electron microscopy (TEM) image of Ga$_2$O$_3$ nanoparticles which are synthesized using a solvothermal process where the dimension of most of the Ga$_2$O$_3$ nanoparticles is within the range of 5–10 nm. Figure 3.1 (f) shows the corresponding selected area electron diffraction (SAED) pattern of Ga$_2$O$_3$ nanoparticles. The synthesized Ga$_2$O$_3$ is detected to be $\gamma$–Ga$_2$O$_3$ using XRD measurements (Figure 3.2).
Figure 3.1 (a) A bulk galinstan droplet kept in DI water. (b) Suspension of micro- to nano-sized liquid metal marble spheres. SEM images of (c) top view of LM/MO frameworks with incorporated Ga$_2$O$_3$ nanoparticles (1 wt%), (d) LM/MO frameworks without incorporated Ga$_2$O$_3$ nanoparticles, inset shows native oxide nanoplatelets, scale bar of the inset is 500 nm. (e) TEM image of solvothermally synthesized Ga$_2$O$_3$ nanoparticles, and (f) TEM diffraction patterns of Ga$_2$O$_3$ nanoparticles.
Figures 3.3 (a) to (d) show the surface morphology of micro-sized galinstan spheres incorporated with different loadings of Ga$_2$O$_3$ nanoparticles. In Figure 3.3 (a), only the native surface oxide layer and native oxide nanoplatelets formed by the sonication process are observed, with zero loading of Ga$_2$O$_3$ nanoparticles. Figure 3.3 (b) shows that Ga$_2$O$_3$ nanoparticles form a relatively uniform distribution on the spherical structure. Increasing the loading of Ga$_2$O$_3$ nanoparticles results in a reasonably uniform coating (Figure 3.3 (c)). From Figure 3.3 (d), it is observed that most of the sphere surface is covered by Ga$_2$O$_3$ nanoparticles when the loading reaches 2 wt %. Low magnification SEM images are presented to show the surface morphology with respect to different loadings of Ga$_2$O$_3$ nanoparticles (Figure 3.4).
Figure 3.3 SEM images of surface morphology of micro–sized galinstan spheres with different loadings of Ga$_2$O$_3$: (a) 0 wt%, (b) 0.2 wt%, (c) 1 wt% and (d) 2 wt%.

Figure 3.4 SEM images of LM/MO frameworks with different loadings of Ga$_2$O$_3$ nanoparticles: (a) 0 wt%, (b) 0.2 wt%, (c) 1 wt% and (d) 2 wt%.

To further characterize the effect of Ga$_2$O$_3$ nanoparticles incorporation, the candidate conducted X–ray photoelectron spectroscopy (XPS) measurements of the LM/MO frameworks with various loadings of Ga$_2$O$_3$ nanoparticles. In the Ga 3d core level spectra (Figures 3.5 (a) to (e)), peaks corresponding to Ga$^{3+}$ (colored as red) and Ga$^0$ (colored as blue) are observed. With the increase of
Ga$_2$O$_3$ nanoparticles, the intensity of Ga$^{3+}$ rises, while the intensity of Ga$^0$ decreases. The Ga$^0$ signal can originate from the core metal as well as the presence of metallic gallium in substoichiometric gallium oxide nanoplatelets and the native oxide layer of LM/MO frameworks. As a result, XPS analysis suggests that it is likely that the incorporation of Ga$_2$O$_3$ nanoparticles changes the stoichiometry of the combined system at the contact boundaries between the metal and nanoparticles (this hypothesis is investigated further using XPS valence band measurements, and is presented later).

UV–visible (UV–vis) spectroscopy is implemented to assess the absorbance of LM/MO frameworks with incorporation of Ga$_2$O$_3$ nanoparticles. LM/MO frameworks with the incorporation of 1 wt % Ga$_2$O$_3$ nanoparticles is chosen for analysis, as it presents a median phase between LM/MO frameworks and Ga$_2$O$_3$ nanoparticles used for the incorporation, according to the XPS spectra. Figure 3.5 (f) shows that there is a strong signal in the deep UV region at less than 220 nm in the absorption spectrum of LM/MO frameworks. The strong signal can be ascribed to the surface plasmon resonances (SPR) of metallic submicron– or nano–sized galinstan spheres. The broad absorption peak spanning the UV and visible wavelengths could be attributed to plasmonic responses from the quasi–metallic sub–stoichiometric gallium oxides inherently formed on the surface of the spheres. The cutoff wavelength of the synthesized Ga$_2$O$_3$ nanoparticles is 260 nm; therefore, the corresponding bandgap of the Ga$_2$O$_3$ nanoparticles is estimated to be $\sim$4.8 eV. The UV spectrum of LM/MO frameworks incorporated with 1 wt % Ga$_2$O$_3$ nanoparticles lies in between the spectra of LM/MO frameworks and Ga$_2$O$_3$ nanoparticles, which is consistent with the result from XPS measurements. The spectrum of the combined system also has a broad absorption peak over UV and visible range. This shows that the system is also capable of efficiently absorbing light.
Figure 3.5 The XPS spectra of Ga 3d of LM/MO frameworks with different loadings of Ga$_2$O$_3$ nanoparticles: (a) 0 wt%, (b) 0.2 wt%, (c) 1 wt% and (d) 2 wt%. (e) The XPS spectrum of Ga 3d of solvothermally synthesized Ga$_2$O$_3$ nanoparticles. (f) UV–Vis absorption spectra

The UV–vis reflectance and transmission spectra of LM/MO frameworks with 1 wt % Ga$_2$O$_3$ nanoparticles are shown in Figure 3.6. The references used for reflectance and transmission measurements are aluminum standard (>99.5% reflectance) and glass (~100% transmission) substrates, respectively. It is shown that around 2% of incoming light is reflected and about 2.5% of the light transmitted through the sample in the visible light range, which means nearly 95 % of light is absorbed.
Congo red (CR) is utilized as the indicative dye to evaluate the photocatalytic performances of LM/MO frameworks incorporated with different concentrations of Ga₂O₃ nanoparticles. Additionally, samples made of pristine Ga₂O₃ and LM/MO frameworks are used as the benchmarks. As shown in Figure 3.7 (a), it is clearly seen that the pristine γ-Ga₂O₃ only decomposes CR at a rate of ∼0.03% h⁻¹ under simulated solar light irradiation, which is attributed to its poor absorption in the solar spectrum owing to its wide energy band gap (∼4.8 eV). The decomposition efficiency of LM/MO frameworks toward CR is close to ∼47% h⁻¹, which is consistent with the previous work.[5] Significantly, the incorporation of Ga₂O₃ nanoparticles into the framework enhances the photocatalytic performance. Starting with as small a concentration as 0.2 wt % Ga₂O₃, the combined system reaches a CR decomposition rate of 50% h⁻¹. As the amount of Ga₂O₃ increases to 1 wt %, complete decomposition of CR is achieved within 1 h (∼100% h⁻¹). Interestingly, further increasing the Ga₂O₃ coating to 2 wt % compromises the performance. It can be observed that the time duration for the complete decomposition of CR rises to 90 min (∼67% h⁻¹). More photocatalytic activity responses can be found in Figure 3.8. Figure 3.7 (b) shows the photocatalytic kinetic curves for the same LM/MO frameworks incorporated with 1 wt % Ga₂O₃ for four consecutive cycles. No significant degradation of CR decomposition efficiency during four consecutive cycles can be observed, confirming excellent stability and reusability of the system for photocatalytic applications. Raw data is presented in Table 3–2.
Figure 3.7 (a) Degradation of 10 µM CR in the presence of Ga$_2$O$_3$ nanoparticles, LM/MO frameworks and LM/MO frameworks incorporated with different loadings of Ga$_2$O$_3$ nanoparticles. (b) Degradation of 10 µM CR in the presence of one sample of LM/MO frameworks with 1 wt% incorporated Ga$_2$O$_3$ in four consecutive cycles. The difference of decomposition rates among four consecutive cycles is less than 2%.

Figure 3.8 Degradation of 10 µM CR in the presence of LM/MO frameworks and LM/MO frameworks with incorporated different loadings of Ga$_2$O$_3$ nanoparticles.

Table 3.2 Raw data of repeatability of photocatalysis.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>C/C$_o$ (Cycle 1)</th>
<th>C/C$_o$ (Cycle 2)</th>
<th>C/C$_o$ (Cycle 3)</th>
<th>C/C$_o$ (Cycle 4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>30</td>
<td>0.2727</td>
<td>0.2705</td>
<td>0.2692</td>
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</tr>
<tr>
<td>60</td>
<td>0.0287</td>
<td>0.0289</td>
<td>0.0288</td>
<td>0.0282</td>
</tr>
<tr>
<td>90</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>120</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
Also, aluminum particles with incorporated Ga₂O₃ nanoparticles are chosen as a control experiment for photocatalytic activity. The outcomes are presented in Figure 3.9. The weight of aluminium particles is kept the same as LM/MO frameworks. It is observed that the photocatalytic efficiency of aluminum particles with 1 wt% Ga₂O₃ is very low, and is almost the same as the sample made of pure Ga₂O₃ nanoparticles.

![Graph showing degradation of 10 µM CR in the presence of Ga₂O₃ nanoparticles, LM/MO frameworks with incorporated 1 wt% Ga₂O₃ and aluminium particles with incorporated 1 wt% Ga₂O₃ nanoparticles.](image)

**Figure 3.9** Degradation of 10 µM CR in the presence of Ga₂O₃ nanoparticles, LM/MO frameworks with incorporated 1 wt% Ga₂O₃ and aluminium particles with incorporated 1 wt% Ga₂O₃ nanoparticles.

The enhancement in photocatalytic activity of the combined system can be related to its band position. The conduction and valence band positions of LM/MO frameworks and Ga₂O₃ nanoparticles are characterized using Mott–Schottky and XPS, respectively. From the Mott–Schottky plots shown in Figure 3.10 (a), the flat band potential of Ga₂O₃ nanoparticles is ~1.0 V more negative than that of LM/MO frameworks, which indicates that the conduction band edge of γ-Ga₂O₃ is ~1.0 eV more positive than that of the frameworks.\[^{6,7}\]
Figure 3.10 (a) Mott–Schottky plots of LM/MO frameworks and Ga₂O₃ nanoparticles measured in Na₂SO₄ solution (0.3 M, pH 7.0). (b) XPS valence band spectra of LM/MO frameworks and Ga₂O₃ nanoparticles. (c) Band structure diagram of the combined system.

Linear sweeps is obtained, and the results are shown in Figures 3.11. As can be seen, during the sweep, the response is capacitive from 0 to −1.2 V range. For voltages lower than −1.2 V, a peak can be observed, which can be ascribed to the reduction of sub–stoichiometric gallium oxide. When the applied voltage is below −1.4 V, the current increases dramatically and hydrogen evolution is observed. For voltages more negative than −2 V, the current is beyond the maximum measurement value, so the plot shows an overflow. In Figure 3.11 (a), the Mott–Schottky plot is linear from 0 to −1.2 V. Once the applied voltage reaches below −1.2 V, the Mott–Schottky plot loses its linear relationship, which can be ascribed to the same electrochemical reactions seen during the I–V measurements. However, the candidate did not observe any obvious hydrogen evolution during the
Mott–Schottky measurements. It is possibly due to the very small dimensions of hydrogen bubbles which could not be observed under the high frequency condition of the Mott–Schottky measurements.

**Figure 3.11** Linear sweep voltammogram of LM/MO framework with incorporated 1 wt% Ga$_2$O$_3$ nanoparticles.

The first 10 cycles of a cyclic voltammogram of LM/MO frameworks with incorporated 1 wt% Ga$_2$O$_3$ nanoparticles are shown in Figure 3.12. After about 8 cycles, the sample was relatively stabilized. The voltage range is from 0 to −1 V. In this range, no metallic stripping peaks are observed and the response appears to be capacitive in nature.

**Figure 3.12** Cyclic voltammogram of LM/MO framework with incorporated 1 wt% Ga$_2$O$_3$ nanoparticles.
From Figure 3.10 (b), the difference in XPS valence band binding energy shows that the valence band edge of Ga$_2$O$_3$ is 0.3 eV more positive than that of the frameworks. As the band gap of Ga$_2$O$_3$ is $\sim$4.8 eV, the candidate therefore estimates that the overall band gap of LM/MO frameworks is $\sim$3.5 eV. XPS valence band spectra of LM/MO frameworks with different Ga$_2$O$_3$ nanoparticle loadings are shown in Figure 3.13, which shows the gradual variation of difference between the Fermi level and valence band.

**Figure 3.13** XPS valence band spectra of Ga$_2$O$_3$ nanoparticles, LM/MO frameworks and LM/MO frameworks with different loading of Ga$_2$O$_3$ nanoparticles.

From Figure 3.10 (b), it is noted that in the XPS valence spectrum of LM/MO frameworks there are two sub–bandgap states centered at 0 and 1.7 eV. Such sub–bandgap states could originate from oxygen vacancies in the sub–stoichiometric native oxides.$^{[8]}$ Therefore, this quasi–metallic part of the frameworks with dominant sub–bandgap states can potentially lead to the formation of pseudo–ohmic contacts in the vicinity of both the semiconducting part of the frameworks and the Ga$_2$O$_3$ nanoparticles, facilitating free carrier transfer.$^{[9]}$

The enhancement of photocatalytic performance for the LM/MO framework incorporated with 1 wt % Ga$_2$O$_3$, in comparison to the performance of the LM/MO framework without Ga$_2$O$_3$ incorporation, is also due to another concurring effect as the plasmon peak decreases after incorporation of Ga$_2$O$_3$.
(Figure 3.5 (f)). To describe the photocatalytic performance, a band structure diagram of the combined system is shown in Figure 3.10 (c). The candidate assumes that, upon irradiation, a considerable amount of electron–hole pairs are generated in the semiconducting part of the frameworks. Because of the observation of broad peaks in the UV–vis measurements, a plasmonic effect should play a role in absorbing light in the UV–vis region in comparison to only Ga$_2$O$_3$ nanoparticles. In light of the pseudo–ohmic contacts induced by the quasi–metallic part of the LM/MO frameworks, the free carrier injection barrier is significantly reduced, therefore allowing nearly free transfer of holes from the frameworks to the valence band of Ga$_2$O$_3$ nanoparticles, where the holes have a higher oxidizing potential. Therefore, this promotes the decomposition of organic species. At the same time, electrons could either transfer to the liquid metal core or remain in the quasi–metallic part of the LM/MO frameworks, thus achieving efficient charge separation.

The variation of overall photocatalytic performance according to the concentration of incorporated Ga$_2$O$_3$ can be explained by a competition between two factors. On the one hand, incorporating Ga$_2$O$_3$ nanoparticles enhances the photocatalytic performance of the combined system due to enabling the higher oxidation potential of the holes which are transferred from the semiconducting part of the LM/MO frameworks through the pseudo–ohmic contacts which is facilitated by the presence of quasi–metallic features. On the other hand, the incorporation of Ga$_2$O$_3$ nanoparticles, which has a poor solar spectrum absorbability compared to LM/MO frameworks, inevitably reduces the available areas of the semiconducting part of the frameworks for efficient generation of electron–hole pairs, thus reducing the overall photocatalytic performance of the combined system. This is evidenced by the lower rate of CR photodecomposition of the combined system when the Ga$_2$O$_3$ loading exceeds 1 wt % (Figure 3.8 (a)).
3.4 Conclusion

The $\gamma$-$\text{Ga}_2\text{O}_3$ nanoparticles were synthesized using a solvothermal process. Different loadings of Ga$_2$O$_3$ nanoparticles were incorporated into LM/MO frameworks made of micro-- to nano--sized galinstan spheres. The photocatalytic performance of the combined system was investigated by decomposing CR under illumination of simulated solar light. It was shown that potentially the plasmonic properties of the frameworks played an important role in their photocatalytic activities. However, it was observed that a concurrent phenomenon helped the LM/MO frameworks with 1 wt % incorporated Ga$_2$O$_3$ nanoparticles to demonstrate the optimum photocatalytic efficiency of $\sim 100\%$ h$^{-1}$ with high reusability, as shown by consecutive catalytic cycles. The investigation of the band structures of Ga$_2$O$_3$ nanoparticles and LM/MO frameworks revealed the potential formation of pseudo–ohmic contacts between the Ga$_2$O$_3$ nanoparticles and liquid metal components, reducing the hole injection barrier. As a result, the higher oxidizing potential and presence of an excess of holes at the valence band of Ga$_2$O$_3$ contributed to the enhancement of CR photodecomposition. The results showed that LM/MO frameworks were capable of serving as a platform for Ga$_2$O$_3$ incorporation to significantly improve its photocatalytic performance and potentially being suitable for incorporating other wide bandgap semiconductors.

In the next chapter, the candidate will present the outcomes of his research on using the LM/MO frameworks with incorporated WO$_3$ for hydrogen gas sensing.
3.5 References


Chapter 4

Liquid Metal/Metal Oxide Frameworks Functionalised with WO$_3$ Nanoparticles for Hydrogen Gas Sensing

4.1 Introduction

Tungsten trioxide (WO$_3$) nanoparticles will be incorporated onto liquid metal (LM) frameworks in order to form hydrogen (H$_2$) gas sensors. These frameworks will be made by breaking down droplets of galinstan, a room temperature liquid alloy of gallium, into micro- and nano-spheres using a sonication method. Afterward, these spheres will be co-sonicated with WO$_3$ nanoparticles to form a coating with this functional oxide. They will be then drop casted onto interdigitated transducers to establish a porous and highly sensitive liquid metal/tungsten oxide (LM/TO) gas sensitive framework. The WO$_3$ nanoparticles will be found to be partially reduced when incorporated onto the surface of liquid metal alloy. These reduced tungsten oxides together with the catalytic metallic core of galinstan will facilitate H$_2$ gas interaction to give a sensing response. At the optimum operating temperature, the sensor will show a fast response and reproducible behaviours. The response will be faster than that of the sensor based purely on WO$_3$ nanoparticles. This work will present a new technology that is based on LM/TO frameworks for H$_2$ sensing that can be expanded to other gases by replacing the functional coating with the desired sensitive material.
In the work of the chapter, WO$_3$ nanoparticles will be incorporated onto the liquid metal frameworks to develop a liquid metal/tungsten oxide (LM/TO) H$_2$ gas sensor. The candidate will study the H$_2$ sensing properties of the LM/TO sensor and discuss the influence of surface morphology and chemical composition that governs the improvement in sensing performance.

A paper has been fully prepared based on the content of this chapter and is under review in the journal of ACS Sensors.

### 4.2 Experimental Details

*Synthesis of LM suspensions with tungsten oxide coating*

A schematic describing the different stages for forming a suspension of LM frameworks with tungsten oxide coating is presented in Figure 4.1. To produce the suspension of LM frameworks, 20 µl of bulk galinstan (Geratherm Medical AG, Geschwenda, Germany) was sonicated in 2 ml of DI water for 20 mins using a bath sonicator. 4 mg of WO$_3$ nanoparticles (NaBond Technologies Co., Limited, particle size ranges from 70–200 nm) was added into the LM framework suspensions. This concentration was used based on previous experiments that provided the most homogenous coating of LM frameworks with WO$_3$ nanoparticles.\[^1\] Then the mixture was sonicated for another 2 min to facilitate the incorporation of WO$_3$ nanoparticles into the native skin of the LM frameworks.
Figure 4.1 Schematic illustration of the synthesis procedure: (a) Adding bulk galinstan to DI water, (b) adding WO$_3$ nanoparticles to the LM frameworks, (c) obtaining the LM/TO suspensions.

Gas sensor fabrication

The substrates were made of an alumina pattern with 8 pairs of platinum interdigitated electrodes (IDE). The spacing between each IDE pair was 200 μm. 100 µl of suspensions of LM frameworks with and without WO$_3$ coating were drop casted onto the substrate. The gas sensor was then annealed in air at 250 °C for 2 hours. A schematic diagram is shown in Figure 4.2 (a). The suspension of WO$_3$ nanoparticles only was also drop casted on another alumina substrate with IDTs to form a reference sensor for comparison.

Characterization

A FEI Nova NanoSEM was utilized for Scanning electron microscopy (SEM). A Bruker D8 DISCOVER micro–diffractometer was used for X–ray diffraction (XRD). For X–ray photoelectron spectroscopy (XPS) measurements, a VG–310F instrument using Al non–monochromated X–rays (20 kV, 15 mA) with a hemispherical energy analyser was set at a pass energy of 100 eV for the survey spectrum and 20 eV for the peak scans.

Gas sensing measurements

The gas sensor was placed in a gas testing chamber connected to a T95 controller (both from Linkam Scientific Instruments), which controlled the testing temperature via an external micro heater beneath
the sensor. The operating system was accessed using Linksys 32 Software Package. The measurement set-up is shown in the schematic diagram in Figure 4.2 (b).

The electrical contact was formed by connecting needle probes to the electrodes. The gas sensor was supplied with a constant bias current of 200 µA in order to measure the dynamic response of the device when it was periodically exposed to ambient air and H$_2$ gas in ambient air with a pulse sequence of concentrations equal to 0.06%, 0.12%, 0.25%, 0.5% and 1%. The gas concentration was controlled using a computerized mass flow controller multi-channel gas calibration system by changing the synthetic air to H$_2$ gas ratio while maintaining a total constant flow rate of 200 SCCM (mL min$^{-1}$). The voltage change was recorded with an Agilent 34410A digital multimeter.

Figure 4.2 Schematic diagram of (a) gas sensor, and (b) gas sensing measurement system.
4.3 Results and Discussion

The surface morphology of the LM/TO sensor is studied using SEM (Figure 4.3). It can be seen that the galinstan droplet is broken down into micro– to nano–sized spherical structures after bath–sonication for 20 min. As shown in Figure 4.3 (a), after drop casting, the galinstan spheres are in close proximity to each other, forming a thin film made of LM/TO frameworks. The average diameter of the galinstan spheres was ~3.5 µm after sonication. For different sonication durations, the average diameter of the galinstan spheres is characterized and is shown in Figure 4.4. The average size of the spheres is observed to reduce from ~13 to ~1 µm with the increase in the sonication duration from 2 to 60 min. However for making sensors, the 20 min sonication time is chosen as the core remained metallic while the size of the spheres is significantly decreased compared to shorter sonication times which is consistent with the previous experiments.[1] The thickness of the film was measured to be ~20 µm. The image of one liquid marble in the framework is shown in Figure 4.3 (b). It is observed that tungsten oxide nanoparticles are incorporated onto the surface of the galinstan spheres, coating the majority of the surface. The existence of tungsten oxide nanoparticles on the surface is also evidenced by X–ray diffraction (XRD) characterisation as shown in Figure 4.5.

![Figure 4.3 SEM images of LM/TO gas sensing film made of micro– and nano–sized LM frameworks with incorporated WO₃ nanoparticles. The sonication duration is 20 min.](image-url)
Figure 4.4 The plot of average diameters of galinstan spheres after different sonication durations.

![Figure 4.4](image)

Figure 4.5 XRD spectrum of the LM/TO framework.

![Figure 4.5](image)

XPS measurements are conducted to investigate the surface chemical composition of the LM/TO gas sensitive film. The original WO₃ nanoparticles and LM frameworks XPS spectra are also presented for comparison. Figures 4.6 (a) and (c) present the XPS spectra of the Ga 3d core level of the LM/MO frameworks without and with WO₃ coating, respectively. The gallium peaks are investigated as it is the main component of galinstan (68.5 wt% Ga, 21.5 wt% In and 10 wt% Sn). The peak at a binding
energy of 18.6 eV corresponds to metallic gallium (Ga\(^0\)), and the peak at 20.7 eV indicates a valence state of Ga\(^{3+}\) showing the existence of Ga\(_2\)O\(_3\).\(^{[2]}\) Compared to Figure 4.6 (a), the candidate finds that the magnitude of the Ga\(^0\) peak intensity in Figure 4.6 (c) is decreased when WO\(_3\) nanoparticles are incorporated onto the framework.

The twin peaks in Figure 4.6 (b) correspond to the W\(^{6+}\) state in the original WO\(_3\) nanoparticles. In addition, two peaks, which correspond to the W\(^{5+}\) state, can be found in Figure 4.6 (d) when WO\(_3\) nanoparticles are incorporated onto the liquid metal spheres.\(^{[3]}\) This can be attributed to the formation of the substoichiometric oxide phase of WO\(_{3-x}\) which is formed after WO\(_3\) nanoparticles are placed in contact with the liquid metal. It has been previously shown that gallium and its alloys can interact with oxides in their vicinity and reduce them.\(^{[4, 5]}\) A similar process also appears to occur here and in principle should have a significant effect on the gas sensing properties of WO\(_3\).

![Figure 4.6](image_url)

**Figure 4.6** XPS spectra of (a) Ga 3d of LM/MO frameworks, (b) W 4f of original WO\(_3\) nanoparticles, (c) Ga 3d of LM frameworks with WO\(_3\) coating and (d) W 4f of LM frameworks with WO\(_3\) coating.
Gas sensing was conducted on LM/TO sensors, LM frameworks and WO₃ nanoparticles. The latter two sensors were included as control experiments. As described in the experimental section the sensors were exposed to H₂ gas of different concentrations. The reference sensor based on the LM frameworks did not show any response to H₂ gas at any selected temperatures, proving that galinstan and its native oxide skin are not sensitive to H₂ gas under the set of conditions presented in this work. Therefore the measurements are not presented here.

The operating temperature is critical to the performance of semiconducting gas sensors. In order to achieve fast response/recovery and reversible responses, elevated operating temperatures are generally required. In this work, the LM/TO sensor is exposed to 1% H₂ gas in synthetic air over a range of temperatures of 150 ºC, 200 ºC and 250 ºC. The results are shown in Figure 4.7 (a). The sensor response (SR) is defined as:

\[
SR = \frac{R_{\text{gas}}}{R_{\text{air}}}
\]  

(1)

where \( R_{\text{gas}} \) and \( R_{\text{air}} \) are the sensor resistance in 1% H₂ and air, respectively. It can be seen that the response magnitude decreased by increasing the operating temperature. At 150 ºC, the LM/TO sensor shows the largest SR of 18%. The SR decreases to 5% at 200 ºC. When the operating temperature rises to 250 ºC, the SR is less than 1% as tungsten oxide does not operate as a gas sensitive layer at such elevated temperatures. This is also an indication that the response is not gallium oxide dominant as this oxide operates best at >250 ºC. It is noted that the LM/TO sensor cannot recover to its initial state at 150 ºC. Taking into account both the magnitude of SR and the ability to fully recover, the candidate choose 200 ºC as the optimum operating temperature for further analysis.

The dynamic responses of the LM/TO sensor and the WO₃ nanoparticles only at 200 ºC are compared to assess whether any enhancement occurred as a result of the presence of the LM frameworks. In a practical sense a direct comparison of the response magnitude is not achievable, as it is impossible to accurately assess the mass of WO₃ in the framework and the nanoparticle only sensors. As a result,
responses are normalized and presented in Figure 4.7 (b) which is a comparison of the dynamic responses.

The response time is defined as the duration for the SR to decrease from ~100% to 10%. The recovery time is defined as the duration for the SR to increase from ~0% to 90%. As can be seen in Figure 4.7 (b), the response time of the reference WO₃ nanoparticle based sensor is 230 s. In contrast, the response time of the LM/TO sensor was 90 s, which is a significant enhancement in the dynamic response. However, no significant improvement is observed for the recovery.

In air, oxygen molecules are adsorbed on the surface of sensitive materials and extract electrons from the conduction band to form oxygen ions. This leads to the formation of an electron depletion region near the surface and hence the increases of resistance:  

\[ O_2(g) \rightarrow O_2(\text{ad}) \]  

\[ O_2(\text{ad}) + e^- \rightarrow O_2^- \]  

After exposure to H₂ gas, the H₂ molecules are adsorbed on the surface of tungsten oxide and split into H⁺ ions and electrons:

\[ H_2(g) \rightarrow H_2(\text{ad}) \rightarrow 2H^+ + 2e^- \]  

H⁺ ions intercalate with tungsten oxide to reduce it, while the injection of e⁻ increases the conductivity. H⁺ ions can react with oxygen ions and form water vapour that leaves the surface at elevated temperature as:

\[ 2H^+ + \frac{1}{2}O^- \rightarrow H_2O \]  

As proven by the XPS measurement, the surface of the LM/TO frameworks is made of WO₃₋ₓ nanoparticles rather than stoichiometric WO₃. Oxygen vacancies have been shown to act as active sites which enhance the gas sensing performance. Another possibility for the enhancement in H₂ sensing can be due to the presence of gallium, indium and tin that act as the catalyst for splitting H₂
gas molecules. It has been previously reported that the surface of LM frameworks can facilitate charge separation and transfer. The candidate believes the generated electrons can either transfer to the liquid metal core or remain in the surface of the LM frameworks, thus achieving a lower response time. As the LM/MO frameworks do not show any response to H$_2$ and also the fact that gallium oxide semiconducting gas sensors generally operate at temperatures above 300ºC, an enhancement due to the formation of a binary compound of gallium oxide–tungsten oxide seems to be unlikely. As such, the candidate believes that the induced oxygen vacancies on the tungsten oxide coating, possibly together with the presence of catalytically active gallium, indium and tin may result in a decrease in the response time of the LM/TO sensor.

![Figure 4.7](image)

**Figure 4.7** (a) The dynamic response of the LM/TO sensor towards 1% H$_2$ gas at different temperatures. (b) The dynamic responses of the LM/TO sensor and original WO$_3$ nanoparticles at 200 ºC.

To assess the performance of the LM/TO sensor, it is exposed to different concentrations of H$_2$ (Figure 4.8 (a)). The concentrations are 0.06%, 0.125%, 0.25%, 0.5% and 1%, respectively. After each exposure to air, recovery to the baseline is observed for all H$_2$ concentrations, demonstrating good repeatability and reproducibility. The response and recovery time of the LM/TO sensor towards H$_2$ with the corresponding concentrations are presented in Figure 4.8 (b). It can be observed that both the response and recovery time increased by increasing the H$_2$ concentration. The recovery time is almost a linearly increasing function of the H$_2$ concentrations for >0.25% H$_2$, while the response time remains relatively unchanged possibility due to the fact that de–intercalation of protons seems to be a
more inhibiting process in the recovery as the reaction with oxygen in the lattice is a slower process and increase in \( \text{H}_2 \) facilitates it.

![Figure 4.8](image)

Figure 4.8 (a) The dynamic response of LM/TO sensor measured with increasing concentrations of \( \text{H}_2 \) gas at 200 °C and (b) response time and recovery time with respect to \( \text{H}_2 \) gas concentration at 200 °C.

### 4.4 Conclusion

The PhD candidate developed a novel LM/TO \( \text{H}_2 \) gas sensor using LM frameworks with incorporated \( \text{WO}_3 \) nanoparticles. The suspensions of LM/TO sensor were realized by sonicating liquid metal galinstan in the presence of \( \text{WO}_3 \) nanoparticles. Then the suspension was drop–casted to form the gas sensitive film. The surface morphology and chemical composition were investigated using SEM, XRD and XPS to reveal that substoichoimetric \( \text{WO}_{3-x} \) was formed as the coating of the micro– and nano–spheres comprising the LM framework. The LM/TO \( \text{H}_2 \) gas sensor was tested at different elevated temperatures to reveal optimum performance at 200 °C. At this operating temperature the LM/TO sensor showed the fastest response to \( \text{H}_2 \) and highly reproducible behaviour. The response time of the LM/TO sensor towards 1% \( \text{H}_2 \) at 200 °C was 90 s, about 2.5 times faster than \( \text{H}_2 \) gas sensors based solely on \( \text{WO}_3 \) nanoparticles. This was ascribed to the formation of oxygen vacancies in substoichoimetric \( \text{WO}_{3-x} \) and also the presence of catalytically active gallium in the liquid core,
facilitating the H₂ redox reaction. Good reproducibility was also demonstrated that presents a viable novel technology for future gas sensing applications.

In the next chapter, the candidate will present the outcomes of his research on using the silver nanoparticle/oleic acid frameworks for SERS enhancement.
4.5 References


Chapter 5

Sonication synthesis of micro–sized silver nanoparticle/oleic acid liquid marbles: a novel SERS sensing platform

5.1 Introduction

As per Chapter 1, liquid marbles are entities made of a small amount of liquid encapsulated by micro/nano scale particles. The functionality of liquid marbles depends on both the core liquid and particle coating. In this chapter, functional silver (Ag) nanoparticles/oleic acid liquid marbles will be developed using Ag nanoparticles to encapsulate micro–sized oleic acid liquid spheres, which will be achieved via sonication. It will be demonstrated that both the size of the encapsulated spheres and the order of the Ag nanoparticles coating are a function of the sonication time. These micro–sized liquid marbles will be investigated for sensing an organic thiolate as a model material. Their capacity for increasing solar light absorption and energy conversion into heat will also be studied. The liquid marbles generated after sonication for a controlled duration will show the strongest Raman peak signals which will originate from the thiolate. They will also demonstrate the highest solar energy absorption. These enhancements will be ascribed to the increased surface area of the Ag Nanoparticles/oleic acid spheres and the optimum order of Ag nanoparticles which will produce the strongest surface enhanced Raman scattering.
In this chapter, the PhD candidate will demonstrate the formation of a suspension of Ag nanoparticles encapsulated oleic acid micro–sized liquid marbles in water. These liquid marbles will be synthesized using sonication and their functional properties will be investigated. It will be shown that this innovative yet simple method can control the dimensions of the marbles and the compactness of the Ag coating as a function of the sonication time. Two model applications will be demonstrated: one will show the possibility of SERS enhancement for the sensing of chemical species and the other will illustrate the illumination induced heating effect.

The content of this chapter was fully reviewed and published in Sensors and Actuators B: Chemical.\[1\]

### 5.2 Experimental Details

**Synthesis of micro–sized Ag nanoparticles/oleic acid liquid marbles**

Figure 5.1 illustrates the process for producing the suspensions of oleic acid micro–sized droplets with a coating of Ag Nanoparticles. To produce the liquid marble suspensions, 1 mL of high purity oleic acid (≥99% Sigma–Aldrich) was added into a glass vial filled with 6 mL of DI water. 6 mg of dry Ag nanoparticles powder (Sigma–Aldrich diameter < 70 nm) were added to the vial. The vial was kept in a sonication bath (UNISONICS AUSTRALIA, FXP10DH, 240V AC, 5 V, 50 Hz) at 25 °C for a desired time.

**Preparation of thiolate suspensions**

The upper layer of the suspensions shown in Figure 5.1 (d) was collected. In the investigation of sonication time effects on Raman signals for thiolate molecules, each testing sample was made by mixing 0.5 mg of sodium 1–phenyl–1H–terazole–5–thiolate (PPT) with 10 µL of Ag Nanoparticles/oleic acid liquid marble suspensions. Four liquid marbles were chosen. They were prepared after sonication for 20, 40, 60 and 80 min, respectively. As a control measurement, 0.5 mg of PPT was dissolved in 10 µL of pure oleic acid. The liquid marble suspensions and oleic acid were
drop casted on glass substrates coated with Au/Ti (100nm/10nm) layers. In addition, 0.5 mg of PPT was also placed on this substrate and measured, as a benchmark. All liquid marbles and oleic acid were incubated together with PTT for 40 min prior to measurement.

In the investigation of different loadings of thiolate, each testing sample was made by mixing different amounts of PPT with 10 µL of the Ag nanoparticles/oleic acid liquid marble suspension after 60 min of sonication. Four different amounts of PPT were chosen, which were 0.4, 0.6, 1.2 and 2 mg. As a control measurement, 0.4 mg of PPT was placed on the glass substrate coated with the Au layer (mentioned above). The extra incubation time of all samples was also 40 min.

**Characterization of light absorption**

Four groups of Ag nanoparticles/oleic acid liquid marble suspensions were prepared (20, 40, 60 and 80 min, respectively) under the same procedure shown in Figure 5.1. Pure oleic acid (7 mL) was also added to a similar glass vial as a control sample. These five glass vials were placed under a simulated solar lamp (Abet Technologies LS150) and illuminated simultaneously for 30 min. The lamp was located at a distance of 10 cm from the top surface of the vials. Thermal images were taken using a FLIR ThermoVision A320 camera. The ambient temperature was 24 °C.

**Other characterization**

Optical images were obtained using a Nikon Eclipse Ti optical microscope. Average sizes of oleic acid spheres were evaluated using the software ImageJ. The candidate utilized a FEI Quanta 200 Environmental scanning electron microscope and a JEOL 2100F High resolution transmission electron spectroscope for Environmental scanning electron spectroscopy (ESEM) and Transmission electron spectroscopy (TEM), respectively. The UV–visible (UV–vis) measurements were conducted using a CRAIC 20/30 microspectrophotometer with a 150 W Xenon lamp source. The candidate used a ×15 mirror lens with a numerical aperture (NA) of 0.28 and a focal distance of 35 mm. Small angle X–Ray scattering (SAXS) measurements were performed on a Bruker Microcalix instrument, using 50 W Cu Ka radiation at a wavelength of 1.54 Å. Scattered light was detected using a Pilatus 100 k detector. Scattering and transmission measurements were performed with 1 hour exposure time. The
Raman spectra were obtained using a Perkin RamanStation 400F with an excitation wavelength of 785 nm. The set laser has a power of 350 mW and the working distance is 15 mm. Each sample was measured 10 times and each time for 5 s exposure. In Raman measurement, centre areas of liquid marbles were chosen to obtain the maximum SERS signals.

![Figure 5.1](image.png)

**Figure 5.1** Schematic illustrating the synthesis of Ag nanoparticles/oleic acid liquid marbles. (a) Adding oleic acid into a glass vial filled with DI water, (b) adding Ag nanoparticles into the vial, (c) positioning the glass vial in a sonication bath for a desired time, and (d) obtaining the micro–sized Ag nanoparticles/oleic acid liquid marble suspension.

### 5.3 Results and Discussion

The optical images of the suspensions of micro–sized Ag nanoparticles/oleic acid liquid marbles are shown in Figure 5.2 (a). It is observed that after sonication for 60 min, the original oleic acid droplet is broken down into micro–sized spheres which are coated with Ag Nanoparticles. Figure 5.2 (b) shows the magnified image. It is seen that the Ag Nanoparticles form a relatively uniform coating on the surface of the oleic acid spherical droplets. The nearly transparent area on some of the spheres could be due to a less dense coating of nanoparticles. Figure 5.2 (c) shows the TEM image of only Ag Nanoparticles. It can be seen that the dimensions of Ag nanoparticles are less than 30 nm. Figure 5.2 (d) shows the selected area electron diffraction (SAED) pattern of Ag nanoparticles. This pattern corresponds to the (1 1 1), (2 0 0) and (2 2 0) planes of Ag.\[^{[2]}\]
Figure 5.2 Optical image of (a) micro-sized Ag nanoparticles/oleic acid liquid marbles after 60 min sonication, and (b) magnified image. (c) TEM image and (d) TEM diffraction pattern of Ag nanoparticles.

To characterize the size distribution of liquid marbles, the candidate compares the optical images of the Ag Nanoparticles/oleic acid liquid spheres synthesized after four different sonication times (Figure 5.3). The average diameters of the liquid marbles are obtained using the software ImageJ. In Figure 5.3 (a), the average diameter of the spheres is ~175 µm. As discussed previously, the transparent areas on the surface of some of the spheres is due to a less dense coating of Ag Nanoparticles. Increasing the sonication time results in a decrease in the diameter of the spheres, which can be observed in in Figures 5.3 (b) and (c). In addition, the coating of Ag nanoparticles tends to be more uniform after longer sonication times. In Figure 5.3 (d), the average diameter of the oleic acid spheres is ~110 µm, after a sonication time of 80 min. The average diameters are included in Figure 5.3 (e). It is seen that the average diameters of the spheres decreases almost linearly as the sonication time increases.
Figure 5.3 Optical images of Ag nanoparticles/oleic acid liquid marbles after sonication for (a) 20, (b) 40, (c) 60, and (d) 80 min. Scale bar = 200 µm. (e) The plot of average diameters of oleic acid spheres coated with Ag nanoparticles at four different sonication times.

Figure 5.4 (a) compares the absorption spectra of Ag nanoparticles/oleic acid liquid marbles synthesized after 20 and 80 min of sonication. The absorption spectrum of Ag nanoparticles powder is also presented as a reference. There is a broad peak at ~500 nm in the spectrum of the reference Ag Nanoparticles, which is generally associated with surface plasmon resonance (SPR) and indicates some aggregation of the Ag nanoparticles. The spectrum of the liquid marbles after 20 min of sonication also has an absorption peak at nearly the same wavelength. However, it is found to be significantly tapered. It seems that at this sonication time the coating is not thick enough to produce a strong signal. Interestingly, the absorption peak for the liquid marbles obtained after 80 min of sonication is located at a much lower wavelength of ~400 nm. This blue shift could be associated with more order for the agglomeration of Ag nanoparticles on the surface oleic acid droplets due to the longer sonication time.

SAXS measurements are carried out to investigate the order of the Ag Nanoparticles coating distribution on the oleic acid spheres. The results are shown in Fig. 5.4 (b). It can be seen that the bandwidth of the lowest peak reduces by increasing the sonication time up to 60 min. This is associated with the higher order of the Ag nanoparticles on the sphere. The Ag nanoparticles in oleic acid appear to be clustering in some complex manner which cannot be simply modelled. The
nanoparticles on the surface of oleic acid spheres show similar behaviour, suggesting that the nanoparticles are clustering. The sonication reduces the clustering, which increases the Ag nanoparticle orders and coat the droplets. The fact that the sample generated after 80 min of sonication show a less ordered behaviour suggests that this process is optimized at 60 min.

![Graph](image)

**Figure 5.4** (a) UV–vis absorption spectra of micro–sized Ag nanoparticles/oleic acid liquid marbles after different sonication times, and Ag nanoparticles powder. (b) SAXS spectra of Ag nanoparticles/oleic acid liquid marbles after four different sonication times. Inset shows the magnified region of interest.

To further investigate the effect of sonication time on surface signals, the candidate obtains and assesses the SERS spectra of PTT on the Ag nanoparticles/oleic acid liquid marbles. The liquid marbles are obtained after 20, 40, 60 and 80 min of sonication. It has been reported that flat hydrophobic substrates are advantageous in concentrating target chemicals. However, in every sample preparation, PPT is mixed with Ag nanoparticles/oleic acid liquid marbles through a same procedure. The samples remain in liquid phase for a long time on the surface of the substrate. As a result, a relatively uniform distribution on surface of liquid marbles is always accessible for measurements. All results are obtained under same condition for consistency. The results are shown in Figure 5.5 (a). The Raman peak shifts associate with PTT are marked with stars. The peaks at 414 and 700 cm$^{-1}$ are ascribed to C–C torsion and C–C–C bending, respectively. The peaks located at 1004,
1501 and 1599 cm\(^{-1}\) are related to vibrational modes of the phenyl ring.\(^6\) N–N and N–C stretching coordinates contribute to the peak at 1094 cm\(^{-1}\).\(^6\)

Figure 5.5 Raman spectra of 0.5 mg PTT on Ag nanoparticles/oleic acid liquid marbles after 20, 40, 60 and 80 min of sonication. The Raman spectra of 0.5 mg of PTT on Au substrate and in oleic acid are presented as control measurements. The Raman spectrum of Ag nanoparticles/oleic acid liquid marbles after 60 min of sonication is also measured. The spectra were shifted vertically for clarity. (b) Raman peaks (1004 cm\(^{-1}\)) intensity of 0.5 mg of PTT on liquid marbles after four different sonication times, and on gold substrate.

As the peak at 1004 cm\(^{-1}\) is the strongest, its intensity is used as an indicator of the signal enhancing ability of the liquid marbles after four different sonication times. The comparison is shown in Figure 5.5 (b). It can be seen that 0.5 mg of PTT on Ag nanoparticles/oleic acid liquid marbles generates a much stronger Raman signal in comparison with the same amount of PTT on Au substrates. Among the four studied groups of liquid marbles, the PPT on the liquid marbles achieved after 20 min of sonication shows the weakest SERS response. The peak intensity shows a slight increase when the sonication time is increased to 40 min. By further increasing the sonication time to 60 and 80 min much stronger SERS responses are obtained, which are almost 10 times greater than those for PTT on the Au substrate. There is no noticeable difference in the responses for liquid marbles generated after sonication for 60 and 80 min.

As shown in Figure 5.3, longer sonication times result in smaller average diameters of the liquid marbles. The decrease in the liquid marble sizes increases the size of oil–water interface, which
allows more Ag nanoparticles to be accessible. As a result, stronger SERS responses can be generated from liquid marbles after sonication for 60 and 80 min. As it has been reported that the enhancement depends on the degree of aggregation of Nanoparticles on the surface, it is likely that longer sonication times result in a more homogenous distribution of Ag nanoparticles, with a more ordered structure (according to the SAXS patterns) that enhance the local electromagnetic field at hot spots and increases the overall SERS signal intensity.

Different loadings of PTT are then incorporated with Ag nanoparticles/oleic acid liquid marbles after 60 min of sonication (the optimum time according to the previous experiments). The results are shown in Figures 5.6 (a) and (b). The control data is also provided. In Figure 5.6 (b), the 0.4 mg of PTT on liquid marbles demonstrates a more intense Raman response, which is nearly 10 times greater than the control experiment. This is consistent with the measurement shown in Figure 5.5. When increasing the amount of PTT from 0.4 to 2 mg, the peak intensity shows a near linear increase. It is believed that the binding between PPT and liquid marbles are by the formation of covalent bonds. Longer incubation time results to higher concentration of bonded chemicals on the surface Ag Nanoparticles. The results are not normalized for comparison in Gervinskas’s way because the Raman measurements are conducted using a set laser.\(^7\) However, all samples were measured 4 times and average is taken to assure the consistency and reliability of measurements.
Figure 5.6 (a) Raman spectra of different loadings of PTT on Ag nanoparticles/oleic acid liquid marbles after at 60 min of sonication. The spectra were shifted vertically for clarity. (b) Raman peaks (1004 cm$^{-1}$) intensity of different loadings of PTT on liquid marbles after 60 min of sonication. Raman peak (1004 cm$^{-1}$) intensity of 0.4 mg of PTT on Au substrate is also presented, shown as a yellow dashed line.

A similar near linear increase is observed from the results of Raman measurements in terms of various incubation durations. The outcomes are shown in Figure 5.7. The amounts of PPT and Ag nanoparticles/oleic acid liquid marbles are kept constant for consistency. The peak intensity also shows a near linear increase when incubation time becomes longer. Longer incubation time results in stronger and more consistent binding.
It is known that the intense absorption of SPR can be utilized for the absorption of solar energy and the conversion of energy to heat. The Ag nanoparticles/oleic acid liquid marbles are evaluated under high intensity illumination of simulated solar light to investigate the light harvesting properties of the liquid marbles obtained after different sonication times. Thermal images are taken of four different liquid marbles under the same illumination conditions. The exposure time is 30 min. The results are shown in Figure 5.8. Pure oleic acid is also included as a control sample. It is observed that the final temperature of oleic acid is the lowest, reaching 32.9 °C. Among the four groups of liquid marbles, the one after 60 min of sonication demonstrates the highest temperature rise, reaching 35.1 °C. Temperatures of liquid marbles after 40 and 80 min of sonication reach very similar temperatures (34.6 and 34.5 °C, respectively), lower than the 60 min sample. The liquid marbles after 20 min of sonication have the lowest temperature rise. The Ag nanoparticles/oleic acid liquid marbles show the highest solar energy absorption efficiency when sonication time is 60 min. This can be ascribed to the higher order of the Ag nanoparticles (according to the SAXS measurements) that is obtained after this sonication time. As the samples have the same concentration of oleic acid and Ag nanoparticles, the temperature rise is most likely to be due to the localized heating effect of the plasmon resonances of

Figure 5.7 (a) Raman spectra of 0.5 mg PTT on Ag nanoparticles/oleic acid liquid marbles after 60 min of sonication. The incubation time is varied. (b) Raman peak (1004 cm⁻¹) intensity of 0.5 mg of PTT on liquid marbles with various incubation durations on a gold substrate.
the more ordered Ag nanoparticles, which is induced by the light radiation.\(^8\) The compositions of four groups of Ag Nanoparticles/oleic acid liquid marbles are similar. Additionally their hue, opaqueness and colour are close. As such, it is reasonable to assume the same thermal emissivity values for those four samples. The results are suggestive that sonication time may vary the order of Ag nanoparticles coating, and different ordering of the nanoparticles may lead to different energy absorption properties. ESEM images of Ag nanoparticles/oleic acid liquid marbles after 60 min of sonication are shown in Figure 5.9. Under the bombardment of electron beam from the environmental scanning electron microscope, it is observed that the encapsulated oleic acid expands in volume and breaks the Ag nanoparticles coating. The candidate ascribes the volume expansion to the heating effect caused by SPR of Ag nanoparticles.

Figure 5.8 Thermal images of Ag nanoparticles/oleic acid liquid marbles after four different sonication times and pure oleic acid under illumination for 30 min. Room temperature is 24 °C.
Figure 5.9 ESEM images of Ag nanoparticles/oleic acid liquid marbles after 60 min of sonication.
5.4 Conclusion

The PhD candidate developed functional Ag nanoparticles/oleic acid liquid marbles using sonication. The micro-sized oleic acid spheres were encapsulated by Ag nanoparticles. He demonstrated that the size of marbles and the order of Ag nanoparticles were functions of the sonication time. The size of liquid marbles showed a near linear decrease from ~175 to ~110 µm when the sonication time was increased from 20 to 80 min. The SAXS measurements showed that the highest order for the Ag nanoparticles was gained after 60 min of sonication time. At this sonication time the Ag nanoparticles/oleic acid liquid marbles also had high surface to volume ratio, which led to its enhanced properties. He demonstrated that the Ag nanoparticles/oleic acid liquid marbles could be utilized as an effective SERS platform for thiolate sensing, with the strongest signals obtained for a sonication time of 60 min. In addition, the candidate also demonstrated that the Ag nanoparticles/oleic acid liquid marbles are capable of absorbing solar energy, which he ascribed to the SPR generated by Ag nanoparticles. After 30 min illumination, the liquid marbles prepared after 60 min of sonication had experienced the highest temperature increase of ~11 °C.

Altogether, his demonstrations showed two important effects of the sonication process: (1) the developed functional Ag nanoparticles/oleic acid liquid marbles had an enhanced surface area for interactions with chemical components and light absorption and (2) the Ag nanoparticles on the surface of the spheres were more ordered than the original powder in a suspension, which resulted in augmented LSPR. The candidate believes that the Ag nanoparticles/oleic acid liquid marbles have great potential in forming future sensing and optical devices, and should be further investigated in order to discover their multi–faceted properties.

In the next chapter, the PhD candidate will present the conclusions of this thesis and the recommendations for possible future work.
5.5 References


Chapter 6

Conclusions and Future Work

6.1 Conclusions

In this work, the candidate successfully achieved the initial aims of his PhD research by creating liquid metal frameworks that were explored for sensing, catalysis and surface enhanced Raman scattering (SERS).

The PhD candidate reviewed literature to establish a well–informed plan for the development of liquid metal frameworks. By delving into literature regarding liquid marbles, he identified a main research gap which was the fact that the interfacial properties of macroscopic liquid marbles are limited in accessibility. This was due to the low surface–to–volume ratio of conventional liquid marbles with millimeter to centimeter size. The candidate demonstrated a facile approach to break down droplets’ bulk liquid core to obtain micro– to nano–sized liquid marble suspensions using sonication. The suspensions containing these micro– to nano–sized liquid marbles were drop casted to realize functional thin films named liquid marble frameworks.

Based on the structure of the liquid marble frameworks, the candidate developed platforms named “liquid metal/metal oxide (LM/MO) frameworks”. The LM/MO frameworks were made of micro– to nano–sized liquid metal galinstan spheres. The candidate studied the surface properties of the LM/MO frameworks and then proved his hypothesis that liquid metal droplets were being oxidized during the sonication process. He also showed that the properties, such as the size and the surface chemical composition, of the micro– to nano–sized liquid metal spheres could be actively controlled.
Functional metal oxides, such as tungsten oxide (WO$_3$) and gallium oxide (Ga$_2$O$_3$), were incorporated to the LM/MO frameworks to form hybrid systems. By using different amounts of coating materials, the surface chemical composition of these systems could be tuned for enhanced performance of different applications. The LM/MO frameworks with incorporated WO$_3$ nanoparticles were highly sensitive to heavy metal ions. These micro- to nano-sized marbles provided significantly improved sensitivity in comparison to their bulk counterparts. The detection limit was lower than the hazardous thresholds of heavy metal ions for humans. This improvement was ascribed to the enhanced surface-to-volume ratio which was enabled by breaking down bulk liquid marbles using sonication. Furthermore, hybrid systems based on LM/MO frameworks coated with WO$_3$ also showed faster response to hydrogen gas at an elevated temperature, compared to sensor based solely on WO$_3$ nanoparticles. This was attributed to the formation of oxygen vacancies in substoichiometric WO$_{3-x}$ and the presence of catalytically active gallium in the liquid core.

The LM/MO frameworks with incorporated Ga$_2$O$_3$ nanoparticles were used for photocatalysis. These systems showed significantly improved photocatalytic efficiency compared to LM/MO frameworks and pure Ga$_2$O$_3$ nanoparticles. Based on the results of band structure study of these hybrid systems, the candidate ascribed the efficiency enhancement to the potential formation of pseudo–ohmic contacts between the Ga$_2$O$_3$ nanoparticles and liquid metal components. The pseudo–ohmic contacts possibly reduced the hole injection barrier and increased the number of holes with high oxidizing potentials.

Silver (Ag) nanoparticles and oleic acid were assembled to form Ag nanoparticles/oleic acid liquid marble frameworks using sonication. The candidate demonstrated that the order of the coating made of Ag nanoparticles was a function of the sonication duration, and the order of the coating could be actively controlled. With an optimum order of Ag nanoparticle coating, the frameworks showed improved SERS responses to the target chemical, compared to pure Ag Nanoparticles. The frameworks were also capable of efficiently absorbing solar energy under illumination of simulated solar source, which was ascribed to the surface plasmon resonances (SPRs) generated by Ag nanoparticles. The augmented performance of the frameworks was ascribed to the formation of an
enhanced surface area and higher order of the Ag nanoparticle coating, which were achieved by sonication.

This PhD project resulted in a number of research outcomes in fields relevant to the liquid marbles. The major outcomes of each stage of this PhD research project are listed as follows:

Stage 1:

- The PhD candidate developed micro– to nano–sized LM/MO frameworks via sonication. The frameworks were made of galinstan core and coatings of metal oxide nanoparticles.
- The PhD candidate found that the surface morphology and stoichiometry of the frameworks were both a function of the sonication duration and therefore could be actively controlled.
- The LM/MO frameworks were incorporated with WO₃ nanoparticles to form a highly sensitive electrochemical platform for heavy metal ion sensing. Results showed that sensitivity of these frameworks towards Pb²⁺ was as low as 100 ppb, which was about 80 times improvement in comparison to the sensitivity of bulk counterparts of the frameworks. This was attributed to the high surface–to–volume ratio and the formation of intense electric fields, which were enabled by sonication.
- The PhD candidate also found that these frameworks demonstrated improved photocatalytic efficiency compared to pure WO₃ nanoparticles. The highest photodegradation efficiency of ~47% h⁻¹ was observed for the LM/MO frameworks prepared after 20 min of sonication. This was ascribed to their excellent visible light absorption properties and the unique LM/MO interfaces that facilitated the charge separation and the suppression of electron–hole recombination.

Stage 2:
• In this stage, the PhD candidate synthesized $\gamma$-$\text{Ga}_2\text{O}_3$ nanoparticles using a solvothermal process. He incorporated different loadings of $\text{Ga}_2\text{O}_3$ nanoparticles to LM/MO frameworks. The LM/MO frameworks were developed using the sonication method.

• The photocatalytic performance of the LM/MO frameworks incorporated $\text{Ga}_2\text{O}_3$ nanoparticles were investigated by decomposing Congo red under illumination of simulated solar light. The PhD candidate found that the photocatalytic efficiency of the hybrid system was enhanced by incorporating $\text{Ga}_2\text{O}_3$ nanoparticles, compared to the efficiency of LM/MO frameworks. The LM/MO frameworks with 1 wt% incorporated $\text{Ga}_2\text{O}_3$ nanoparticles demonstrated the optimum photocatalytic efficiency of $\sim100\% \text{ h}^{-1}$ with a high reusability. It was also shown that the photocatalytic efficiency was a function of loading of incorporated $\text{Ga}_2\text{O}_3$ nanoparticles.

• The PhD candidate investigated the band structures of $\text{Ga}_2\text{O}_3$ nanoparticles and LM/MO frameworks. The results revealed the potential formation of pseudo–ohmic contacts between the $\text{Ga}_2\text{O}_3$ nanoparticles and liquid metal components. The candidate found that those contacts reduced the hole injection barrier and therefore enhanced the photodecomposition of Congo red.

Stage 3:

• In this stage, the PhD candidate developed a liquid metal/tungsten oxide (LM/TO) hydrogen ($\text{H}_2$) gas sensor by incorporating $\text{WO}_3$ nanoparticles to LM/MO frameworks. He characterized the surface morphology and chemical composition of the hybrid system. The results of characterization indicated that the incorporated $\text{WO}_3$ nanoparticles were partially reduced and then became substoichoimetric $\text{WO}_{3-x}$.

• The LM/TO sensors were exposed to $\text{H}_2$ gas at different elevated temperatures. Optimum operating temperature was found to be 200 °C. At this operating temperature, the LM/TO sensors showed the fastest response to $\text{H}_2$ and highly reproducible behaviour. The response time of the LM/TO sensor towards 1% $\text{H}_2$ was 90 s, which was approximately 2.5 times faster than $\text{H}_2$ gas sensors based solely on $\text{WO}_3$ nanoparticles.
• The PhD candidate ascribed the improved sensing response to the formation of oxygen vacancies in substoichiometric WO$_{3-x}$ and also the presence of the catalytic gallium in the liquid core. They facilitated the H$_2$ redox reaction. When exposed to increasing concentrations (from 0.06% to 1%) of H$_2$ gas, the LM/TO sensor was capable of recovering to its initial baseline, which showed good reproducibility.

Stage 4:

• In this chapter, the PhD candidate developed Ag nanoparticles/oleic acid liquid marbles frameworks using sonication. The micro–sized oleic acid spheres were encapsulated by Ag nanoparticles. It was demonstrated that the size of marbles and the order of Ag nanoparticle coating were functions of the sonication duration. Optimum order of Ag nanoparticle coating was obtained at 60 min sonication.

• The candidate demonstrated that Ag nanoparticles/oleic acid liquid marbles were an effective SERS platform for thiolate sensing. With sonication duration of 60 min, the Ag nanoparticles /oleic acid liquid marbles showed the strongest SERS responses. The SERS enhancement of the liquid marbles was ascribed to an enhanced surface area and higher order of Ag nanoparticle coating.

• The candidate also showed that the Ag nanoparticles/oleic acid liquid marbles frameworks were capable of efficiently absorbing solar energy. After 30 min illumination of a simulated solar source, the liquid marbles sonicated for 60 min experienced the highest temperature increase of ~11 °C. This was ascribed to the SPRs from Ag Nanoparticles.
6.2 Publications

The outcomes of this PhD research were published in prestigious journals with high impact factors. A list of these publications is as follows:


6.3 Recommendations for future works

Significant advancements in the field of liquid marbles were achieved during the course of this PhD project. However, there are still many opportunities for continuing research in alignment with those presented in this thesis. The recommendations for future works are listed as follows:

- The degree of construability of the micro– to nano–sized liquid marbles can be increased. The PhD’s approach to control the frameworks during synthesis process is mainly changing the sonication duration. The candidate believes that the surface morphology and chemical composition can be affected by other variables, such as the frequency of sonication and ambient temperature in solution. Taking into account these factors, properties of the micro– to nano–sized liquid marbles can be further engineered on demand.

- Different types of solvents can be chosen as the media for liquid metal during the sonication process. In this PhD research, DI water was chosen because of its compatibility with the processes. The candidate suggests that sonication of liquid metals in organic solvents can result in the formation of organic bonds on surface of liquid metals. This may offer new opportunities to form novel functional frameworks for sensing applications.

- The interactions between individual micro– to nano–sized liquid marbles can be investigated. In this project, micro– to nano–sized liquid marbles are assembled and investigated as a whole system. There could be certain effects and reactions between individual marbles in the frameworks, which contributes to the collective performance and are still unknown.

- The interfacial properties of micro– to nano–sized liquid marbles can be further investigated. The PhD candidate mainly focuses on the surface chemical composition of these liquid marbles in this project and demonstrates the catalytic properties of the liquid metal core. However, he believes that further study on the properties of the interface between liquid core and incorporated nanostructures will lead to better understanding of the mechanisms that govern the hybrid systems.
• The application of sonication enabled liquid marble frameworks can be extended by using different types of liquid cores and coatings. The PhD candidate suggests that the combinations of liquid core and coating should not be limited by the choices presented in this project. New opportunities will be possible if other components and materials will be used.