Porphyrin-based nanomaterials and their applications for photocatalysis

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

Duong Duc La
M. Sc. (Chemistry & Nanotechnology)

School of Science
College of Science, Engineering and Health
RMIT University

10/2017
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.

Duong Duc La

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List of Abbreviations

GNPs ........................................................................................................ Graphene nanoplatelets
H2TCPP ....................................................................................................... Tetrakis(4-carboxyphenyl)porphyrin
RhB ........................................................................................................... Rhodamine B
MO ............................................................................................................ Methyl Orange
TCPP .......................................................................................................... Tetrakis (4-carboxyphenyl) porphyrin
EtOH ......................................................................................................... Ethanol
MeOH ......................................................................................................... Methanol
(LUMO) ...................................................................................................... Lowest unoccupied molecular orbital
(HOMO) ...................................................................................................... Highest occupied molecular orbital
MOF .......................................................................................................... Metal-organic framework
CuTCPP .................................................................................................... Cu(II) tetrakis(4-carboxyphenyl)porphyrin
Cu(OH)2 .................................................................................................... Copper hydroxide
2D .............................................................................................................. 2 Dimensions
H-bond ........................................................................................................ Hydrogen bond
TiO2 ........................................................................................................... Titanium Oxide
CTAB ......................................................................................................... Cetyltrimethylammonium bromide
TiCl4 ......................................................................................................... Titanium tetrachloride
OAPs ......................................................................................................... Ocatalkylporphyrins
TFA ........................................................................................................... Trifluoroacetic acid
(NH4)2S2O8 .............................................................................................. Amonium persulfate
HCl ........................................................................................................... Hydrochloric acid
KOH ........................................................................................................... Potassium hydroxide
NaOH ........................................................................................................ Sodium hydroxide
Na2S2O8 .................................................................................................. Sodium persulphate
SAS ......................................................................................................... Self-assembly
rGO ........................................................................................................ Reduced graphene oxide
THF ........................................................................................................ Tetrahydrofuran
ZnT(4-Py)P ............................................................................................... Zinc meso-tetra (4-pyridyl) porphyrin
H₄TPPS²⁻ ................................................................................................. Tetrasulfonatophenylporphyrin
FTIR ........................................................................................................ Fourier transform infrared spectroscopy
XPS ............................................................................................................ X-ray photoelectron spectroscopy
EDX ........................................................................................................ Energy dispersive X-ray Spectroscopy
AFM ...................................................................................................... Atomic Force Microscopy
SEM ...................................................................................................... Scanning Electron Microscopy
TEM .................................................................................................... Transmission Electron Microscopy
XRD ...................................................................................................... X-Ray Diffraction
UV-Vis ................................................................................................. Ultraviolet-Visible
FL ........................................................................................................... Fluorescence
Abstract

The design and fabrication of organic-based supramolecular nanoassemblies is a powerful method for the fabrication of nanostructured materials with tunable morphologies. The resulting materials often have unique optical and electronic properties, which can be used for potential applications including but not limited to, optoelectronic nanodevices, energy storage, catalysis, sensors, and photonics. Among the numerous organic-based supramolecular nanoassemblies described in the literature, π-conjugated porphyrins have attracted great attention as organic building blocks for the construction of soft materials. Porphyrin-based nanomaterials in particular have been extensively studied for visible-light photocatalysis due to their intrinsic optical properties. This thesis describes the synthesis of Porphyrin derived nanostructures, and reports on their properties, using a variety of methods. A particular focus is the design and fabrication of composite materials, which combine the properties of self assembled porphyrins with other materials.

Firstly, a facile synthetic protocol to grow thin films of Cu(II) tetrakis(4-carboxyphenyl)porphyrin (CuTCPP) metal-organic frameworks (MOF) from a tetrakis(4-carboxyphenyl)porphyrin (H₂TCPP) solution and a Cu(OH)₂ nanoneedle array formed on a Cu substrate at room temperature is described. The formation of Cu-centered TCPP ligands and crystalline platelet-like Cu MOFs were characterised by SEM, XRD, FTIR, UV-vis, and XPS. The formation process from Cu(OH)₂ was monitored by using SEM images obtained at different reaction times during the first 24 h, allowing the proposal of a possible reaction pathway involving Cu(OH)₂ dissolution followed by the reprecipitation of CuTCPP MOFs at the near surface. By using self-assembly with the assistance of Arginine porphyrin, (TCPP)-based supramolecular nanobelts are produced that show enhanced photocatalytic activity for the photodegradation of pollutant Rhodamine B under simulated visible-light.

Graphene has received considerable attention as a platform for studies concerning photocatalytic activity due to favorable properties imparted by its 2D geometry and large surface area. Graphene-based materials have shown excellent charge transfer properties, and have also been used as a scaffold for enhancement the photocatalytic
activity of semiconductors. Hence, in this thesis, graphene is used as a substrate for porphyrin nanomaterials for enhanced photocatalytic performance. An industrial-scale method of mass production of graphene nanoplatelets is developed by chemical exfoliation of natural graphite flakes in a single step using sodium persulfate and sulphuric acid at room temperature followed by washing with dry acetone. The produced GNP s (~100%) are tens of microns in diameter with a thickness of around 10-20 nm. The structure of the so-formed GNPs was confirmed by SEM, TEM, and AFM microscopy. Using these good quality graphene nanoplates, well-dispersed porphyrin nanorods were assembled of the GNPs by surfactant-assisted self-assembly of tetrakis (4-carboxyphenyl) porphyrin (TCPP). The assembled TCPP nanorods, with a 50 nm diameter and 200 nm in length were well-distributed on the GNPs and thoroughly characterised by SEM and TEM. The resulting hybrid material showed enhanced visible-light photocatalytic activity compared to free standing TCPP nanorods for the degradation of Rhodamine B (RhB). In addition, the photodegradation mechanism of RhB when using GNPs-supported TCPP nanorods catalyst was proposed. A GNPs@porphyrin nanofibre composite was also fabricated via arginine-mediated self-assembly of tetrakis(4-carboxyphenyl) porphyrin (TCPP) on graphene nanoplates (GNPs). The visible-light photocatalytic activity for the degradation of Rhodamine B (RhB) and methyl orange (MO) was studied, which indicated that GNPs@porphyrin nanofibre composite can be used as a photocatalyst for highly efficient degradation of dyes.

Anatase (TiO2) has emerged as a promising material for applications in environmental pollutant degradation via oxidative or reductive methods in the presence of UV light, due to its photoactivity, non-toxicity, high stability and low cost. The mechanistic pathways for pollutant degradation have been discussed in the literature. In this thesis, the synergistic photocatalytic activities of porphyrin aggregates in visible light and TiO2 particles in the UV region was investigated. A TiO2@porphyrin hybrid material was synthesized by surfactant-assisted co-assembly of monomeric porphyrin molecules with TiO2 nanoparticles. The obtained TiO2@porphyrin composite showed the excellent integration of TiO2 particles with diameters of 15-30 nm into aggregated porphyrin nanofibers, which have a width of
70-90 nm and are several µm long. This material exhibited efficient photocatalytic performance under simulated sunlight. A plausible mechanism for photocatalytic degradation was also proposed and discussed.

Finally, the combination of graphene, porphyrin, and TiO$_2$ as one composite for enhanced photocatalytic efficiency was studied. The composite was fabricated via self-assembly of TCPP porphyrin on the graphene surface in the presence of TiO$_2$ with the assistance of a CTAB surfactant. The photocatalytic performance of the graphene@TiO$_2$@porphyrin composite under sunlight conditions was investigated. TiO$_2$ and porphyrin aggregates are shown to be active for UV and visible light, respectively, resulting in a high performing composite. The possible photocatalytic mechanism of RhB degradation by graphene@TiO$_2$@porphyrins composite was discussed.

This thesis has thus provided a comprehensive understanding of the fabrication of porphyrin-based nanomaterials and composites via self-assembly, as well as the mechanism for photocatalysis of selected new materials. The composites of porphyrin with graphene and/or TiO$_2$ have been studied in some detail to increase our knowledge in this area and opened up new strategies for using the unique properties of porphyrins in materials science.
Chapter I

Introductions

This chapter contains the author’s rationale for the thesis. This chapter provides a summary of the relevant literature of porphyrins, the fabrication of porphyrin-based nanomaterials via self-assembly and applications. The application of graphene and TiO$_2$ for photocatalysis along with an overview of these materials is also presented.
1.1 Porphyrin

The majority of animal and plant life that exists on our planet today results from a class of compounds called porphyrins, which are involved in processes such as light absorption, gas transport, and catalysis. Chlorophyll and haem are two key biological molecules which contain tetra-pyrrolic units known as chlorins and porphyrins, respectively (Figure 1.1).\textsuperscript{1-2} Taking inspiration from these, many technologies using synthetic chlorins or porphyrins to mimic photosynthesis artificially, requiring molecules with a range of photophysical and redox characteristics, have been developed. However, porphyrin-based materials, due to their ease of synthesis and versatility of the oxidized porphyrin systems, as well remarkable chemical and physical properties have been widely employed for this purpose.

\textbf{Figure 1.1: Molecular structures of tetra-pyrrolic molecules, chlorophyll and haem A.}

The first porphyrin was isolated from blood, demonstrating they were pyrrole derivatives in late 1871 by Hoppe-Seyler, and the structural similarities between chlorophyll and haem were considered in 1879. However, the correct structure for porphyrins was only proposed by K\"uster in 1912, even though at that time it was not accepted. In 1918, the first general synthesis of porphyrins was reported by Milroy.\textsuperscript{3} In 1929, Hans Fischer proposed the synthesis of porphyrins which confirmed the structure reported by K\"uster almost twenty years earlier.\textsuperscript{4} Fischer was awarded the Nobel Prize in 1930 for this work.
1.1.1 Structure and properties of porphyrins

Porphyrins are cyclic organic compounds, which consist of 4 pyrrole rings connected by methylene groups at the α pyrrolic positions. The methylene carbon is assigned the meso position, while the pyrrolic carbons in the porphyrin macrocycle are termed α and β. The simplest porphyrin is known as porphin, with all other porphyrin derivatives having substituents in the β-pyrrolic and/or meso positions (Figure 1.2).\textsuperscript{5}

\textbf{Figure 1.2: The structure of the simplest porphyrin, porphin.}

Porphyrins consist of 22 π-electrons in the planar aromatic core though only 18 are required for an aromatic system.\textsuperscript{6} The allows for chemical interconversion with the free-base porphyrin I, (Figure 1.3) leading to equivalent pyrrolic nitrogens. The free-base porphyrin which has 2 protons bound to pyrrolic nitrogens is able to accept 2 protons to form a dicationic species II.\textsuperscript{7} In basic conditions, the conjugated porphyrin ring is able to produce a dianionic species III, and this open cage (species III) is capable of coordinating to metal ions to form metalloporphyrins IV.

\textbf{Figure 1.3: Acid-base, metalation and tautomerization characteristics of porphyrins.}
The delocalisation of electrons around the large ring system and the aromaticity of the porphyrin ring are responsible for high chemical and thermal stability, the characteristic electronic absorption spectra and the unique 1H nuclear magnetic resonance (NMR) spectra of porphyrin derivatives. The high molar extinction coefficients of porphyrins can be explained by the 4-orbital model. The unique electronic absorption porphyrin spectrum is derived from the transitions between two lowest unoccupied molecular orbitals (LUMO) and highest occupied molecular orbitals (HOMO). Orbital mixing of the HOMOs (the a1u and a2u orbitals) and LUMOs splits the energy states and as a result, gives rise to 2 distinct spectral regions. In the high energy state region, the dominating porphyrin Soret band between 380-420 nm ($\varepsilon > 200\,000 \text{ L mol}^{-1}\text{ cm}^{-1}$) is formed, and the low energy state gives rise to the lower intensity Q bands. A free-base porphyrin usually generates 4 Q bands between 500 and 700 nm ($<30\,000 \text{ L mol}^{-1}\text{ cm}^{-1}$), while upon insertion of metals into the porphyrins ring to form metalloporphyrins, the absorption spectrum is altered to form 2 Q bands (Figure 1.4). The metal center and substituents on the porphyrin core significantly affect the energy transitions between the HOMO and LUMO, affecting the electronic absorption spectra of porphyrins.

Figure 1.4: Typical UV-visible spectrum of a porphyrin.

The 1H NMR spectrum can be significantly affected by the aromatic ring system. One of the major effects is the position of the pyrrolic NH signal, which is shifted from a highly deshielded region to approximately -2.7 ppm in porphyrins due to the
shielding of the induced ring current (Figure 1.5).\textsuperscript{10} Other factors such as the β-pyrrolic and meso phenyl protons are also affected by the porphyrin ring current, with a downfield shift of these protons observed relative to pyrrole and benzene.

**Figure 1.5:** \textit{1H NMR chemical shifts of tetraphenyl porphyrin (TPP) in CDCl\textsubscript{3}.}

The chemical and physical properties of the porphyrin macrocycle can be adjusted through functionalization. For example, the light harvesting capabilities of the dye can be enhanced by withdrawing and/or donating electrons at the meso position of porphyrins with aromatic substituents. The porphyrin core usually incorporates with surface binding substituents to assist with light harvesting applications.

### 1.1.2 Photophysical properties of porphyrin

The interaction of light with the matter has caught the wide interest of scientists since the early 15th century. Generally, it was widely accepted that electrons were particles and the light was a wave till the end of the 19th century. However, at the beginning of the 20th century, Planck determined that blackbody radiation was limited to finite values of energy, which meant that energy was quantized. This changed the prevailing view of light, showing it could act as a wave. Later, Einstein cemented the idea of light having wave and particle by discovering the photoelectric effect. The Maxwell wave equations discovered in 1860 generally explain most of the light-related phenomena. In 1924, de Broglie theorize that all particles act as waves based on these findings. This led to the introduction of the Schrödinger equation in 1924 which
enabled the description of the wave nature of electrons mathematically. These
discoveries have dramatically changed our understanding of atomic and molecular
structure.

Photosynthesis has enabled plants, algae, and cyanobacteria to efficiently convert
sunlight into chemical energy, which is responsible for sustaining life on earth for the
last 3 billion years.\textsuperscript{11} Generally, photosynthesis is considered as a process to convert
sunlight, H\textsubscript{2}O, and CO\textsubscript{2} into carbohydrates and O\textsubscript{2}. However, this process is
performed by one of the most complex systems ever found in nature, which is a
biological machine. The biological machine that is responsible for photosynthesis can
be divided into two components: Photosystem I is responsible for light absorption and
Photosystem II is responsible for H\textsubscript{2}O splitting and carbon fixation, respectively.

When interacting with matter, light can be reflected, transmitted or absorbed by the
material. The absorption properties can provide important information regarding the
electronic molecular structure of a molecule. When matter absorbs a photon, this
photon will promote an electron from a ground state to a higher energy level, named
an excited state. The difference of value in energy between these two energy levels is
equal to the energy of the absorbed photon. This allows for clarification of the
molecular energy levels of a molecule. The energy of a photon is proportional to the
frequency of an electromagnetic wave as described in equation 1.1 as following:

\[ E = h\nu = \frac{hc}{\lambda} \]  \hspace{1cm} (1.1)

Where E is the photon energy, h is Planck’s constant, \nu is the frequency, c is the
speed of light, and \lambda is the photon wavelength.

The ground state electrons often absorb photons of different wavelengths with
different efficiencies due to the limit of the electronic energy levels of a molecule. The
efficiency when a certain wavelength of light is absorbed is described by the molar
absorptivity as following equation 1.2:

\[ A = \epsilon b C \]  \hspace{1cm} (1.2)
Where $A$ is the absorbance, $b$ is the path length of absorption, $\varepsilon$ is the molar absorptivity (units of M$^{-1}$ cm$^{-1}$), and $C$ is the molar concentration of the absorbing compound.

Another important principle to understand is the Franck-Condon principle. This principle is used to explain the appearance of the broad absorption bands in molecules instead of the expected sharp peaks based on the discrete electronic energy levels.

**Figure 1.6:** Potential energy curves for electronic transitions. A) Electronic transitions between states of similar equilibrium nuclear geometry. B) Electronic transitions between states of different equilibrium nuclear geometry. Adopted from$^{12}$

This equation is illustrated by potential energy curves of the ground and excited states as a function of equilibrium geometry. The electronic transitions are termed
“vertical” to illustrate absorption occurring without any changes in the equilibrium geometry, which allows electrons to be promoted to higher excited states regardless of any differences in equilibrium geometry between the ground and excited state. After absorption, the molecule will relax to the lowest vibrational excited state (v’ = 0). This relaxation results in a loss of energy and is the reason why the energy between the ground state (v” = 0) and some vibrationally excited state (v’ > 0) will always be higher in energy than the 0-0 transition.

1.1.3 Synthesis of Porphyrins

Since Fischer first confirmed the porphyrin structure in 1929, there was a need for developing practical and efficient synthetic methods for the preparation of porphyrins. The novel biological roles and photophysical properties of porphyrins had caught the attention of researchers for decades, but because of the limited synthetic availability, the exploration of these compounds has been severely restricted. This inspired synthetic chemists to develop simple and efficient synthetic methods for the preparation of porphyrins. Therefore, understanding the history and synthetic development made in this field is necessary. Figure 1.7 show the most common substitution patterns found around the porphyrin core for the synthesis of porphyrin derivatives.

![Figure 1.7: A) β- and meso-unsubstituted porphine B) β- substituted OAPs C) meso-aryl substituted porphyrin.](image-url)
The preparation of porphyrins are divided into three main categories, which are the β- and meso-unsubstituted porphine, β-substituted porphyrins referred to as octalkylporphyrins (OAPs) and finally meso-aryl substituted porphyrins. The first functionalised porphyrin was synthesized in 1936 by reaction of benzaldehyde with pyrrole in a sealed tube at 150°C for 24 hours to form TPP. In this protocol, only small yields were obtained and because of aldehyde decomposition, the use of more sensitive aldehydes could not be studied. In 1967, a milder methodology to produce porphyrin derivatives was proposed by Adler and Longo by reaction between benzaldehyde and pyrrole in refluxing propionic acid for 30 minutes (min) (Figure 1.8). The yields from this method were around 20% with molecular oxygen acting as the oxidant required for porphyrin oxidation. The new methodology not only produced higher yields but also enable greater numbers of substituted aldehydes to be employed. With the mild reaction conditions, this method could be used on a large scale, however, but the method does not allow for acid-sensitive aldehydes. Moreover, the product does not precipitate out of the reaction solution, therefore purification is difficult.
Figure 1.8: Adler-Longo and Lindsey porphyrin syntheses.\textsuperscript{15-16}(i) Propionic acid, O$_2$, reflux, 30 min. (ii) CH$_2$Cl$_2$, boron trifluoride etherate or TFA, room temperature (RT), 3 h. (iii) p-chloranil or DDQ, 30 min.

Synthesis of meso-Substituted Porphyrins

Although meso-substituted porphyrins provided chemists and other scientists with many applications and fundamental insights because of their simplicity in their preparation as one-pot synthesis, they are not naturally occurring compounds. Furthermore, the preparation of naturally relevant porphyrins is rather complicated and difficult.\textsuperscript{17} Therefore, much attention has been paid to the preparation of meso-substituted porphyrins due to their symmetry, which enables their simple synthesis from starting materials such as pyrrole and benzaldehyde.\textsuperscript{5}

In 1935, the first meso-substituted porphyrins was reported by Rothemund, who developed a method for the synthesis of meso-tetramethyl porphyrin by heating acetaldehyde and pyrrole in methanol at 95°C.\textsuperscript{18} Later, by using this method he included a variety of aromatic aldehydes, including benzaldehyde to yield H$_2$TPP.\textsuperscript{13} In 1941, Rothemund described a detailed preparation protocol of H$_2$TPP with a yield of 7-9\% by heating 20 mL of benzaldehyde and 10 mL of pyrrole in 20 mL of pyridine at 220°C for 48 hours.\textsuperscript{19} However, the Rothemund method often used high concentrations of reactant at high temperatures in the absence of an added oxidant.

Improvements in the synthesis of meso-substituted porphyrins did not occur until the mid-1960s when Alder and Longo developed a new method, which used lower reactant concentrations compared to the Rothemund method. This method enabled the preparation of a variety of meso-substituted porphyrins with a yield of up to 30-40\% by heating reactants in acidic solvents with the use of unsealed reaction vessels.\textsuperscript{16, 20} Good yields were obtained by increasing the reactant concentrations and using a high boiling point acidic solvent such as propionic acid (bp 141°C) rather than other lower boiling point acidic solvents like acetic acid.\textsuperscript{14} Dolphin then examined the condensation of 3,4-dimethylpyrrole with benzaldehyde in refluxing acetic acid in the absence of oxygen. This led to the formation of the porphyrin precursor called octamethyltetraphenyl porphyrinogen, which could then be oxidized to form
octamethyltetraphenylporphyrin.\textsuperscript{21} This provides strong evidence for the formation of the porphyrin followed by the oxidation of the porphyrinogen precursor.

However, the standard for meso-aryl substituted porphyrin only came in the late-1980s when Lindsey \textit{et al.} reported a new synthetic method.\textsuperscript{15, 22} The new approach allows for a wide variety of substituted aldehydes to be incorporated into the porphyrins macrocycle. The reaction is highly reproducible with yields of about 30-40\% and is able to scale up to gram-scale quantities. This method is a single flask two-step reaction based on equilibrium cyclizations and biomimetic studies of porphyrin biosynthesis as shown in Figure 1.5. In the first step, the intermediate was formed by the acid catalyzed condensation, and the porphyrin was formed upon the addition of an external oxidant such as DDQ or chlorinal.

The method was based on the idea that tetraphenyl porphyrinogen would be the thermodynamically favored product from the condensation of pyrrole and benzaldehyde under favorable conditions. It is also important to keep mild reaction conditions due to benzaldehyde and pyrrole being reactive molecules, and high temperatures are unnecessary. This enabled new functionalities on substituted benzaldehydes to be compatible with the given reaction conditions. The previous methods used harsh reaction conditions which limited the scope of possible substituents available at the meso-position.

1.1.4 Application of Porphyrins

The ability to incorporate differing levels of functionality, bind metals and form highly ordered complex structures has made porphyrins one of the most promising and applicable molecules in practical applications. Use as catalysts for organic reactions have been a significant application field for porphyrins, specifically oxidation and reduction reactions. Iron and ruthenium porphyrins have shown promise as catalysts for organic oxidation reactions.\textsuperscript{23-24} Manganese(III) porphyrins exhibited high selectivity towards the epoxidation of alkenes, with activated hydrocarbons also undergoing selective oxidation reactions.\textsuperscript{25} Cobalt porphyrins have been used in the reduction reaction of molecular \(\text{O}_2\) to \(\text{H}_2\text{O}\). Moreover, face-to-face cobalt porphyrin
dyads have been designed to facilitate the electroreduction of H₂O, with other porphyrin derivatives capable of producing hydrogen peroxide.²⁶

Due to their light absorption characteristics and the ease of synthetic method to incorporate functional groups onto the porphyrin core, porphyrins have been used extensively in dye sensitized solar cells (DSSCs).²⁷ Porphyrin dyes for DSSCs commonly relate to including a linker that connects a binding group to the highly aromatic porphyrin core, and carboxylic acid binding groups in porphyrin are used as anchors to bind the porphyrin to semiconductor surfaces. Push-pull functional groups are also employed to ensure efficient charge injection from the porphyrin excited state into the conduction band of a semiconductor (Figure 1.9).²⁸

![Figure 1.9: Porphyrin chromophore for DSSC applications. Adapted from ²⁸](image)

Another major application of porphyrins is for the treatment of cancer by photodynamic therapy. Photodynamic therapy uses a sensitive porphyrin-based drug for a treatment of tumors. Due to the high energy absorption characteristics of porphyrins, they can have a cytotoxic effect and potentially destroy the unwanted cancer tissue. In order to compatible with biological conditions, which is necessary to treat tumor tissue, porphyrin-based drugs have to be soluble in water. Therefore, many organic chemists have found ways to incorporate a water-soluble group into the drug. Once cancer cells are reached, the sensitisation drug allows the formation of singlet O₂ and as a result, the cancerous cell is oxidized and destroyed. Water-soluble porphyrin compounds were also utilized for biological intercalation of deoxyribonucleic acid (DNA) for targeted cancer cell death as well as biological imaging of both tumors and lymph nodes.²⁹⁻³⁰
The development of porphyrins with the water-soluble capability and the applications of porphyrins as light harvesters open a promising application of porphyrins in an artificial photosynthetic system, which is the ability to convert H$_2$O to molecular O$_2$ or the reduction of CO$_2$ to a fuel.

1.2 Self-Assembly of Porphyrin Nanostructures

1.2.1 Driving forces for porphyrin self-assembly

All scales of the structural organization come from self-assembly, and the formation of the nanostructure can be described as a self-assembling optimization between sub-systems using all of the available valence electrons.$^{31}$ Molecular self-assembly such as the driven or spontaneous association of molecules is the basis of many successful self-organized nano- and mesoscopic structures. All processes such as programmed self-organization, the necessary information for the self-assembly to occur, and the algorithm the process follows, must be operative via selective molecular interactions that are intrinsic to the components.$^{32}$ Thus, based on molecular recognition events, systems may be considered as programmed molecular or supramolecular complexes that generate organized species by following a well-defined plan.$^{32}$ Typically, self-assembly of organic and organic-inorganic structures takes place in solution and/or solid state via various interactions such as donor-acceptor (D-A) interactions, hydrogen bonding, $\pi$ - $\pi$ Interactions, coordination bonding, and electrostatic interactions. During the self-assembly of a porphyrin, two of the main driving forces we consider here are hydrogen bonds and $\pi$ - $\pi$ Interactions.

*Self-Organization by Hydrogen Bonds*

One of the most important driving forces for the self-assembly of porphyrins is hydrogen bonding. The nature of H-bonds still remains an active topic, which attracts considerable interests from researchers, e.g. to determine the degree of electrostatic character.$^{33-34}$ H-bonds are commonly utilized for the formation of porphyrin assemblies because of their wide range of interaction energies and directional structure. These interaction energies are controllable by changing H-bonds’ relative
orientation, number of hydrogen bonds, and position in the overall structure.\textsuperscript{35-37} For example, the cooperative dipolar interactions of hydrogen bonds in the center of protein helices is about 20 kcal mol\textsuperscript{-1}.\textsuperscript{35, 38} H-bonds can be divided into two categories, which are Intramolecular H-Bonding and Intermolecular H-Bonding.

\textit{Intramolecular H-Bonding}

In porphyrin systems, linking components or intramolecular H-bonds of a backbone can help to build the primary geometry of molecules by binding a guest,\textsuperscript{39} reversibly positioning the chromophores\textsuperscript{40} or locking the ends of a rotaxane.\textsuperscript{41} For example, a 3-component system can be formed by tuning intramolecular H-bonds in the oligoamide spacer of a Zn porphyrin dimer, which controls the molecular formation as a result, and pre-organizes the metalloporphyrin to bind the pyridyl rotaxane ends. The nanoarchitecture of the host can be reinforced through the binding of the guest.\textsuperscript{41}

\textit{Intermolecular H-Bonding}

Many H-bonding donor and acceptor groups of porphyrins have been extensively studying as components of new functional materials for many applications,\textsuperscript{42} and to investigate the fundamental photophysical properties of these systems.\textsuperscript{43} The design of various structures can be implemented by controlling the rigid H-bonding moieties and their relative orientation through the robustness of the porphyrin macrocycle. For example, H-bond groups directed on the 5,10-meso positions and along the plane of the macrocycle form a molecule with a rigid right angle structure.\textsuperscript{44-45} On the other hand, a linear morphology can be formed by placing these groups on the 5- and 15-meso positions. Furthermore, vertical structures can be afforded by directing the H-bond groups above and/or below the plane of the macrocycle. The pre-organization of supramolecular structures using H-bonds is a primary driver of the nanostructure, allowing the formation of a range of morphologies from open to closed topologies such as sheets, film, tubes, wires, rods, and even complex 3-D structures. Similar to other porphyrin systems, nonspecific or designed intermolecular interactions also are used to mediate the structure of solid-state supramolecular morphology. The formation of rigid materials can be obtained by the synergistic combination of different intermolecular interactions (for example, \(\pi\)-stacking with H-bonding and
coordination of metal ion). These self-assembled architectures can be utilized in many potential applications including, but not limited to, molecular sieves, photocatalysis, sensors, photonics, and catalysis.

**Porphyрин self-assembly by π - π Interactions**

The porphyrinoids, which are large, planar aromatic macrocycles, are useful building blocks for self-assembly by π-stacking. The interaction energy of porphyrins is approximately 5 kcal mol\(^{-1}\) per face. The π-π interactions have distinctive absorption and emission properties, which can be an edge-to-edge interaction (J-aggregates) or face-to-face interaction (H-aggregates). π-π interactions and dispersion forces in simple porphyrins and metalloporphyrins can result in a large number of crystal architectures. Conversely, amorphous materials, which are obtained from spontaneously assembly and precipitation of porphyrin molecules have been rarely studied by researchers. In order to purify hydrophobic porphyrins, a large amount of water is commonly added to the reaction solution to induced the precipitation. This host /guest process reveals that nanoscale materials can be formed through kinetically trapping the aggregates in dispersions with a stabilizing agent, e.g. a short polyethylene glycol. Nanomaterials obtained this way can be stable for over a year. However, because of variation in the media of the particles, which lead to self-organization by dispersion forces, the resultant nanoparticles can separate or further assemble into amorphous solids. For amorphous porphyrin aggregation, both J- and H-type interactions can be observed by changes in electronic spectra. The size, stability and macrocycle self-assembled properties of the nanostructures are greatly affected by the intermolecular forces between the porphyrins, the solvents, and the stabilizer. The design of programmed nano-architectures usually needs additional specific intermolecular interactions, as π-π interactions of simple porphyrins are generally not precise enough to enable fine tuning of architecture. As an example, the formation of nano-aggregates originating from π-stacking of perylene-di-carboxamides on the para position of TPP was due to the coplanarity of the perylenes with the porphyrin. The results show that the charge in the nanoparticles is delocalized. In order to obtain ordered structures, other localized interactions such as
dipolar and electrostatic interactions also need to be considered. Complex architectures using $\pi$-interactions can be achieved by a combination of electrostatic interactions, coordination chemistry, and hydrogen bonding. Based on this strategy, various self-organized structures have been fabricated, such as nanotubes, nanorods, nanowires, spherical structures such as micelles, and rings. Other architectures such as ordered 2D or 3D nanostructures-containing porphyrins are also reported.

1.2.2 Methods for self-assembly of porphyrin nanostructures

Self-assembly of porphyrin nanostructures has attracted much attention from scientists in recent years. Porphyrin nanostructures can be fabricated by various methods, such as reprecipitation, ionic self-assembly, coordination polymerization, or others.

Reprecipitation method

The reprecipitation method is the simplest and the most widely used method to produce organic nanomaterials containing one type of porphyrins. Many nanostructures of porphyrins have been prepared by using this method. In 2002, Gong and co-workers reported the preparation of hydrophilic and hydrophobic mesoarylporphyrin nanoparticles for the first time by the self-assembly in a solvent mixture of DMSO and water with the assistance of (polyethylene) glycol (PEG) as the stabilizing reagent (Figure 1.10). In a typical process, the porphyrin compound was first dissolved in DMSO, then a certain amount of the solution was mixed with a large amount of water causing the precipitation of the porphyrin aggregates, which formed nanostructures.

![Figure 1.10: The procedure of producing porphyrin nanoparticles by the solvent mixing method. Adapted from 51](image)
In 2007, Wang’s group reported preparation of porphyrin nanosheets from SnIV5-(4-pyridyl)-10,15,20-triphenylporphyrin (SnPyTriPP) by using a reprecipitation method without surfactants (Figure 1.11). The obtained square nanosheets are 0.3 to 1.0 µm in edge length and of uniform thicknesses ranging from 7 to 12 nm. The aspect ratios of the porphyrin sheets are not constant, and it can be up to 100. Different morphologies of micron cubes with hollow faces could be obtained by changing the self-assembly conditions.

![SnPyTriPP dichloride in ethanol](image)

**Figure 1.11**: The protocol of producing porphyrin nanosheets by the solvent mixing method. Adapted from

The reprecipitation method was also employed to produce porphyrin nanorods from the diaryl substituted porphyrin H$_2$DBuPP. Nanorods 5.02±1.94 µm long and 360±130 nm wide were obtained upon addition of a 3.5 mM solution of H$_2$DBuPP in toluene to acetonitrile solvent (volume ratio is 1: 9) and sonicated for 30 min at 15°C. Interestingly, fibres 27.2 ± 6.9 µm in length and 890 ± 270 nm in width could also be achieved after leaving the solution containing nanorods for 6 days and subsequently stirring for 5 min. The self-assembled porphyrin nanorods were also prepared by Gao and his colleagues by reprecipitation of the free base or zinc complex of DP(CH$_3$COSC$_5$H$_{10}$O)$_2$P. The nanorods were produced by injecting a small volume of a Zn29 solution in chloroform into methanol as shown in Figure 1.12. In the instance of H229, the nanorods (nanoribbons) can be fabricated by the introduction of a chloroform solution into n-hexane.
In some instances, surfactants were added to assist the self-assembly process. Hollow hexagonal nanoprisms were fabricated by the reprecipitation reaction of zinc meso-tetra (4-pyridyl) porphyrin (ZnT(4-Py)P) via the assistance of cetyltrimethylammonium bromide (CTAB) surfactant. The resultant nanoprism is 529 ± 12 nm long, 95 ± 3 nm wide with an aspect ratio of 5.6 (Figure 1.13). The thickness of the nanoprisms walls was approximately 30 nm. While the width of the nanoprisms remains unchanged when adjusting the CTAB concentration, their length was significantly changed. In particular, when reducing the surfactant concentration by 50%, nanoprisms were with a length up to 720 ± 15 nm and an aspect ratio of 8.0. When the surfactant concentration increased 2-fold, the length of the nanoprisms decreases to 340 ± 10 nm with an aspect ratio of only 3.5.
Lee et al. also used a surfactant to adjust the sizes and shapes of assembled porphyrin nanostructures. In this case, the ratio of an amphiphilic Sn porphyrin and a triblock copolymer Pluronic F127 as the surfactant during the reprecipitation can be used to control the aspect ratio of the porphyrin nanowires (Figure 1.14). Typically, a solution of SnDiPyP in ethanol was dropped into water at a high temperature to produce mono-dispersed crystalline square-faced rods a length of 500 nm and diameter of about 120 nm. The length of the as-produced nanowires could be controlled by using various F127 concentrations in hot water. A dependence of morphology on the Pluronic F127 concentration up to 0.5 mM was also revealed. The porphyrin nanowires were formed by the self-organization of porphyrins in the hydrophilic channels between cylindrical micelles of Pluronic F127. When surfactant concentration increases, the average length of the Pluronic F127 micelles increased. This explained why the length of nanorod increased along with the F127 concentration. Other factors such as reaction temperature, type of solvent, and the concentration of the initial porphyrin monomers also affected the nanostructures of the assembled porphyrin.
Figure 1.14: The SEM images showing the porphyrin nanowires prepared at various Pluronic concentrations. (a) 0, (b) 0.01, (c) 0.05, (d) 0.1, (e) 0.18, (f) 0.25 and (g) 0.5 mM of Pluronic F127 in water. The bottom-right panel is a plot showing the relationship between the length of the nanowires and the Pluronic concentration.

Adapted from

Ionic self-assembly method

Several research groups have utilized self-assembly using electrostatic interactions of different ionic building blocks to fabricate porphyrin-based nanomaterials. Unlike reprecipitation techniques, where a single type of porphyrin is used in the self-assembly, two porphyrins including a porphyrin cation and a porphyrin anion as the starting materials are usually involved in ionic self-assembly. In this method, the ionic interaction of the porphyrin ions plays an important role during the assembly process.

The most relevant porphyrin self-assembly of this kind was the ionic self-assembly of tetrasulfonatophenylporphyrin (H₄TPPS²⁻) in the diacid form. In 2004, Wang and co-workers reported the fabrication of porphyrin nanostructures such as porphyrin nanotubes and porphyrin nanofiber bundles prepared via ionic self-assembly. Porphyrin nanotubes can be obtained by simply mixing equal proportions of metal-free tetrakis(4-sulfonatophenyl)porphyrin (H₄TPPS²⁻) and tin meso-tetra(4-pyridyl) porphyrin (SnTPyP²⁺), in aqueous solution (Figure 1.15). The prepared nanotubes have diameters of about 50–70 nm and a length in the micrometer range. The thickness of the walls of the hollow tubes is approximately 20 nm, with a concentric layered structure.
Figure 1.15: The preparation of porphyrin nanotubes via the ionic interaction between $H_4TPPS^2-$ and SnTPyP$^{2+}$. The right panel shows the TEM image of the nanotubes. Adapted from 75

Porphyrin nanofiber bundles were obtained from mixing oxo-antimony(V) porphyrin (SbOTPP$^+$) and the divalent metal complexes or a free base porphyrin ($H_2TPPS^4-$). 76 Figure 1.16 shows the TEM images of the resulting nanofibers. This indicated that the obtained bundles of nanofibres are approximately 70–140 nm in width and 1–2 µm in length.

Figure 1.16: The preparation of porphyrin nanofiber bundles through the interaction between SbOTPP$^+$ and $H_2TPPS^4^-$. The right panel shows the TEM image of the nanofiber bundles. Adapted from 76

Interestingly, Wang’s group also reported on the assembly of porphyrins in the shape of four-leaf clovers by the ionic self-assembly of Zn$^{II}$T(N-EtOH-4-Py)P$^{4+}$ and the tin(IV) complex of TPPS$^4$ (Sn$^{IV}$TPPS$^4$) at 23°C (Figure 1.17). 77 Leaf-like, stem, and vein-like structures on the leaves can be clearly seen in the SEM image. The
cloves have a diameter of about $5 \pm 2 \, \mu m$ with elaborate nanoscale features. The clover morphology can be tuned to the temperature and other solution conditions. However, the concentrations of the porphyrins do not have a significant effect on the final morphology of clover. These clover-like morphologies are produced from equal proportions of porphyrin ions with the $(\text{Zn}^{II}\text{T(N-EtOH-4-Py)}\text{P}^+4\text{)}$ as a donor and $(\text{Sn}^{IV}(\text{OH})_2\text{TPPS}^4\text{)}$ as an acceptor. The metal incorporated into the core of the porphyrin ring and the porphyrin substituents are responsible for the donor-acceptor abilities of the porphyrins.

![Figure 1.17: The preparation of porphyrin clovers via the interaction of ZnT(N-EtOH-4-Py)P+4 and Sn(OH)-2TPPS-4. Adapted from 77](image)

**Figure 1.17:** The preparation of porphyrin clovers via the interaction of ZnT(N-EtOH-4-Py)P+4 and Sn(OH)-2TPPS-4. Adapted from 77

**Coordination polymerization method**

A peripheral substituent on porphyrin macrocycles (e.g., the pyridyl groups of T(4-Py)P), which use an exogenous metal complex or the metal ion of another porphyrin to induce polymerization, is usually utilized to form porphyrin-based coordination polymers. Although the crystal architecture of porphyrin coordination polymers has been extensively studied; 78-84 there are very few studies of porphyrin coordination polymer nanostructures in the range of 100 - 500 nm. In 2005, Sun’s group successfully synthesized nanospheres from the coordination polymerization of p-phenylenediamine and chloroplatinic acid (H$_2$PtCl$_6$) as shown in Figure 1.18. 85 The particle size and shape can be controlled by the molar ratio and reactant concentrations. The uniform nanospheres were produced at the molar ratio of 1:1 and moderate concentration.
Figure 1.18: (a) Low magnification SEM image and size distribution (inset), (b) high magnification SEM image, and (c) TEM image of the resultant particles; (d) local magnification of a single colloid. Adapted from 85

Following this work, porphyrin coordination polymer nanospheres were also obtained by the reaction of MT(4-Py)P complexes (M = SnIV, FeIII, CoIII) with chloroplatinic acid. 86 Figure 1.19 shows the SEM image of the aggregate produced from the reaction of SnT(4-Py)P and H2PtCl6. It clearly indicates that the precipitate is uniform nanospheres approximately 161.1 ± 12.8 nm in diameter. The nanospheres are stable over a wide range of pH (2–12) or in organic solvents such as dichloromethane.

Figure 1.19: Structures of the porphyrin starting materials (a) (M = SnIVCl2);(b) SEM image of SnT(4-Py)P: Pt coordination-polymer nanospheres (inset: size distribution histogram of the nanospheres). Adapted from 86
Similarly, coordination polymer nanospheres were produced by the reaction between $\text{Co}^{\text{III}}\text{T}(4\text{-Py})\text{P}$ or $\text{Fe}^{\text{III}}\text{T}(4\text{-Py})\text{P}$ with chloroplatinic acid. The obtained nanospheres with $\text{Fe}^{\text{III}}\text{T}(4\text{-Py})\text{P}$ are also uniform and about $153 \pm 9.6$ nm in diameter. This is somewhat larger than the diameter of spheres produced from the Sn complex. On the other hand, nanospheres obtained from self-assembly of $\text{Co}^{\text{III}}\text{T}(4\text{-Py})\text{P}$ were not uniform and were much smaller ($67.3 \pm 17.7$ nm) than those produced with $\text{Sn}^{\text{IV}}\text{T}(4\text{-Py})\text{P}$.

Other methods

Other self-assembly methods can be also utilized to produce porphyrin nanostructures. For example, acidification of porphyrins which have acidic groups such as sulfonic acids or carboxylic acids as peripheral substituents result in aggregation of the porphyrins in aqueous solution. In 2003, Schwab et. al. produced either single nanorod $3.8 \pm 0.3$ nm in height or bundles of nanorods by increasing the ionic strength of aqueous solutions of $\text{H}_4\text{TPPS}_4^{2-}$ as shown in Figure 1.20. The height of the single porphyrin nanorods can be well-controlled by tuning experimental conditions that affect self-assembly.

![Figure 1.20: a) Structures of the diacid ($\text{H}_4\text{TPPS}_4^{2-}$, forms of tetrakis(4-sulfonatophenyl)porphine, (b) AFM images illustrating the morphologies of $\text{H}_4\text{TPPS}_4^{2-}$ aggregates. Adapted from 62](image)

In another method, a polyethylene glycol or non-ionic surfactant can be exploited to produce porphyrin nanoparticles.51-52, 87 In 2008, Sandanayaka et al. successfully fabricated self-assembled porphyrin nanoparticles with well-controlled sizes and
shapes by EG surfactants with different chain lengths using an effective and facile method. In this method, the host solution was prepared by dissolving H$_2$TCPP in THF containing the ethylene glycol (EG) derivative, and water was the guest solution. The host and guest solution were mixed with a ration of 1:15 and the concentration of porphyrin in the final mixture was 0.05 mM. Figure 1.21 shows TEM images of the obtained aggregate. It is obvious to observe the change in the average size of the nanoparticles along with the length of the EG chain. Interestingly, the H$_2$TCPP nanorods about 50 nm in diameter and approximately 500 nm in length were formed in the absence of EG (Figure 1.21D).

Figure 1.21: (Left) Molecular structures of H$_2$P(CO$_2$H)$_4$ and ethylene glycol derivatives with different chain lengths. (Right) TEM images of (A) H$_2$P(CO$_2$H)$_4$/TriEG, (B) H$_2$P(CO$_2$H)$_4$/TetraEG, (C) H$_2$P(CO$_2$H)$_4$/HeptaEG, and (D) pristine H$_2$P(CO$_2$H)$_4$ composite assemblies: [H$_2$P(CO$_2$H)$_4$] = 0.05 mM in H$_2$O/THF (15/1, v/v). Adapted from 88

The vapor deposition method has also been used to produce porphyrin structures with nanoscale features. The vapor deposition approach was extensively employed to produce highly crystalline nanostructures of porphyrins and phthalocyanines. This method is applied to the fabrication of devices such as field effect transistors on the large scale. In this method, the porphyrin molecules are vaporized without the
presence of a solvent and then condensed on a substrate. Using this method, single-crystal rectangular porphyrin nanotubes were formed by the vapour deposition process of 5, 10, 15, 20-tetra(4-pyridyl)porphyrin (H$_2$TPyP) by Yoon’s group in 2009. In this procedure, H$_2$TPyP powder is heated to 450°C in an argon environment and placed at the end region of the furnace where the temperature is about 350°C. As a result, the rectangular nanotubes were formed on the carbon-coated Si(100) substrate. The SEM images of the rectangular nanotubes fabricated on Si (100) substrate are shown in Figure 1.22.

![Figure 1.22: Low and high-resolution SEM images of porphyrin rectangular nanotubes. Adapted from 89](image)

In another example, Zhang et al. reported single-crystalline nanoribbon aluminum oxide membranes of copper hexadecafluorophthalocyanine (F$_{16}$CuPc) and rubrene by using the vapor deposition method (Figure 1.23).
1.3 Applications of Self-Assembled Porphyrin Nanomaterials

Self-assembled porphyrin nanomaterials which have structural and functional properties are useful for many practical applications. Porphyrin nanostructures are able to be fabricated in well-organized and uniform in sizes and shapes, which is important in practical applications. Furthermore, these materials can be also further functionalized while retaining the morphology of the nanostructure (e.g., for coordination polymer nanospheres, cobalt or iron porphyrins can be substituted for the photocatalytic tin porphyrin to enable electrocatalytic activity).

1.3.1 Hydrogen production

The absorptivity of porphyrin nanomaterials is useful for efficient harvesting of light, which can be used for solar water splitting. Moreover, the high surface areas of nanoscale materials are also an important factor to increase surface photocatalytic reaction rates and efficiency. Therefore, porphyrin nanostructures are promising for this kind of application. The Pt@tin porphyrin nanohybrid obtained from mixing Pt colloids with a solution of tin porphyrin in the presence of an electron donor can be used as a catalyst to generate hydrogen from protons. When these nanomaterials were subject to visible light in the presence of ascorbic acid as an electron donor, hydrogen gas was clearly observed in the sealed reaction vessel. Later, a water-splitting nanodevice in which the porphyrin nanostructure serves as a light-harvesting antenna have also been reported by Wang et al. In this study, the author produced coordination-polymer nanospheres and used them as the light-harvesting components for hydrogen production. While platinization of the nanospheres gives a nanocomposite as the basis of the photosynthetic system, addition of anthracene-9-carboxylic acid (AA-) to a suspension of the nanospheres served as an excitation-energy transfer molecule.

Porphyrin nanomaterials may also be used as organic semiconductors to produce hydrogen. The photoconductivity of the cooperative binary ionic solis Zn–Sn clovers
was demonstrated to be promising as organic semiconductor.\textsuperscript{77, 91} For example, with the donor–acceptor Zn–Sn clover nanocomposite, in the absence of electron donors, only small amounts of H\textsubscript{2} are observed as a result of direct electron transfer from the photoexcited clovers to the Pt nanoparticles on the surface. Because of the short length of the charge-carrier diffusion, which is typically less than 20 nm in organic semiconductors, only a small amount of hydrogen is detected.

### 1.3.2 Photocatalytic applications

Porphyrin nanostructures with well-defined and controlled shape, size, and function can be obtained by the design of molecular and supramolecular structures. These structures are built due to intramolecular and intermolecular noncovalent interactions such as hydrogen bonding, van der Waals forces, π–π stacking, and electrostatic interactions. Porphyrin-based nanomaterials have been extensively studied for visible-light photocatalysis.\textsuperscript{55, 92–94} In 2012, Guo \textit{et al.} successfully fabricated zinc-tetra (4-pyridyl) porphyrin (ZnTPyP) nanostructures by using the reprecipitation method with the assistance of a surfactant.\textsuperscript{93} The obtained ZnTPyP nanostructure shows the effects of morphology on photocatalytic behavior. In another study, 1D ZnTPyP fibers showed higher photocatalytic efficiency towards degradation of rhodamine B (RhB) pollutants than ZnTPyP nanoparticles. Different morphologies of porphyrin nanostructures such as rods, spheres, flakes and flowers can be also obtained by the assembly of \textit{meso}-tetra (4-carboxyphenyl) porphyrin with control of the stirring time during the acid-base neutralization process.\textsuperscript{95} The degradation rates of RhB of the sphere-, rod-, flake- and flower-shaped TCPP nanomaterials were calculated to be 56\%, 81\%, 79\% and 71\%, respectively. Similarly, tin porphyrin can be self-assembled into various hierarchically-structured nanocrystals, which show high activity for photodegrading MO.\textsuperscript{96} Another example was also proposed by Chen’s group who fabricated 1D organic single-crystal p/n nano-heterojunctions by using a one-step physical vapor deposition (PVD) method of tetraphenyl porphyrin (H\textsubscript{2}TPP, p-type) and N,N-(dicyclohexyl) perylene-3,4,9,10-tetracarboxylic diimide (CH-PTCDI, n-type) for photocatalytic degradation.\textsuperscript{97}
1.3.3 Chemical sensors

Many works have been reported for sensing using assembled porphyrin nanomaterials. It has been shown that nanotubes are suitable for sensing applications as the three-dimensional structure can incorporate different guests inside the cavity, or the induced modification of the skeletal interaction after analyte binding. For example, Dini et al. used porphyrin nanotubes as an optical sensing probe for the detection of chemical analytes\(^9\). The J-aggregate structure of the nanotubes may be changed when interacting with analytes, significantly affecting optical properties. Initial work focused on studies of optical absorption when chemical analytes interact with the nanotubes. In order to carry out these measurements, the nanotubes were commonly dispersed into a polymer (polydimethylsiloxane disterate) matrix by direct deposition of a layer of the porphyrin nanotubes in a film, resulting in an excessive optical density. Absorption spectra of the polymer-dispersed nanotubes showed a J-type aggregate band characteristic. Several analytes such as acetic acid, triethylamine, toluene, ethanol, and NOx were investigated.

1.3.4 Carbon Dioxide Reduction

Besides hydrogen production, sensing, and photocatalytical applications, self-organized porphyrin nanomaterials can also be employed for the reduction of carbon dioxide and used for carbon-based liquid fuel production. For example, numerous studies on the self-assembly of cobalt porphyrin nanomaterials can be used catalysts for the electrochemical reduction of CO\(_2\) to CO.\(^{99-101}\) The carbon monoxide produced from this process can be utilized as a feedstock for the production of carbon-based liquid fuels through syngas reactions. Ryba’s group confirmed that cobalt porphyrins can be coated onto electrodes and used for the electrocatalytic reduction of CO\(_2\) to CO under aqueous conditions.\(^{102}\) Recently, by employing quantum chemical studies, the mechanism of the electrochemical reduction of carbon dioxide using the Co porphyrin as an electrocatalyst was also confirmed.\(^{103}\)

1.3.5 Electrocatalysts for fuel Cells

The highly reductive photocatalytic activity of porphyrins and porphyrin nanostructures can also be utilized as catalysts for fuel cells. Tin porphyrins and its
nanostructures have been using as photocatalysts for producing platinum nanostructures in the last decade. Cobalt porphyrin–platinum nanocomposites can be also used as hybrid fuel cell electrocatalysts. The electrodes modified with cobalt porphyrin have been utilized as catalyst for the reduction reaction of oxygen, which suggest the use of Co porphyrin–Pt hybrid membrane electrode for fuel cells.

1.4 Application of Graphene in Photocatalysis

Graphene is a nanomaterial that has attracted significant interest in recent years due to its potential applications in many interdisciplinary areas in physics, chemistry and engineering. Graphene possesses a range of useful properties such as thermal conductivity and mechanical stiffness, and may challenge graphite itself in its broad range of applications. The individual graphene scaffolds have excellent electronic properties which are essential for various applications such as sensors, transistors, batteries, as well as conducting polymer composites for solar cells.

This has led to many studies attempting to develop techniques to create single layer graphene. Three general routes have been employed, which include (i) mechanical peeling, (ii) epitaxial graphene growth and (iii) solution-based reduction of graphene oxide. Mechanical peeling can repeatedly produce single graphene sheets of up to 10 μm in planar size, whereas the epitaxial method produces graphene by treatment of silicon carbide wafers at high temperatures. It is important to note that these two techniques are extremely time consuming and can only produce very small amounts of graphene with the quality depending on the type of substrate employed. The third method is the solution-based approach, which has emerged as a promising route to produce large quantities of graphene. Commonly in this approach graphite oxide (GO: a product from oxidation of graphite) is used as a medium to obtain stable graphene dispersion in a solvent. Another solution based approach is the conversion of graphite to graphite intercalation compounds (GICs), in which intercalation expands graphite and lessens the adhesive forces between the constituent graphene layers, thereafter GIC’s are introduced into a liquid and upon sonication afford partially exfoliated graphite. However, both these methods suffer drawbacks. Firstly oxidation of graphite to produce GO results in diminished performance of its
excellent electrical properties and ultimately becomes an electrical insulator due to formation of a distorted sp$^3$-hybridized geometry.$^{126}$ For the GICs, the technique described previously mechanical, and not chemical, therefore the degree of delamination is very low and can often be inconsistent. The use and application of graphene is hampered by the lack of efficient processes for its mass production and there is therefore a need to develop a simple and straightforward method to produce graphene of consistent quality in high quantities.

Recently, graphene sheets have be employed as a platform for semiconductor materials to enhance the photocatalytic activity due to its large surface area, large number of adsorption sites, good charge transfer properties and band-gap energy tunability.$^{127-130}$ During the past decade, a variety of strategies have been employed to combine graphene with semiconductor photocatalysts to enhance their photocatalytic performance.$^{127, 131-134}$ For example, Kamat et al. successfully fabricated GO–TiO$_2$ nanocrystalline composites by sonicating dispersed TiO$_2$ nanoparticles and GO in ethanol, and demonstrated the feasibility of using graphene as an electron-transfer medium in the graphene/TiO$_2$ composite photocatalysts.$^{131-132}$

Graphene can be also intergrated with porphyrin nanoassemblies for photocatalysis applications. For example, Chen et al. employed vacuum filtration methods to integrate porphyrin nanoparticles into reduced graphene oxide (rGO) for use in photocatalysis (Figure 1.24).$^{135}$
Figure 1.24: TEM images of p-THPP NPs (A) and rGO sheets (B), and insets are the corresponding electron diffractions. Low (C) and high resolution (D) TEM images of the p-THPP/rGO nanohybrid. Adapted from\textsuperscript{86}

Visible-light photocatalytic activity of one-dimensional porphyrin nanoassemblies assisted \textit{via} graphene oxide has also successfully been investigated by Guo \textit{et al} (Figure 1.25).\textsuperscript{136}

Figure 1.25: (A) Molecular structure of ZnTPyP and (B) GO. (C) Illustration for self-assembly of GO-based porphyrin into 1D supramolecular nanostructure. Adapted from\textsuperscript{87}
1.5 Photocatalysis of TiO$_2$

There are three forms of TiO$_2$ in nature: brookite, anatase and rutile. Anatase and rutile have been widely demonstrated to be the most effective photocatalysts, with anatase showing a higher photocatalytic efficiency over rutile. Generally, TiO$_2$ consists of either pure anatase or a mixture of both rutile and anatase. The photocatalytic activity of TiO$_2$ depends on both the particle size and the crystalline form. Rutile can be obtained by heating anatase and brookite.

Two major challenges, which can limit the application of TiO$_2$ in practical photocatalysis are:

- The immobilisation of TiO$_2$ such that the material can be easily removed and recycled. Many immobilisation substrates have been employed including, but not limited to carbon-based materials (graphene, CNT), metal-organic framework, aerogel…

- The development of visible light sensitised photocatalytic activity for TiO$_2$. Currently, UV light is required for TiO$_2$ to be active as a photocatalyst, which heightens the cost of the process significantly. Achieving visible light sensitised photocatalysts can be done in many ways such as doping with metals, or coating with dyes. Overcoming these drawbacks is the present focus of research in TiO$_2$ photocatalysis.

In recent years, TiO$_2$ has been shown capable of harvesting visible/solar light by coating with visible light sensitised materials. Many works have been reported for the sensitisation of TiO$_2$ with various conjugated conducting polymers. Depending on the number of units, the absorbance of these polymers can be further red shifted, and modification of TiO$_2$ by these polymers allows sensitisation by visible light. These polymer modified TiO$_2$ materials show considerable promise in photo voltaic cells. For example, Qui et al., Xu et al. and Liao et al. (opal crystal-polymer hybrid) have shown its potential for photocatalytic degradation of textile dyes and phenol. Other sensitising materials which have been considered are organic dyes such as methylene blue, rhodamine B, Chryosidine G and also macrocyclic sensitising...
molecules such as phthalocyanines and porphyrins.\textsuperscript{141-143} Porphyrins and phthalocyanines are well-known for their use as photosensitising molecules and their application stretches from PDT, photovoltaic cells, contrast/imaging agents, to non-linear optics.\textsuperscript{144-145} In terms of their photo-sensitising ability, generally metal phthalocyanines and metal porphyrins are employed due to their higher stability and improved photocatalytic activity over the metal free form.\textsuperscript{146} TiO\textsubscript{2} can be anchored with sensitisers via physisorption, chemisorption, and covalent binding. The resultant sensitising TiO\textsubscript{2} materials have been successfully used in photocatalytic degradation of various organic dyes, nitrophenols and chlorophenols, and lignins.\textsuperscript{146-149}

Conjugated $\pi$-electron donor-bridge-acceptor structures of TiO\textsubscript{2}/porphyrin systems have been extensively studied for various applications such as dye-sensitized solar cells,\textsuperscript{150-152} and photochemical solar cells\textsuperscript{153-154}. Recently, these dye-sensitized systems have also been considered as an alternative material for visible-light photocatalysis.\textsuperscript{155} Shabana \textit{et al.} demonstrated that self-assembled monolayers of TCPP on anatase coated-cotton fabric exhibits efficient photocatalytic activity for the degradation of methylene blue and coffee stains.\textsuperscript{151} In another study, porphyrin-sensitized TiO\textsubscript{2} was successfully studied for photocatalytic degradation of acid chrome blue K.\textsuperscript{156} However, both of these studies only investigated the visible light-sensitized property of monomeric porphyrin molecules to enable UV-activated TiO\textsubscript{2} photocatalyst having photocatalytic activity under visible light.

\subsection*{1.6 Objectives of the Present Study}

The objective of the present study is to enhance our understanding of structure/function relationships in porphyrin nanostructures and hybrids for real world applications. This will be achieved by developing several protocols to fabricate porphyrin-based nanomaterials from \textit{meso}-tetra(4-carboxyphenyl) porphyrin (TCPP). To achieve this, Cu(II) tetrakis(4-carboxyphenyl)porphyrin (CuTCPP) nanosheet metal-organic frameworks (MOF) will be fabricated on Cu substrate by reaction between tetrakis(4-carboxyphenyl)porphyrin (TCPP) solution and the copper hydroxide (Cu(OH)\textsubscript{2}) nanoneedle array at room temperature. Other types of TCPP porphyrin nanostructures such as nanobelts can also be obtained via self-assembly.
with the assistance of arginine or surfactants (CTAB). The resultant porphyrin nanomaterials will then be investigated for photocatalytic properties toward pollutant degradation under visible light irradiation. Self-assembly of porphyrins with other materials such as TiO$_2$ and graphene to enhance photocatalytic activity will be also employed. For this purpose, a TiO$_2$@TCPP nanofiber hybrid material will be fabricated by CTAB surfactant-assisted co-assembly of monomeric TCPP molecules with TiO$_2$ nanoparticles. The TiO$_2$@TCPP hybrid material will be tested for its photocatalytic performance under sunlight conditions due to synergistic photocatalytic activities of the both porphyrin aggregates in visible light and TiO$_2$ particles in UV light. In order to enhance photocatalytic performance, graphene will be employed as substrate to increase the surface area of porphyrin photocatalysts, as well as increase the efficiency of charge separation. A new method to fabricate graphene nanoplates on the industrial scale will be developed. Porphyrin nanostructures will be formed on these graphene nanoplates via self-assembly of porphyrin molecules with the assistance of surfactants such as CTAB or Arginine. Finally, the combination of porphyrin nanomaterials, TiO$_2$, and graphene will be investigated in detail. The photocatalytic performance of obtained hybrid materials will be studied, and compared to materials that do not show any synergy.

1.7 Thesis Structure

The results achieved in this thesis are divided into three main sections: (1) fabrication of TCPP nanomaterials including CuTCPP nanosheets and TCPP nanobelts; (2) synthesis of graphene@TCPP nanorods hybrid materials and its application for photocatalysis; and (3) fabrication of TiO$_2$@TCPP nanofibers and Graphene@TiO$_2$@TCPP composites.

The thesis is broken down into the following chapters:

Chapter II provides details of the work performed the synthesis of porphyrin (TCPP)-based nanostructures. This chapter is divided into two sub-chapters. Chapter II-A describes a facile synthetic protocol to grow thin films of Cu(II) tetrakis(4-carboxyphenyl)porphyrin (CuTCPP) nanosheet metal-organic frameworks (MOF) from a tetrakis(4-carboxyphenyl)porphyrin (TCPP) solution and the copper hydroxide.
(Cu(OH)$_2$) nanoneedle array formed on a Cu substrate at room temperature. **Chapter II-B** presents the arginine-induced fabrication of porphyrin (TCPP)-based supramolecular nanostructures. These self-assembled porphyrin nanostructures such as nanobelts show enhanced photocatalytic activity for the photodegradation of the pollutant Rhodamine B under simulated visible-light irradiation.

**Chapter III** presents the fabrication of graphene@TCPP hybrid materials. This chapter is split into three sub-chapters. **Chapter III-A** deals with the development of a new and efficient method of mass production of graphene nanoplatelets by chemical exfoliation from natural graphite flakes in single step using sodium persulfate and sulphuric acid at room temperature, followed by washing with dry acetone. The method described is very simple and avoids toxic reagents for the production of defect free and few-layered GNPs. Importantly, no chemical oxidation of graphite occurs when sodium persulfate/sulphuric acid is used for mass production of GNPs. **Chapter III-B** describes the fabrication of well-dispersed porphyrin nanorods on the surface of graphene nanoplates (GNPs) by surfactant-assisted self-assembly of tetrakis (4-carboxyphenyl) porphyrin (TCPP). The formation and crystallisation of GNPs-supported TCPP nanorods were successfully characterized by SEM, XRD, FTIR, UV-vis and fluorescence spectroscopy. The photocatalytic activity of the resultant hybrid materials toward the degradation of Rhodamine B is investigated. In addition, the photodegradation mechanism of RhB when using GNPs-supported TCPP nanorods catalyst is also proposed. **Chapter III-C** describes the fabrication of a graphene@porphyrin nanofibre composite via arginine-mediated self-assembly of tetrakis(4-carboxyphenyl) porphyrin (TCPP) on graphene nanoplates (GNPs). The formation and crystallisation of the graphene@porphyrin nanofibre composite was fully characterized by SEM, TEM, XRD, FTIR, UV-vis and fluorescence spectroscopy. The visible-light photocatalytic activity for the degradation of Rhodamine B (RhB) and methyl orange (MO) was studied.

**Chapter IV** deals with the fabrications of TiO$_2$@TCPP nanofiber hybrid materials by CTAB surfactant-assisted co-assembly of monomeric TCPP molecules with TiO$_2$ nanoparticles. The obtained TiO$_2$@TCPP hybrid material exhibits efficient
photocatalytic performance under sunlight conditions due to the synergistic photocatalytic activities of both porphyrin aggregates in visible light and TiO$_2$ particles in UV light. The mechanism for photocatalytic degradation is also proposed and discussed.

Chapter V presents a detailed study on the fabrication of a nanostructured graphene@TiO$_2$@porphyrin composite via surfactant-assisted self-assembly. The obtained nanostructures were fully characterized by UV-vis, fluorescence emission spectroscopy, SEM, XRD and FTIR techniques. The applications of the three component (graphene@TiO$_2$@porphyrin) based nanostructure in photocatalytic pollutant degradation Rhodamine B is reported, where TiO$_2$ and porphyrin aggregates are shown to be activated for UV and visible light respectively, resulting in a high performing composite. The possible photocatalytic mechanism of RhB degradation by graphene@TiO$_2$@porphyrins composite is discussed.

Chapter VI provides a summary of the results completed during the PhD candidature, summarises the main contributions to knowledge of the thesis suggests scope for future work.
Chapter II

This chapter described in detail of the work performed on the synthesis of porphyrin TCPP nanostructures.
Chapter II-A

Facile fabrication of Cu(II)-porphyrin MOF thin films from tetrakis(4-carboxyphenyl)porphyrin and Cu(OH)$_2$ nanoneedle array

This sub-chapter reports a facile synthetic protocol to grow thin films of Cu(II) tetrakis(4-carboxyphenyl)porphyrin (CuTCPP) metal-organic frameworks (MOF) from a tetrakis(4-carboxyphenyl)porphyrin (H$_2$TCPP) solution and a copper hydroxide (Cu(OH)$_2$) nanoneedle array formed on a Cu substrate at room temperature.
2.1 Introduction

In the last two decades, the synthesis of metal-organic frameworks (MOFs) has attracted immense attention of researchers because of their high surface area as well tunable porosity and chemical properties.\(^{157}\) These materials have exhibited a great potential for gas storage and separation, catalysis, drug delivery, fuel cells, solar cells, sensors and electronic devices.\(^{158-161}\) Until now, most of MOFs have been generally prepared in a powder form. However, thin films of highly porous MOFs are preferred in many applications in order to fully employ their outstanding properties.\(^{162-165}\) Many efforts have already been initiated for the formation of MOF thin films with a high quality.\(^{166-168}\) There exist several techniques for the deposition of MOF thin films including the direct growth from precursor solutions, the self-assembly of precursors, and the layer-by-layer growth onto a substrate.\(^{169-175}\) For example, Cu\(_3\)(BTC)\(_2\) (BTC = 1,3,5-benzenetricarboxylate, also called by HKUST-1) crystals were successfully deposited and patterned on a substrate from the precursor solutions, spatially confined by the micro-contact printing technique via in-situ crystallization.\(^{17}\)

Recently, new synthetic strategies have been applied to fabricate MOF thin films through the direct conversion from insoluble metal precursors formed on a substrate, thus providing a fast reaction and a well-controlled architecture of the precursors in the mesoscale.\(^{176-178}\) Toyao \textit{et al.} reported the formation of patterned Cu\(_3\)(BTC)\(_2\) thin films through the positioning of the insoluble Cu-based ceramic presursors on glass and polymer substrates, followed by treatments with an alcoholic H\(_3\)BTC solution at room temperature. Majano \textit{et al.}\(^{177}\) also found that Cu\(_3\)(BTC)\(_2\) MOFs synthesized by adding a slurry of Cu(OH)\(_2\) in water into an ethanolic solution of H\(_3\)BTC via dehydration process. Most recently, Okada \textit{et al.}\(^{179}\) developed a facile synthetic route for the formation of Cu\(_3\)(BTC)\(_2\) thin films on a copper substrate through the two step reactions: anodizing of surface Cu atoms into Cu(OH)\(_2\) nanotubes and then their conversion into the MOFs by the reactions between the Cu(OH)\(_2\) and H\(_3\)BTC. To the best of our knowledge, these approaches do not be employed to grow other Cu-based MOF layers except for Cu\(_3\)(BTC)\(_2\) although they have been proved to be fast, cost-effective and versatile. This is possibly due to insolubility or low solubility of other
organic ligands, which limits a transformation rate of the insoluble metal precursors to MOFs.

Herein, we have reported the growth of new Cu-based MOF thin films with using the porphyrin-derivative ligand of tetrakis(4-carboxyphenyl)porphyrin (H₂TCPP) at room temperature for the first time. As illustrated in Fig. 1, the formation of CuTCPP MOF thin films was preceded by two steps: the oxidative transformation of surface Cu into insoluble Cu(OH)₂ needles and the subsequent recrystallization of Cu(OH)₂ into CuTCPP MOFs near at a substrate surface. The latter process was interpreted by “dissolution-reprecipitation” mechanism.

**Figure 2.1:** Graphical illustration of the formation of CuTCPP MOF thin films on a copper substrate.

2.2 Materials and methods

2.2.1 Materials

Copper foil (99.99 % purity) was procured from Chem Supply. Ethanol, sodium hydroxide (NaOH), ammonium persulphate ((NH₄)₂S₂O₈), methanol
were purchased from Ajax Finechem. All chemicals were used as received. Tetrakis(4-carboxyphenyl)porphyrin (H₄TCPP) was synthesised in house.

2.2.2 Synthesis of H₂TCPP

![Synthesis scheme of 4,4′,4″,4‴-(porphyrin-5,10,15,20-tetrayl)tetrabenzoic acid](image)

**Figure 2.2: Synthesis scheme of 4,4′,4″,4‴-(porphyrin-5,10,15,20-tetrayl)tetrabenzoic acid**

**Step-1:** Synthesis of tetramethyl 4,4′,4″,4‴-(porphyrin-5,10,15,20-tetrayl)tetrabenzoate, 3.

Pyrrole 1 (1.26 mL, 18.16 mmol) and 4-carboxyester benzaldehyde 2 (3.0 g, 18.16 mmol) was heated together in propionic acid (200 mL) at 180 °C for 2 h. After 2h heating, resultant reaction mixture was kept in the refrigerator for 16 h. Methanol was added to it. Purple colour solid precipitates out was filtered and washed with plenty of methanol. Solid obtained was dried completely under vacuo to get 3 (1.6 g, 10.4%). All spectroscopic data matches with literature values.⁵¹

To a stirred suspension of 3 (0.5 g, 0.591 mmol) in THF: H₂O: EtOH (1:1:1, 9 mL) was added NaOH (0.141 g, 3.549 mmol) and KOH (0.030 g, 0.590 mmol). The resultant reaction mixture was allowed to heat at 90 °C for 16 h. Reaction completion was checked by TLC analysis. After completion, the solvent was removed on
rotavapour for complete dryness. The crude residue obtained was dissolved in water (3 mL) and neutralised (pH = 7) using 1N HCl. A solid precipitate that formed was filtered, washed with water and dried completely under vacuo to obtain 4 as a purple coloured solid (0.42 g, 90.12 %). All spectroscopic data matched with literature values.\textsuperscript{S1}

![Figure 2.5: $^1H$ NMR of 4](image)

2.2.3 Synthesis of Cu(OH)$_2$

A polycrystalline copper foil (1 x 1 cm$^2$) was degreased with acetone and ethanol by sonication in 5 minutes for each solvent, followed by washing with a solution of HCl 2M, deionized water and dried with air stream. Copper substrates were then immersed in 10 ml aqueous solution of NaOH 2M and ((NH$_4$)$_2$S$_2$O$_8$ 0.5M for 60 minutes at a temperature of 15°C. Samples were rinsed thoroughly with Ethanol and water, and then dried in a stream of N$_2$ gas. Samples were stored at ambient environment.

2.2.4 Syntheis of CuTCPP
Prepared Cu/Cu(OH)$_2$ nanoneedles array was immersed in 10 ml of saturated H$_4$TCPP solution in H$_2$O/Ethanol mixture solvents (volume ratio of H$_2$O:Ethanol is in range of from 4:6 to 6:4) for 8 hours at room temperature. The surface of the sample turned from light blue to dark purple in colour indicating the conversion from Cu(OH)$_2$ to CuTCPP. The sample was rinsed several times with deionized water and dried in a stream of N$_2$ gas prior to characterization.

**2.2.5 Characterizations**

The crystal structures and elemental composition of Cu(OH)$_2$ and CuTCPP were studied by scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) using an EDX-equipped FEI Nova NanoSEM (Hillsboro, USA). Fourier transform infrared (FTIR) was performed on a PerkinElmer D100 spectrometer in attenuated total reflectance mode. X-ray photoelectron measurements (XPS) were carried out using a K-Alpha XPS instrument using monochromatic Al as the X-Ray source. The C 1s, Cu 2p, N 1s and O 1s core level spectra were recorded with an overall resolution of 0.1 eV. The core level spectra were background corrected using Shirley algorithm and chemically distinct species were resolved using a nonlinear least squares fitting procedure. Thermal analysis was performed on the TGA instrument with furnace and microbalance from Perkin-Elmer and operating temperature from 35 - 800 °C at a heating rate of 20 °C/min. A BrukerAXS D8 Discover instruments with a general area detector diffraction system (GADDS) using Cu Kα source were utilized to obtain XRD patterns of Cu(OH)$_2$ and CuTCPP. Ultraviolet-visible (UV-vis) measurements of TCPP and CuTCPP in solution (dissoloved in dimethylformamide-DMF) and in solid state were carried out using a Cary 50 Bio spectrophotometer with a cell of 1 cm path length and The UV–visible a CRAIC 20/30 microspectrophotometer with a 150 W Xenon lamp source used a ×15 mirror lens with a numerical aperture (NA) of 0.28 and a focal distance of 35 mm, respectively. The N$_2$ specific BET surface areas and pore size of the CuTCPP MOF were measured on a Micromeritics (ASAP 2000) analyzer.
2.3 Results and Discussion

Scanning electron microscopy (SEM) analysis clearly exhibited the formation of a Cu(OH)$_2$ needle array after the first anodization process (see Fig. 2.6A and Fig. 2.7).

**Figure 2.6: SEM images of (A) Cu(OH)$_2$ nanoneedle array and (B) Cu-based porphyrin MOFs. The insets show magnified images obtained from the same samples.**

**Figure 2.7: Side-view SEM images of (A) Cu(OH)$_2$ nanoneedles array and (B) Cu-based porphyrin CuTCPP.**

The obtained Cu(OH)$_2$ needles had an average diameter of approximately 1 µm and a length of 10 - 15 µm. A light blue colour (Fig. 2.8A) of the anodized surface was changed to dark purple (Fig. 2.8B) after the chemical treatment in the H$_2$TCPP solution, suggesting the formation of a Cu-based MOF thin film. In the low resolution SEM image of the thin film (Fig. 2.6B), the resultant MOFs look like a surface morphology consisted of micron and submicron-sized particles. In the magnified inset,
however, the crystals clearly display a cubic-like crystal structure formed by the stacking of square sheets with a diameter of 1 - 2 µm and a thickness of about 30 nm, being consistent with the morphology of CuTCPP MOFs reported by Rahimi.\textsuperscript{180}

\textbf{Figure 2.8:} Optical images of (A) Cu(OH)$_2$ array nanoneedles, (B) CuTCPP MOF nanosheets

Fig. 2.9 show the EDS studies of prepared CuTCPP MOF. EDS spectra (Fig. 2.9A) obtained from CuTCPP crystals show characteristic C Kα, N Kα, O Kα and Cu Lα energy lines at 0.277, 0.392, 0.525 keV and 0.930 keV, respectively, which suggests the formation of a CuTCPP MOF. The distribution of elements constructing the MOFs is confirmed by EDS mapping images (Fig. 2.9B-F).
Figure 2.9: (A) EDS spectrum. EDS mapping of CuTCPP thin film: (B) overlapping elements distribution i.e. carbon, oxygen, copper and nitrogen. Separate element distribution of (C) C (carbon = red), (D) O (oxygen = green), (E) Cu (copper = faint blue) (F) N (nitrogen = purple).

To understand the conversion process from Cu(OH)$_2$ nanoneedles to Cu-based MOF crystals, morphologies of the samples obtained at different reaction times were investigated. Unlike the fast formation of Cu$_3$(BTC)$_2$ MOFs from the Cu(OH)$_2$ and H$_3$BTC precursors within only few minutes, the MOF growth from H$_2$TCP occurred at a much lower rate that required more than 6 h to complete the process. Fig. 2.10A shows surface nanostructures of the initial Cu(OH)$_2$ needles preferentially grown along the vertical direction. After the reaction time of 15 min, the surface of
Figure 2.10: Surface SEM image of (A) original Cu(OH)$_2$ nanoneedles and (B) - (F) time-evolved images at different reaction times of 15 min, 1 h, 3 h, 6h and 12 h, respectively.

Cu(OH)$_2$ became rough and was decorated by many small-sized debrises, indicating the dissolution of Cu(OH)$_2$ and the formation of new products in the acidic environment (Fig. 2.10B). These decorated particles seemed to grow to very thin nanosheets of Cu-mediated MOF at the 1 h reaction time as shown in Fig. 2.10C. These nanosheets grown on the Cu(OH)$_2$ surface became larger and thicker through the stacking of platelets, which resulted in the morphology change from the vertically oriented needle shape to a thin packed layer during the additional reaction time up to 12 h (Figs. 2.10D-F). The final product exhibits a uniform cubic-like morphology with a diameter of 1 – 2 µm and a thickness of ca. 500 nm. There observed no significant change in morphology during the reaction time of 12 – 24 h (see Fig. 2.11). The formation of completely different morphology suggests the MOF growth proceeds by the dissolution of Cu(OH)$_2$ to Cu$^{2+}$ ions followed by the reaction with the H$_2$TCPP ligands at near the surface for producing insoluble MOF crystals.
Figure 2.11: SEM images of CuTCPP formation after immersion of Cu(OH)$_2$ in $H_4$TCPP solution for (A) 12 hours and (B) 24 hours, which shows no significant change in morphology

Figure 2.12A shows the FTIR spectra of Cu(OH)$_2$, H$_2$TCPP and Cu-based MOF thin films. The 3564 and 3298 cm$^{-1}$ peaks of Cu(OH)$_2$ and the 3642 cm$^{-1}$ of H$_2$TCPP reflects the stretching modes of hydroxyl groups. These stretches were disappeared in the MOF sample, indicating the occurrence of dehydration reactions between Cu(OH)$_2$ and H$_2$TCPP. Furthermore, a strong C=O stretching band at 1707 cm$^{-1}$ was observed in pristine H$_2$TCPP, however, this peak almost was suppressed in the MOF sample. Two new stretches at 1620 and 1400 cm$^{-1}$ were observed instead, supporting the formation of coordination bonds between Cu$^{2+}$ ions and the carboxyl groups of H$_2$TCPP ligand. The XRD pattern of the MOF thin film is shown in Fig. 2.12B together with that of Cu(OH)$_2$. The peaks observed at 2θ = 5.55, 7.96, 9.24, 11.03, 13.24, 15.7, 18.3, 20.23, and 22.02 ° could be indexed to the TCPP-mediated Cu MOF planes of (100), (110), (001), (200), (220), (300), (002), (320) and (400), respectively. In addition, the peaks designated by asterisks indicate the existence of Cu(OH)$_2$ crystals underneath the MOF thin film. The narrow-scanned N 1s XPS spectrum of H$_2$TCPP exhibited two peaks at 400 and 398 eV for the protonated and unprotonated N atoms (=-N and –NH–) of the porphyrin ring center, respectively (Fig. 2.12C). However, the two peaks was merged to one band centered at 398.5
Figure 2.12: (A) FTIR spectra, (B) XRD patterns, (C) N 1s XPS spectra, and (D) UV-vis absorptions of the CuTCPP MOF and related samples.

eV in the spectrum of the MOF sample, indicating the coordination of Cu evenly by four N atoms of the porphyrin center, i.e., the formation of CuTCPP through the exchange reaction of Cu$^{2+}$ with the two protons located at the center of H$_2$TCPP ligand during the MOF synthesis. The Cu 2- core level XPS spectrum (Fig. 2.13) also suggests the presence of the Cu$^{2+}$ oxidation state in the centre of TCPP and in the binding with (COO-) group. Fig. 2.12D shows UV-vis spectra of H$_2$TCPP and CuTCPP MOFs in the N,N- dimethylformamide (DMF) solution. The H$_2$TCPP sample exhibits one strong absorption peak at 418 nm and four weak peaks in range of from 500 - 700 nm which was assigned to Soret and Q bands, respectively. Interestingly,
only one relatively strong Q band at 545 nm was observed in CuTCPP MOF. It can be interpreted with the symmetry change of porphyrin molecule from $D_{2h}$ to $D_{4h}$, which further supports the symmetric coordinations of Cu$^{2+}$ ions at the center of TCPP$^{2-}$ ring. Additionally, UV-vis spectra in solid state of H$_2$TCPP and CuTCPP MOF thin film is also shown in Figs. 2.14.

**Figure 2.13:** Core level of Cu 2p XPS spectrum in Cu(OH)$_2$ and CuTCPP

Thermal properties of the obtained MOF were investigated by thermogravimetric analysis. Illustrated in Fig. 2.15 are the TGA curves of pristine Cu(OH)$_2$ and CuTCPP. The TGA spectrum of Cu(OH)$_2$ shows a 18% weight loss from 150 - 200°C indicates the dehydration of Cu(OH)$_2$. In the TGA of CuTCPP, there is also a 7.5% weight loss in
Figure 2.14: The UV-vis spectra of $H_4$TCPP, CuTCPP thin film MOF and Cu(OH)$_2$ array. This also conversion of from 4 $Q$ bands in TCPP to 1 strong $Q$ band in CuTCPP, which indicates the metalation of porphyrin that induce the change in the symmetry from $D_{2h}$ to $D_{4h}$ by incorporating Cu$^{2+}$ ions in the center of TCPP.

Figure 2.15: Thermogravimetric analysis (TGA) of Cu(OH)$_2$ and CuTCPP MOFs.

the temperature range of 150 - 200$^\circ$C, which is in agreement with the above discussion concerning the remaining of Cu(OH)$_2$ in Cu-based thin film MOFs. A gradual decomposition with a loss of 30% weight is observed between 200 and 500$^\circ$C.
This can be ascribed to the loss of CuTCPP through decomposition. From the N$_2$ sorption measurement of the CuTCPP MOF, the BET surface area was found 408 m$^2$/g. The solubility of the resultant CuTCPP MOF was tested by immersing in aqueous media for 24 hours. The sample was taken out and the resulting SEM images are shown in Fig. 2.16. It can be clearly seen that there is an insignificant change in morphology of the sample before and after immersion in water. This results indicate that the CuTCPP MOF is stable in aqueous solution.

![Figure 2.16: SEM images of the obtained CuTCPP MOF before (A) and after (B) immersion in water for 24 hours.](image)

To optimize the condition of the MOF fabrication, the effect of ethanol/H$_2$O volume ratio on the formation of CuTCPP crystal was studied using SEM images (Fig. 2.17). It can be concluded that the optimized ratios of ethanol/H$_2$O to obtain a uniform thin film and homogeneous MOF crystal are from 60/40 - 40/60 regarding to the volume percentage.
Figure 2.17: Effects of volume ratio of Ethanol/Water on morphologies of CuTCPP: Ethanol/Water = (A) 100/0, (B) 80/20, (C) 60/40, (D) 40/60, (E) 20/80.

2.4 Conclusions

In conclusion, we have developed a new and facile synthetic route for growing the porphyrin-based Cu MOF thin films with a high specific surface area for the first time. Through the various material analysis techniques, the MOFs were confirmed to have Cu-centered TCPP ligands that were participated to generate the structure of binuclear Cu$_2$(COO)$_4$ paddle wheels.$^{165,180}$ This approach offers a simple and effective protocol to prepare CuTCPP-based MOF thin films at room temperature, which are a promising candidate in various applications such as sensors, catalysts and separation devices.
Chapter II-B

Arginine-induced porphyrin-based self-assembled nanostructures for photocatalytic applications under simulated sunlight irradiation

This sub-chapter investigates the arginine-induced fabrication of porphyrin (TCPP)-based supramolecular nanstructures. These self-assembled porphyrin nanostructures such as nanobelts show enhanced photocatalytic activity for the photodegradation of pollutant rhodamine B under simulated visible-light irradiation.
2.5 Introduction

The fabrication of soft nanomaterials via supramolecular self-assembly of porphyrin-based materials has been shown to be an effective protocol to design functional structures.\textsuperscript{87, 186-189} Such supramolecular nanostructure formations can be achieved via diverse self-assembly bottom-up approaches.\textsuperscript{190-192} Several non-covalent interactions such as hydrogen bonding, van der Waals interactions, aromatic $\pi$-$\pi$ stacking, and coordination bonds are involved to produce supramolecular nanostructures via self-assembly. Synthetic porphyrin derivatives that self-assemble into well-defined discrete nanostructures such as nanorods, nanotubes, nanofibre bundles, nanoprisms, nanosheets, nanospheres, nanoparticles, nanowires and nanoclovers with well-defined shape and size have been reported.\textsuperscript{193} Nanomaterials synthesized from self-assembly of porphyrins exhibit unique optical and electronic properties, with potential applications deriving from the materials obtained e.g. optical devices, sensors, photoelectronics, solar energy conversion, energy or information storage, nanocatalysts and photodynamic therapy.\textsuperscript{186, 194-202} Furthermore, porphyrins play an important role in functional biological systems such as catalysis and light-harvesting.\textsuperscript{203-207} Therefore, the fabrication of self-assembled supramolecular nanostructures from porphyrins with potential applications in photocatalysis is a research area of continued importance. Recently, self-assembled nanostructures of porphyrin have received much attention for visible-light photocatalysis reactions.\textsuperscript{92-93, 96, 135, 208} Literature searches reveal that various self-assembled nanostructures such as nanosheets, octahedral, and microspheres were also employed for visible-light photocatalytic reactions.\textsuperscript{92-93, 208} The photodegradation of the model pollutant Rhodamine B (RhB) under visible light irradiation was achieved by using self-assembled nanostructures of \textit{meso}-tetra(4-carboxyphenyl) porphyrin (TCPP).\textsuperscript{209}

In our earlier report, we have successfully fabricated well-dispersed TCPP nanorods on graphene nanoplates by CTAB-assisted self-assembly, which could be an efficient catalyst for photocatalytic degradation of RhB.\textsuperscript{210} In continuation
of our efforts to this end, herein we report our new findings, that TCPP in presence of L-/D-arginine forms one-dimensional, self-assembled supramolecular nanobelts with well-defined morphology. Under visible light, these nanobelts display good photocatalytic activity for the photodegradation of RhB. Our results imply that the nanobelts obtained by two component assemblies may provide new opportunities for photocatalysis reactions based on supramolecular self-assembled nanomaterials.

2.6 Materials and Methods

Materials

All chemicals were used as received without any further purification. L-/ D-arginine were obtained from Sigma Aldrich (Bengaluru, Karnataka, India). Chemicals such as dry acetone, propionic acid, dichloromethane, chloroform, sodium hydroxide (NaOH), potassium hydroxide (KOH) and ethanol were purchased from Ajax Finechem. Australia.

H₂TCPP supramolecular nanostructures via arginine-induced self-assembly

First, 8 mg of TCPP was dissolved in 1 mL of 0.2 M NaOH solution. This is assigned as the guest solution. The host solution was prepared by dissolving L-/D-arginine with various concentrations in 20 mL of 0.01 M HCl solution. Subsequently, the guest solution was added dropwise into the host solution under stirring at room temperature in the dark for 1 hour. The obtained green aggregates were, then, filtered and dried for further characterizations.

Photocatalytic Investigation

Photocatalytic performance of the porphyrin nanobelt was evaluated by the degradation of RhB in aqueous solution. In a typical photodegradation measurement, 0.1 mg of hybrid material was dispersed in a 20 mL aqueous solution of RhB dye with a concentration of 5 mg L⁻¹. The dispersion was stirred in the dark for 30 minutes to establish an adsorption/desorption equilibrium before irradiation. The sunlight source for the photocatalytic reaction was a 1500 W air cooled Xenon lamp. At appointed times, 1.5 mL of dispersion aliquots were taken out and centrifuged to remove...
photocatalyst. The photocatalytic performance of the as-fabricated samples for RhB degradation was evaluated by recording the real-time absorptivity of RhB at a wavelength of 553 nm.

**Characterizations**

*UV-Vis Spectrophotometer*

Ultraviolet-visible (UV-vis) absorption measurements of samples in solution and in solid state were carried out using a Cary 50 Bio spectrophotometer with a cell of 1 cm path length.

Furthermore, UV-vis absorption measurements were also employed to record the photocatalytic performance for Rhodamine B degradation.

*Fluorescence Spectrofluorophotometer*

Horiba JobinYvonFluroMax®-4 Spectrofluorometer was used to record fluorescence emission spectra of TCPP titration with L-/D-arginine. All experiments were performed in a quartz cell with a 1 cm path length upon excitation at 420 nm wavelength.

*Scanning Electron Microscope*

The supramolecular self-assembled nanostructure morphology of TCPP in presence of L-/D-arginine were studied by scanning electron microscopy (SEM) using an FEI Verios 460L (operating under HV and Stage bias condition of 1 KeV, using stage bias and Circular Backscatter Detector for low conductive samples).

*Transmission Electron Microscope*

TEM samples were prepared and measured by paper blotting method followed by solvent evaporation on a holey carbon coated copper grid. The micrographs were investigated using a Jole 1010 100 kV transmission electron microscope.

*XRD Measurements*

A BrukerAXS D8 Discover instrument with a general area detector diffraction system (GADDS) using a Cu Kα source was utilized to obtain XRD patterns of TCPP nanobelts.
2.7 Results and Discussion

UV-vis absorption spectroscopy was employed to investigate the optical properties of the sample (Fig. 2.18a). Absorption spectra of the TCPP molecule showed a strong Soret band at 416 nm due to \( \pi-\pi^* \) transition and four Q bands in the range of 500 to 700 nm. Upon addition of D-arginine, the characteristic Soret band intensity reduced and a loss of fine structure was observed which broadened with the addition of 7 to 9.5 equiv. of arginine, indicating the formation of a supramolecular assembly due to arginine addition. The fluorescence emission properties of the TCPP molecules were measured upon excitation of the solution at 400 nm. Two characteristic emission peaks at 655 nm and 714 nm were observed (Fig. 2.18b). With the addition of D-arginine the emission peaks at 655 nm and 714 nm merged to form a broad peak at 680 nm. Upon incremental addition of arginine, the peak at 680 nm blue-shifted, and fluorescence emission is quenched completely at 9.5 equiv. of arginine. These blue shifts and broadening in the emission peaks are attributed to the self-assembly of TCPP into aggregates in the presence of arginine.

The UV-vis and fluorescence spectroscopy result clearly shows that the self-assembly of phrphyrin with arginine is via face-to-face \( \pi-\pi \) stacking of the
porphyrin core along with electrostatic attraction between the carboxylic group of the porphyrin and the \(-\text{NH}_3^+\) group of the arginine moieties. The assembly of TCPP in the presence of D-arginine was carried out using an aqueous medium. Field emission scanning electron microscopy (FE-SEM) was used to characterise self-assembled nanostructures. SEM images of structures obtained from the solutions are as shown in Fig. 2.19A-B and Fig. 2.20. The SEM image reveals self-assembled in several micrometres in length with diameters of about 20-30 nm have been produced. Similarly, belt-like morphology of TCPP was also observed in the presence of L-arginine (Fig. 2.21). These results clearly suggest that self-assembled nanobelt morphology could be directly fabricated by adding either D- or L-arginine to TCPP solutions.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure2.19.pdf}
\caption{Scanning electron micrographs of TCPP microstructures showing belt-like morphology in the presence of D-arginine: (A) low resolution and (B) high resolution.}
\end{figure}
resolution images, respectively.

Figure 2.20: SEM images of D-arginine assisted TCPP nanobelts.

![SEM images of D-arginine assisted TCPP nanobelts](image)

Figure 2.21: SEM images of L-arginine assisted TCPP nanobelts.

![SEM images of L-arginine assisted TCPP nanobelts](image)

To gain further insight into the nanostructure of TCPP in presence of D- or L-arginine, TEM spectra were collected as shown in Fig. 2.22 A,B and Fig.2.23 A,B, respectively. TEM images clearly support formation of TCPP nanobelts of several micrometres in length in the presence of D-arginine (Fig. 2.23D) as well as similar nanobelt of TCPP was also observed with L-arginine (Fig. 2.23B). The consistency in FESEM and TEM images confirms the well-ordered structures i.e. nanobelts.
Figure 2.22: TEM images of D-arginine induced nanobelt morphology of TCPP nano aggregates.

Figure 2.23: TEM images of TCPP nano aggregates assembled with L-arginine (A and B) and D-arginine (C and D)
The crystal structure of TCPP within the nanostructure in presence of D-arginine was further characterized by X-ray diffraction (XRD) to characterise the self-assembly (Fig. 2.24). The XRD spectrum reveals that the diffraction peaks are not observed for TCPP monomers, which implies that monomeric TCPP molecule is non-crystalline in nature. The XRD data of self-assembled TCPP in presence of D-arginine contain two intense, sharp peaks at approximately 31° and 45°. These peaks are attributed to the crystalline structure of TCPP in its aggregated nanobelts, indicating that π-π stacking and electrostatic interactions lead to the formation of well-ordered nanobelts of the TCPP molecules in the presence of arginine.

![XRD Spectrum](image)

**Figure 2.24:** XRD of D-arginine induced morphology of TCPP aggregates.

Furthermore, we investigated the photocatalytic degradation of the pollutant RhB under visible-light using our supramolecular self-assembled TCPP-arginine nanobelts. At first, photodegradation of RhB was carried out without catalyst (black curve in Fig. 2.25). It is obvious that without a catalyst, negligible RhB degradation could be observed, suggesting that the self-sensitized photodegradation of RhB does not occur readily under these
conditions. When TCPP monomers are used as a photocatalyst, a decrease in RhB concentration of only about approximately 15% was observed after 3 hours. However the photocatalytic performance increases significantly when the TCPP nanobelts obtained from self-assembly of monomeric TCPP in addition of L- and D-Arginine are used, and RhB degradation reaches about 80% and 90%, respectively. This indicated that the free standing TCPP nanobelts have a high photocatalytic activity under visible irradiation.

![Figure 2.25](image)

**Figure 2.25:** Photocatalytic activity of D-arginine induced morphology of TCPP nano aggregates: (a) the black curve is controlled reaction (no catalyst); (b) red is molecular TCPP; (c) the green curve is assembled TCPP with L-arginine and (d) blue curve is assembled TCPP with D-arginine.

The reason for the higher photocatalytic activity of the TCPP nanobelts compared to amorphous TCPP was ascribed to porphyrin aggregates, which have a molecular structure that is comparable to photoactive molecules such as chlorophyll in many biological energy transduction processes in plants and algae, where arrays arranged in such a way that the charge separation is better as compare to chlorophyll monomer.\textsuperscript{211-212} It has been well demonstrated that
for the J-type assembly of π-conjugated organic dyes, that electronic delocalization spans over the aggregated molecules as a result of the strong intermolecular π–π interactions,93, 213 which gives J-aggregated porphyrins photosemiconductor properties. Thus, J-type porphyrin assemblies can serve as organic semiconductors, which can harvest light, especially in the visible range, to generate electron-hole pairs under irradiation.61-63 It also is known that porphyrin aggregates may increase charge separation due to exciton-coupled charge transfer processes in J-type porphyrin nanobelts.214-215 Based on the well-documented understanding and above discussions, we propose a possible mechanism for the enhanced photocatalytic activity of the TCPP nanobelts hybrid material as shown in Fig. 2.26. When the TCPP nanobelts are irradiated

![Figure 2.26: The possible mechanism of TCPP nanobelts photocatalyst for Rhodamine B degradation.](image)

under sunlight conditions, TCPP nanobelts absorb photon energy from visible light to generate e-/h+ pairs, by electrons jumping from the valence band (VB) to the conduction band (CB).216 The generated electrons reduce the oxygen in H2O to ‘O2’ and RhB molecules are oxidatively degraded on the surfaces of the TCPP nanobelts by the holes generated from sunlight illumination of the TCPP nanobelts material.
2.8 Conclusion

In summary, we have successfully fabricated porphyrin nanobelts by the self-assembly of monomeric TCPP with arginine. The obtained nanobelts show well-defined and ordered structure with a diameter of about 30 nm and a length of several micrometres. TCPP nanobelts exhibit efficient photocatalytic performance under sunlight conditions with a maximum RhB degradation up to 90% after 3h. This work will certainly contribute more insight into the fabrication of organic semiconducting materials by a simple method of self-assembly. The obtained nanobelts are a promising class of new materials, easily fabricated under mild conditions that are promising candidates for applications in environmental catalysis.
Chapter III

This chapter presents the fabrication of graphene@TCPP hybrid materials. This chapter is split into three sub-chapters i.e. III-A, III-B and III-C, respectively. In which, chapter III-A proposes a new approach for mass production of graphene nanoplates, chapter III-B studies the fabrication of graphene@TCPP hybrid materials via CTAB-assisted self-assembly, and chapter III-C reveals arginine-mediated self-assembly of porphyrin on graphene. The photocatalytic performance of the resulting hybrid materials are also discussed in this chapter.
Chapter III-A

Improved and a simple approach for mass production of graphene nanoplatelets material

This sub-chapter describe mass production of graphene nanoplatelets (GNPs) by exfoliation of natural graphite flakes in a single step using sodium persulfate and sulphuric acid at room temperature followed by washing with dry acetone. The produced GNPs (~100%) are tens of microns in diameter with thickness are about 10-20 nm. We have also evaluated role of water for exfoliation of graphite. The formed GNPs were confirmed by SEM, TEM, AFM microscopy.
3.1 Introduction

Graphene is a nanomaterial has attracted significant interest in recent years due to its potential applications in many interdisciplinary areas in physics, chemistry and engineering.\textsuperscript{107-112} Graphene possesses a range of useful properties such as thermal conductivity and mechanical stiffness and may challenge graphite itself in its broad range of applications. The individual graphene scaffolds have excellent electronic properties which are essential for various applications such as sensors, transistors, batteries, as well as conducting polymer composites for solar cells.\textsuperscript{113,114}

This has led to many studies attempting to develop techniques to create single layer graphene. Three general routes have been employed, which include (i) mechanical peeling, (ii) epitaxial graphene growth and (iii) solution-based reduction of graphene oxide. Mechanical peeling can repeatedly produce single graphene sheets of up to 10 $\mu$m in planar size, whereas the epitaxial method produces graphene by treatment of silicon carbide wafers at high temperature.\textsuperscript{115-116} It is important to note that these two techniques are extremely time consuming and can only produce very small amounts of graphene with the quality depending on the type of substrate employed. The third method is the solution-based approach, which has emerged as a promising route to produce large quantities of graphene.\textsuperscript{117-119} Commonly in this approach graphite oxide (GO: a product from oxidation of graphite) is used as a medium to obtain stable graphene dispersion in a solvent.\textsuperscript{120} Another solution based approach is the conversion of graphite to graphite intercalation compounds (GICs), in which intercalation expands graphite and lessens the adhesive forces between the constituent graphene layers, thereafter, GIC’s are introduced into a liquid and upon sonication afford partialy exfoliated graphite.\textsuperscript{121-125} However, both these methods suffer drawbacks. Firstly oxidation of graphite to produce GO results in diminished performance of its excellent electrical properties and ultimately becomes an electrical insulator due to formation of distorted sp\textsuperscript{3}-hybridized geometry.\textsuperscript{126} For the GIC’s technique describe previously is mechanical one, not chemical, therefore the degree of delamination is very low and can often be inconsistent. The use and application of graphene is hampered by the lack of efficient process for its mass production and there
is therefore a need to develop a simple and straightforward method to produce graphene of consistent quality, in sufficient quantity.

Here, we describe a simple technique for synthesis of graphene nanoplatelets (GNPs) and few-layer graphene ($G_{\text{few-layer}}$) in quantitative yield with the flakes being about tens of microns in size. Typically, 1 g of natural graphite flakes (from PressolGmbH, with particles size > 100 mesh) was dispersed in 80 mL of sulphuric acid (98%) thereafter 6 g of sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$) was added and reaction mixture gently stirred for 3 h at room temperature, followed by direct filtration, washing with dry acetone (3x10 mL), followed by Milli-Q water (5 mL) and dried at 60 °C in open air gave a quantitative yield of GNPs (Fig. 3.1).

![Synthetic route of the graphene nanoplatelets from graphite.](image)

**Figure 3.1:** Synthetic route of the graphene nanoplatelets from graphite.

This method avoids the use of expensive, toxic oleum,\textsuperscript{217} avoids conversion of graphene back to graphite,\textsuperscript{218} and uses of a simple stirring method (saves two thirds of the time required in the conventional method). Furthermore, the filtrated solution containing $\text{H}_2\text{SO}_4$ and $\text{Na}_2\text{S}_2\text{O}_8$ could possibly be reused for the graphite exfoliation, allowing for a more “green” approach. The method developed in this study a simple, efficient and is faster than conventional method\textsuperscript{23} for production of mass GNPs from natural graphite as illustrated in Figure 3.2.
Chapter III

3.2 Experimental Section

**Materials:** All following chemicals were used as received without any further purification. Natural graphite flakes was supplied from Pressol Gmbh, with particles size > 100 mesh. Chemicals such as dry acetone, concentrated acid sulphuric (98%), ethanol and sodium persulphate (Na$_2$S$_2$O$_8$) were purchased from Ajax Finechem.

**Detailed procedure for fabricating graphene nanoplates:** Typically, 1 g of natural graphite flakes was dispersed in 80mL of sulphuric acid 98% with swirling for 10 minutes in a 250 mL reactor. Thereafter 6g of sodium persulfate (Na$_2$S$_2$O$_8$) was gradually added and reaction mixture gently stirred for 3h at room temperature. The mixture, then, was filtrated directly by a glass sintered filter (Duran® sintered with disc filter funnel capacity 50 mL, max pore size 4-5 μm) without quenching. The filtrated solution was separated and use for next graphite exfoliation. GNP's was rinsed with dry acetone (3x10 mL), followed by 5 mL water to remove any residual acid in the GNP's, and dried at 60°C in open air. The product was then weight for yield evaluation of process. Then 2 mg of obtained GNP's was dispersed in 100 ml ethanol

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**Figure 3.2:** Comparision of the standard method (obtained from Journal of Life Cycle Assessment 2014 19, 1226) and method described in this work.
by sonication for 10 minutes and dropped on the Si wafer for SEM and EDS, on the carbon membrane-coated copper grid for TEM characterization. The dry GNPs powder was used for other characterizations.

**Characterization:** The crystal structures and elemental compositions of GNPs obtained from exfoliation of graphite flakes were characterized by scanning electron microscopy (SEM) images and energies dispersive X-ray (EDX) spectra using an EDX-equipped FEI Nova NanoSEM (Hillsboro, USA). TEM images were obtained on a JEOL 1010 TEM instrument operated at an accelerating voltage of 100 kV. Thermal analysis was performed on the TGA instrument with furnace and microbalance from Perkin-Elmer and operating temperature from 35 - 800 °C at a heating rate of 20 °C/min Fourier transform infrared (FTIR) measurements were performed on a PerkinElmer D100 spectrometer in attenuated total reflectance mode. Raman spectra were obtained by using PerkinElmer Raman Station 200F. A BrukerAXS D8 Discover instruments with a general area detector diffraction system (GADDS) using Cu Kα source were utilized to obtain XRD patterns of CuTCNQF₄. X-ray Photonelectron spectra (XPS) were obtained from a K-Alpha XPS instrument using a monochromated Aluminium as the X-Ray source. Thickness of nanoplates was investigated by using a AFM (Bruker Multimode 8 with PF TUNA).

### 3.3 Results and Discussion

The formation of GNPs was confirmed by scanning electron microscopy (SEM) as shown in Figure 3.3. Figure 3.3A shows the typical nature of graphite flakes with a thick lateral structure. However, GNPs retained their expanded exfoliated states confirmed by SEM imaging (Fig. 3B and 3C). The low-magnification image (Fig. 3.3B) of GNPs shows a very consistent crumpled and wrinkled morphology with lateral size of 10-50 µm, which indicate that the GNPs only contain a few graphene layers in each stack, such morphology has also been reported by Müllen group. The high-magnification image of GNPs shows semitransparency to the electron beam, which clearly show GNPs with less than 10-40 layers in the stack (Fig. 3.3C). The thermogravimetric analysis (TGA) data is shown in Fig. 3.3D, and typically the GNPs exhibit a 2.3% weight loss in the 120-230 °C temperature interval and this
weight loss is typical for graphene oxide and attributed to decomposition of some oxygen functionalities along with the loss of trapped water. The weight loss of about 2\% after 230 °C is attributed to the loss of intercalated H\textsubscript{2}SO\textsubscript{4}, Na\textsuperscript{+}, S\textsubscript{2}O\textsubscript{8}\textsuperscript{2-} within the GNPs.

**Figure 3.3:** SEM images of (A) natural graphite flakes, (B) and (C) GNPs and G\textsubscript{few-layer}, and (D) TGA of GNPs at 20 °C min\textsuperscript{-1} in air atmosphere.

Figure 3.4 and 3.5 shows a AFM images of the GNPs. The average height and thickness ratio of GNPs gained from AFM image is ~ 18 nm, which is about 36 GNPs as shown in Figure 3. The GNPs synthesised are not uniformly flat due to their wrinkled morphology. This therefore leads to the top graphene layers “jumping” out of Si wafer surface.\textsuperscript{217}

The X-ray-diffraction (XRD) analysis of GNPs only shows a broad peak at about 26.5° (Fig. 3.6A and Fig. 3.7). The broad peak as compared to graphite (sharp peak observed for graphite) between 25-28° 2\(\theta\) angle areas indicative of a less orderly structure, which is consistent with SEM image. The XRD comparison clearly shows that 002 diffraction signals of the GNPs are significantly broader and weaker
compared to that of graphite flakes (Fig. 3.6A). These results clearly indicate that although GNPs hold multilayered flakes the ordered interlayer structure, the

Figure 3.4: Topographic AFM image of graphene nanoplatelets and the height profile taken across the white line on the AFM image.

Figure 3.5: (A) Topographic tapping mode AFM scans of Graphene nanoplates: (A) and (B) 2D images; (C) 3D images
constituent graphene layers as seen in graphite, no longer exists. The morphology of GNPs was further confirmed by transmission electron microscopy (TEM) analysis. TEM images clearly show that the formed GNPs have a wrinkled structure with corrugation and scrolling which is typical to graphene (Fig. 3.6B and 3.8). The semitransparency of GNPs observed in TEM images also confirms that the GNPs comprise very few layers of graphene, overlaid side by side.

**Figure 3.6:** (A) XRD spectrum of graphite flakes (Black) and graphene nanoplatelets (Red); (B) TEM image of GNPs; and XPS spectra of GNPs: (C) survey scan and (D) C 1s.

Furthermore, the quality of the as-fabricated GNPs was confirmed by X-ray photoelectron spectroscopy (XPS) as shown in Fig. 3.6C. A survey scan of GNPs, confirms the appearance of Na⁺, Sulfur and O trapped between GNPs layers with 86% of Carbon, 13% of Oxygen, 0.7 % of Sulfur and 0.3 % of Sodium. This atomic ratio is in good agreement with EDS data with atomic percentage of C and O are 89% and 11% respectively. The C 1s spectrum (Fig. 3.6D) shows only one peak of binding
energy at 284.5 eV, which corresponds to C-C bonds indicating the final product is pure GNPs. The absence of peaks at 285.5 eV or 286.6 eV indicates that there is no oxidized carbon species existed in obtained Graphene NPs.
In an earlier report by the Tour group\textsuperscript{218}, they suggested that water has an influence in exfoliating graphite when ammonium persulfate/sulphuric acid (98\%) intercalation compounds were used. With this method they observed that the formation of graphite intercalation compounds is reversible upon washing with water. In another report they have also suggested that use of oleum as a dehydrating agent within the reaction would overcome this issue and increase the yield of GNPs to near quantitative.\textsuperscript{217} From these two reports it is clear that water plays a significant role in exfoliation of graphite flakes.

We therefore investigated the effects of varied water content in H\textsubscript{2}SO\textsubscript{4} for the exfoliation of graphite as shown in Figure 3.9 (A-E). SEM and optical images (glass vial) exhibit a slight expansion of graphite flakes when >2\% H\textsubscript{2}O content in H\textsubscript{2}SO\textsubscript{4} is used. However, the graphitic structures are similar for GNPs obtained from H\textsubscript{2}SO\textsubscript{4} of both 98\% and 100\% (Fig. 3.9D and 3.9E). Figure 3.9F displays the TEM image of few layers GNPs obtained from 100\% H\textsubscript{2}SO\textsubscript{4}, which is similar to GNPs obtained from

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure3_9.png}
\caption{SEM image of GNPs obtained from exfoliation of graphite flakes with different concentration of H\textsubscript{2}SO\textsubscript{4}: (A) 80\%, (B) 90\%, (C) 95\%, (D) 98\%, (E) 100\% (H\textsubscript{2}SO\textsubscript{4} 98\% + oleum 65\% SO\textsubscript{3} free), and (F) TEM image of graphene nanoplatelets synthesized from H\textsubscript{2}SO\textsubscript{4} 100\%.
}
\end{figure}
H₂SO₄ 98% (Fig. 3.9A and 3.9C). Although water appears to have an effect on the exfoliation of graphite, the reverse reaction does not occur when sodium persulfate is used as an intercalator.²¹⁷, ²²² This phenomenon can be explained by the participant ion in intercalation²²³ and subsequently exfoliation of graphite flakes overcoming the Na⁺ hydrophobic force of 2% H₂O, the main factor preventing exfoliation when ammonium persulfate was used.²¹⁷ From this experiment, we concluded that there is no need to use expensive and toxic oleum for exfoliation of graphite (see Fig. 3.10). It is important to note that after exfoliation washing with water should be avoided otherwise shrinking/aggregated graphene will be produced (see Fig. 3.11).²¹

**Figure 3.10:** SEM and optical images of Graphene nanoplates obtained from H₂SO₄ 98% with (A) NH₄S₂O₈ and (B) Na₂S₂O₈

**Figure 3.11:** SEM and optical images of Graphene nanoplates obtained from chemical exfoliation in H₂SO₄ 98% and Na₂S₂O₈ with (A) quenching and wash with water; (B) without quenching following with acetone and water wash
3.4 Conclusion

In conclusion, we have developed a new and efficient method of mass production of graphene nanoplatelets with later size of ~10-20 nm thick. The method described is very simple and avoids toxic reagents for the production of defect free and few-layered GNPs. Importantly, no chemical oxidation of graphite occurs when sodium persulfate/sulphuric acid is used for mass production of GNPs.
Chapter III-B

Well-Dispersed Assembled Porphyrin Nanorods on Graphene for Enhanced Photocatalytic Performance

This sub-chapter reports a facile synthetic protocol for the fabrication of well-dispersed porphyrin nanorods on the surface of graphene nanoplates (GNPs) by surfactant-assisted self assembly of tetrakis (4-carboxyphenyl) porphyrin (TCPP). The formation and crystallisation of GNPs-supported TCPP nanorods were successfully characterized by SEM, XRD, FTIR, UV-Vis and fluorescence spectroscopy.
3. 5 Introduction

Organic based supramolecular nanoassemblies are a powerful method for the fabrication of nanostructure materials with tunable morphologies. The resulting materials have unique optical and electronic properties, which can be used for potential applications including, but not limited to, optoelectronic nanodevices, energy storage, catalysis, sensors and photonics. Among numerous organic-based supramolecular nanoassemblies, \( \pi \)-conjugated porphyrins have been attracting great attention as organic building blocks for the construction of solid-state soft materials. Various assembly protocols have been successfully employed to form nanostructured porphyrins, including ionic self-assembly, surfactant-assisted self assembly (SAS), reprecipitation, etc. Owning to the unique planar geometry, well-understood Soret-band in visible region and the inherent capability to mimic biological processes, porphyrin assemblies have many potential applications such as photoelectronics, optical devices, sensors, solar energy conversion. Most recently, self-assembled porphyrin nanostructures have been extensively reported for visible-light photocatalysis. Mandal et al. fabricated different morphologies of assembled structures (spherical, rods, flakes, and flowers) of meso-tetra(4-carboxyphenyl) porphyrin (TCPP) and used them for the photodegradation of pollutant Rohdamine B (RhB) under visible light irradiation. Visible-light photocatalytic performances of various hierarchically structured porphyrin nanocrystals such as nanosheets, octahedral, and microspheres were also investigated by Zhong et al.

It is well known that graphene sheets can be employed as a platform for semiconductor materials to enhance the photocatalytic activity due to it has large surface area, high adsorption sites and capability, good charge transfer properties and band-gap energy tunability. To the best of our knowledge, up to now very few studies have reported on integrating porphyrin nanoassemblies the graphene for photocatalysis applications. Chen et al. employed vacuum filtration methods to integrate porphyrin nanoparticles into reduced graphene oxide (rGO) for use in photocatalysis. Visible-light photocatalytic activity of one-dimensional porphyrin
nanoassemblies assisted via graphene oxide has also successfully been investigated by Guo et al.\textsuperscript{136} However, both of these studies faced a disadvantage of either in-direct integrating or poor distribution of the porphyrin nanoassemblies on the graphene substrate.

Herein we present the successful fabrication of well-dispersed porphyrin nanorods on the surface of graphene nanoplates by direct self assembly of the monomeric TCPP molecules on graphene with the assistance of CTAB surfactant. Firstly graphene nanoplates (GNPs) were suspended in a solution of TCPP monomers in NaOH by sonication (guest solution). The TCPP-adsorbed GNPs suspension was the, added dropwise in a host solution of CTAB in HCl under vigorous stirring to form uniform TCPP nanorods on the GNPs (Fig. 3.12). The detailed experimental procedure can be found in the SI. The photocataytic performance of the prepared GNP-supported TCPP nanorods was investigated by the degradation of RhB under visible light irradiation condition.

\textbf{Figure 3.12:} Possible mechanism of surfactant-assisted self assembly of porphyrin nanorods.
3.6 Experimental Section

**Materials**

All chemicals were used as received without any further purification. Natural graphite flakes were supplied from Pressol Gmbh, with particles size > 100 mesh. Chemicals such as dry acetone, concentrated acid sulphuric (98%), propionic acid, tetrahydrofuran (THF), sodium hydroxide (NaOH), potassium hydroxide (KOH), ethanol and sodium persulphate (Na$_2$S$_2$O$_8$) were purchased from Ajax Finechem. tetrakis(4-carboxyphenyl)porphyrin (H$_2$TCPP) was synthesised in house. All chemicals were used as received.

**Synthesis of graphene nanoplates (GNPs)**

The preparation of GNPs was obtained according to previous known method.$^1$ Typically, 1 g of natural graphite flakes was dispersed in 80mL of sulphuric acid 98% with swirling for 10 minutes in a 250 mL reactor. Thereafter 6g of sodium persulfate (Na$_2$S$_2$O$_8$) was gradually added and reaction mixture gently stirred for 3h at room temperature. The mixture, then, was filtrated directly by a glass sintered filter (Duran® sintered with disc filter funnel capacity 50 mL, max pore size 4-5 μm) without quenching. The filtrated solution was separated and use for next graphite exfoliation. GNPs was rinsed with dry acetone (3x10 mL), followed by 5 mL water to remove any residual acid in the GNPs, and dried at 60°C in open air.

**Synthesis of GNPs-supported TCPP nanorods**

GNPs-supported TCPP nanorods were fabricated by a typical surfactant-assisted acid-base neutralization strategy. First, 8 mg of TCPP was dissolved in 1 mL of 0.2 M NaOH solution. Then, 0.1 mg of graphene nanoplates were dispersed in TCPP solution by sonication for 30 minutes. This is assigned as guest solution. The host solution was prepared by dissolving 70 mg CTAB in 19 mL of 0.01 M HCl solution. Subsequently, the guest solution was added dropwise into the host solution under rigorous stirring at room temperature in the dark for 30 minutes. Certain amounts of solution were taken out at appointed times to investigate the changing morphologies...
of TCPP aggregates. Free standing TCPP nanorods were also fabricated using a similar strategy without addition of GNPs, for comparative purposes.

**Photocatalytic investigation**

Photocatalytic performance of GNPs-supported TCPP nanorods were evaluated by the degradation of RhB in aqueous solution. In a typical photodegradation measurement, 0.1 mg of hybrid material was dispersed in 20 mL aqueous solution of RhB dye with a concentration of 5 mg L\(^{-1}\). The dispersion was stirred in the dark for 30 minutes to establish an adsorption/desorption equilibrium before irradiation. The visible light source for the photocatalytic reaction was a 1500 W air cooled Xenon lamp with a UV cutoff filter, which only allowed wavelengths of > 400 nm to penetrate. At appointed time, 3.5 mL of dispersion aliquots were taken out and centrifuged to remove photocatalyst. The photocatalytic performance of the as-fabricated samples for RhB degradation were evaluated by recording real-time UV-vis adsorption spectra of RhB at a wavelength of 553 nm.

**Characterization**

The crystal structures and elemental compositions of samples were studied by scanning electron microscopy (SEM) using an FEI Nova NanoSEM (Hillsboro, USA). TEM images were obtained on a JEOL 1010 TEM instrument operated at an accelerating voltage of 100 kV. Fourier transform infrared (FTIR) was performed on a PerkinElmer D100 spectrometer in attenuated total reflectance mode. A BrukerAXS D8 Discover instruments with a general area detector diffraction system (GADDS) using Cu K\(\alpha\) source were utilized to obtain XRD patterns. Ultraviolet-visible (UV-vis) measurements of samples in solution (dissolved in dimethylformamide-DMF) and in solid state were carried out using a Cary 50 Bio spectrophotometer with a cell of 1 cm path length. UV-vis spectrophotometer was also employed to investigate the photocatalytic performance for Rodhamine B degradation. Fluorescence emission spectra were recorded on a Horiba Jobin Yvon FluoroMax®-4–Spectrofluorometer. All experiments were performed in a quartz cell with a 1 cm path length with 420 nm excitation wavelength. All the solutions were prepared in a similar manner to that in the UV–vis study.
3.7 Results and Discussion

As illustrated in Fig. 3.13A graphene nanoplates (GNPs) were synthesized from the chemical exfoliation of natural graphite flakes in a mixed solution of sodium persulfate and sulphuric acid. The obtained GNPs are tens of microns in diameter with thickness of about 10-20 nm. The morphology and distribution of self assembly porphyrin crystals TCPP are observed by TEM and SEM images as shown in Fig. 3.13B-D and Fig. 3.14. It clearly shows that well-dispersed

![Figure 3.13:](image)

TCPP nanorods with an average diameter of 50 nm and lengths of approximately 200 nm are uniformly assembled on the surface of GNPs. Unlike in CTAB-assisted self assembly of TCPP without GNPs, which demonstrated the formation of flakes and flowers TCPP aggregated structures as a function of
stirring time,\textsuperscript{209} in our case GNPs-assisted assembly of TCPP aggregated nanorods are almost unchanged in morphology and size even after 24 hours of stirring time (Fig. 3.15). This suggests that presence of GNPs may help to avoid further aggregation of TCPP once the nanorods are completely formed.

\textbf{Figure 3.14:} SEM images (A,B) and TEM images (C,D) of graphene-supported assembled TCPP nanorods
**Figure 3.15:** SEM images of graphene-supported assembled TCPP nanorods after 30 min (A) and 24 hours (B) of surfactant-assisted assembly time.

UV-vis spectra of monomeric TCPP molecules and GNPs@TCPP nanorods are exhibited in Fig. 3.16A. In the UV-vis spectrum of monomeric TCPP molecules, there is one strong Soret absorption peak at 416 nm as a result of a transition from $\alpha_1 \pi$ to $e^* \pi$, and four weak peaks in range of from 500 - 700 nm which are attributed to Q bands of $a_{2u} \pi$ to $e^* \pi$ transition.\textsuperscript{135, 248} After self assembly with assistance of surfactant and GNPs, UV-vis spectrum displays characteristic absorption peaks of both GNPs and TCPP nanorods. While a broad peak at the wavelength of around 300 nm is ascribable to the GNPs,\textsuperscript{249} a strong absorption peak at 424 nm and four weak peaks between 500 - 700 nm are attributed to Soret band and Q bands of aggregated TCPP crystals, respectively. Compared with the Soret band of monomeric TCPP molecules, there are distinct bathochromic and hypsochromic shifts by 8 nm from 416 nm to 424 nm indicating that most of the TCPP building blocks form J-aggregates supramolecular assemblies with assistance of CTAB surfactant and GNPs.\textsuperscript{136, 241, 250} The red-shift in Q bands also suggests well-defined J-type assemblies of TCPP monomers on the GNPs surface. The optical property of TCPP nanorods on GNPs was further...
Figure 3.16: (A) UV-vis absorption spectra and (B) Photoluminescence (PL) spectra of monomeric TCPP molecules (black line) and GNPs-supported TCPP nanorods (red line).

investigated by photoluminescence (Fig. 3.16B). The fluorescence spectrum of TCPP molecules in DMF solution shows two characteristic emission peaks at 655 and 714 nm. Interestingly, there are three emission peaks at 644, 674, and 710 nm observed in the photoluminescence spectrum of GNPs-supported TCPP nanorods with significant decrease in emission intensity. This new emission peak is likely due to the coupling from the spatial packing of the TCPP porphyrins. Furthermore, the decrease in emission intensity can be ascribed to the quenching effect by GNPs, suggesting an efficient photoinduced process of electron injection from TCPP to GNPs.

The crystallinity of TCPP monomers and surfactant-assisted TCPP aggregates on GNPs was determined by XRD measurement as depicted in Fig. 3.17. The XRD pattern of TCPP monomers (black line) show no diffraction peak, indicating the non-crystalline nature of monomeric TCPP molecules. However, strong refraction peaks are observed in the self-assembled TCPP nanorods on GNPs indicating that the resulted aggregates are crystalline in nature, which may be due to aromatic $\pi-\pi$
stacking between the porphyrin molecules. Fourier transform infrared (FTIR) spectra of monomeric TCPP molecules and GNPs-supported TCPP nanorods also reveal characteristic bands for both GNPs and porphyrin components (Fig. 3.18).

![Figure 3.18: FTIR spectra of monomeric TCPP molecules (black line) and GNPs-supported TCPP nanorods (red line).](image)

TCPP porphyrin aggregates comprise of a similar molecular structure to photoactive molecules such as chlorophyll, which show photocatalytic property in many biological energy transduction processes in plants, algae. Moreover, the photocatalytic activities of TCPP aggregates of different morphologies were also well-studied previously, which demonstrated that TCPP aggregates only exhibit photocatalytic properties under visible light condition and TCPP nanorods show the highest photocatalytic activity compared to other morphologies. The band gap energy of free standing TCPP aggregates and GNPs-supported TCPP nanorods were also calculated from the UV-visible spectrum in Fig. 3.16A to be ca. 2.88 and 2.68 eV, respectively, which indicates that the photocatalysis can be performed under visible light and the introduction of graphene decreases the band gap energy. Thus, in this work we evaluate the photocatalytic performances of as-prepared GNPs-supported TCPP nanorods in comparison with GNPs and free standing TCPP aggregates for the degradation of RhB dye. The decrease in the absorption peak of 553 nm of dye as a
function of time is monitored to assess the photocatalytic performance. Fig. 3.19A shows the $C/C_0$ vs. time plot of RhB in the different photocatalytic reaction conditions, where $C_0$ is the initial concentration of RhB and $C$ is the concentration at time $t$. The plot of $\ln \left( \frac{A_t}{A_0} \right)$ vs. time was also drawn to determine the kinetics of the photocatalytic reaction, where $A_t$ is the peak intensity at time $t$, and $A_0$ is the intensity at time zero (Figure 3.19B). For the blank experiment without photocatalyst, negligible RhB degradation could be observed, suggesting that the self sensitized photodegradation of RhB does not occur under these conditions. When free standing GNPs and TCPP aggregates are used as photocatalysts, a decrease in RhB concentration of 25% and 50% were observed, respectively.

![Figure 3.19: (A) Photocatalytic performance for RhB degradation and (B) kinetic simulation curve of a) control without catalyst, b) GNPs, c) free standing TCPP nanorods, d) GNPs-supported TCPP nanorods.](image)

While the decrease in RhB concentration with GNPs is likely due to adsorption of RhB molecules on GNPs,\textsuperscript{136} RhB degradation with free standing TCPP aggregates reveal photocatalytic activity under visible irradiation.\textsuperscript{209} However the photocatalytic performance increases significantly when GNPs-supported TCPP aggregates are used, and RhB degradation reaches 80%, with a rate constant is ca. $7.3 \times 10^{-3}$ min$^{-1}$. These
results indicate that well-dispersed TCPP self assembly on the GNPs exhibit enhanced photocatalytic activity in comparison with TCPP aggregates.

It is well-known that the J-type assembly of π- conjugated organic dyes that are electronic delocalization spans over the aggregated molecules as a results of the strong intermolecular π-π interations,\textsuperscript{235, 241} which makes J-aggregated porphyrins photosemiconductors. Thus, J-type porphyrin assemblies can serve as organic semiconductors, which can harvest light to generate electron-hole pairs under irradiation.\textsuperscript{235, 250, 254-255} The enhanced photocatalytic performances of GPNs@TCPP compared to free-standing TCPP aggregates may be attributed to the unique physicochemical properties of graphene that can act as an ideal support and promoter.\textsuperscript{128-129, 256} Therefore, graphene could improve the charge sepparation by the suppressing the recombination of electron-hole pair generated from irradiation of the porphyrins and hence serve to increase the lifetime of the charge carriers.\textsuperscript{130, 246} Graphene also plays an important role in enhancing the efficiency of RhB adsorption and the interfacial charge transfer to the absorbed agent.\textsuperscript{246, 257}

Based on the well-documented understanding and above discussions, we propose a possible mechanism for enchanced photocatalytic activity of GNPs-supported TCPP nanorods as shown in Fig. 3.20. When GPNs@TCPP nanorods hybrid material is
Figure 3.20: The possible mechanism of GNPs-supported photocatalyst for Rhdamine B degradation.

Irradiated with visible light, electrons from valence band (VB) of TCPP nanorods cross band gap to the conduction band (CB) resulting the formation of e/h+ pairs.216 The generated electron in CB, then proceed to the graphene sheets. The oxidation reaction of RhB molecules to RhB+ degraded products occurs on the surface of both TCPP nanorods, while oxygen in H2O is reduced on the graphene sheet by the electrons generated from visible light illumination of TCPP nanorods.18

3.8 Conclusions

In short, we have successfully synthesized a well-dispered TCPP nanorods on the surface of graphene by surfactant-assisted self-assembly of TCPP monomers adsorbed on graphene. The resulted TCPP nanorods with an average diameter of 50 nm and the length of 200 nm are uniformly distributed on the surface of graphene nanoplates. The prepared graphene-supported TCPP nanorods show enhanced photocatalytic performance compared to free standing TCPP aggregates under visible light irradiation, due to the improved charge separation and charge transfer with introduction of graphene nanoplates. The photocatalytic mechanism is also discussed and the mechanism of action warrants further investigation. This study will be a considerable contribution to artificial photocatalysis, organic/graphene hybrid nanocatalysts and also provides a possible solution to solving environmental issues.
This sub-chapter describes the fabrication of graphene@porphyrin nanofibre composite via arginine-mediated self-assembly of tetrakis(4-carboxyphenyl) porphyrin (TCPP) on graphene nanoplates (GNPs). The formation and crystallisation of the graphene@porphyrin nanofibre composite was fully characterized by SEM, TEM, XRD, FTIR, UV-vis and fluorescence spectroscopy. The enhanced visible-light photocatalytic activity and the mechanism for photocatalysis is also discussed in this chapter.
3.9 Introduction

Supramolecular self-assembly of porphyrin-based materials has attracted intensive interest from scientists as an effective protocol to design functional structures during the past decade.\textsuperscript{87, 187, 258} \(\pi\)-conjugated porphyrins have been extensively studied as building blocks for the construction of solid-state nanostructured materials \textsuperscript{234-235, 238-239, 259}, which can be utilized in many application such as optoelectronic nanodevices, energy storage, catalysis, photodynamic therapy, sensors and photonics \textsuperscript{229-233}. Supramolecular nanostructures via self-assembly are usually produced via non-covalent interactions such as hydrogen bonding, electrostatic, van der Waals interactions, \(\pi-\pi\) interactions, and coordination. These soft materials are fabricated by self-assembly protocols including ionic self-assembly \textsuperscript{240}, surfactant-assisted self-assembly (SAS) \textsuperscript{241}, and reprecipitation \textsuperscript{242-243}. Many well-defined and controlled nanostructures such as nanoprisms, nanotubes, nanofibre bundles, nanorods, nanosheets, nanospheres, nanoclovers, nanowires and nanoparticles have thus been reported \textsuperscript{51, 67, 72-75, 193}. Recently, visible-light photocatalytic applications of self-assembled porphyrin nanostructures have been extensively reported \textsuperscript{135, 209, 246}. Zhong and colleagues reported the dependence of photocatalytic performance on various hierarchically structured porphyrin nanocrystals such as nanosheets, octahedrons, and microspheres \textsuperscript{96}. More recently, we successfully fabricated porphyrin nanobelts via arginine-induced self-assembly of tetrakis (4-carboxyphenyl) porphyrin (TCPP), and used the structure for the photodegradation of model pollutant Rhodamine B (RhB) under visible light irradiation \textsuperscript{260-261}.

Graphene, due to its large surface area, high number of adsorption sites, and good charge transfer properties has been demonstrated to be a good platform for semiconductor materials to enhance the photocatalytic activity \textsuperscript{127-130, 262-265}. However, only a few studies have been reported so far on combination of porphyrin nanostructures with the graphene for photocatalytic applications. For example, Chen \textit{et al.} employed vacuum filtration methods to integrate porphyrin nanoparticles into reduced graphene oxide (rGO) for use in photocatalysis \textsuperscript{135}. In another study, Guo’s group studied visible-light photocatalytic activity of a one-dimensional porphyrin...
formed by self-assembly assisted by graphene oxide. However, these studies faced disadvantages, being poor integration or poor distribution of the porphyrin nanostructures on the graphene substrate. Recently, we reported well-dispersed TCPP nanorods on graphene for enhanced photocatalytic performances.

Herein, we fabricate a GNPs@porphyrin nanofiber composite via arginine-mediated reprecipitation of TCPP on the graphene surface, and use the material as a photocatalyst for degradation of a dye.

3.10 Materials and Methods

Materials

All chemicals were used as received without any further purification. D- arginine was obtained from Sigma Aldrich (Bengaluru, Karnataka, India) and graphene nanoplates (GNPs) were purchased from VNgraphene. Chemicals such as dry acetone, propionic acid, dichloromethane, chloroform, sodium hydroxide (NaOH), methyl orange (MO), Rhodamine B (RhB), potassium hydroxide (KOH) and ethanol were purchased from Ajax Finechem. Australia.

Arginine-mediated self-assembly of TCPP on the graphene surface

First, 8 mg of TCPP and 4 mg of GNPs were dissolved and sonicated in 1 mL of 0.2 M NaOH solution for 15 minutes. This is assigned as the guest solution. The host solution was prepared by dissolving 16 mg of D- arginine in 20 mL of 0.01 M HCl solution. Subsequently, the guest solution was added dropwise into the host solution under stirring at room temperature in the dark for 1 hour. The obtained dark green aggregates (GNPs@TCPP nanofibers) were, then, filtered and dried for further characterizations (Fig. 3.21).

Photocatalytic Investigation

The photocatalytic performance of the GNPs@TCPP nanofibers was evaluated by the degradation of RhB and MO in aqueous solution. In a typical photodegradation measurement, 0.1 mg of composite was dispersed in a 20 mL aqueous solution of dye with a concentration of 5 mg L⁻¹. The dispersion was stirred for 30 minutes and left overnight in the dark to establish an adsorption/desorption equilibrium before
irradiation. The simulated sunlight source for the photocatalytic reaction was a 1500 W air cooled Xenon lamp. At appointed times, 1.5 mL of dispersion aliquots were taken out and centrifuged to remove photocatalyst. The photocatalytic performance of the as-fabricated samples for dyes degradation was evaluated by recording the real-time absorptivity at a wavelength of 553 nm for RhB and 446 nm for MO.

**Figure 3.21: Schematic diagram of arginine-mediated self-assembly of porphyrin nanofibers on graphene surface.**

**Characterization**

The supramolecular self-assembled nanostructure morphology of GNPs@TCPP nanofiber were studied by scanning electron microscopy (SEM) using an FEI Nova NanoSEM (Hillsboro, USA, operating under HV and Stage bias condition of 15 KeV with Pt coating). TEM samples were prepared and measured by paper blotting method followed by solvent evaporation on a holey carbon coated copper grid. The micrographs were investigated using a Jole 1010 100 kV transmission electron microscope. Ultraviolet-visible (UV-vis) absorption measurements of samples in solution and in solid-state were carried out using a Cary 50 Bio spectrophotometer with a cell of 1 cm path length. Furthermore, UV-vis absorption measurements were
also employed to record the photocatalytic performance for dyes degradation. Horiba JobinYvonFluoroMax®-4 Spectrofluorometer was used to record fluorescence emission spectra of obtained materials. All experiments were performed in a quartz cell with a 1 cm path length upon excitation at 420 nm wavelength. A BrukerAXS D8 Discover instrument with a general area detector diffraction system (GADDS) using a Cu Kα source was utilized to obtain XRD patterns of GNPs@TCPP nanofibers.

3.11 Results and Discussion

Fig. 3.22A shows the SEM image of graphene nanoplates (GNPs) obtained from VNgraphene. It is clear that the GNPs have a wrinkled, crumpled structure with a lateral diameter of tens of microns. The semitransparency of GNPs to the electron beam also suggest that the thickness of GNPs is approximately 5-15 nm. Fig. 3.22B is the SEM image of free-standing arginine-mediated self-assembly of porphyrins dropped onto a silicon wafer. The assembled porphyrins have similar morphology to our previous work, which is best described as a belt-like morphology several microns in length, with diameters of about 20-30 nm.

![Figure 2.22: SEM images of (A) graphene nanoplates, (B) free-standing arginine-induced TCPP aggregates.](image)

The morphology and distribution of the arginine-mediated self-assembly porphyrin TCPP on the graphene are observed by SEM and TEM images in Fig. 3.23, Fig. 3.24 and 3.25. It is seen that the porphyrins nanofibers were densely and uniformly distributed on the surface of the GNPs with a diameter ranging from 50-200 nm and several micrometers in length. In contrast to Arginine-assisted self-assembly
of TCPP with GNPs, which demonstrated the formation of well-dispersed porphyrin nanorods with 50 – 100 nm in diameter and about 200 nm in length on the GNPs surface,\textsuperscript{210} in this case the diameter of the TCPP aggregates are almost unchanged. This suggests that the presence of arginine helps to elongate the aggregation of TCPP to form nanofibers with length on the micron scale.

**Figure 3.23:** (A) Low and (B) High resolution SEM images of arginine-induced self-assembly of TCPP on the graphene surface, respectively.

**Figure 3.24:** SEM images of D-arginine-assisted TCPP nanofibers on graphene.
Figure 3.25: TEM images of D-arginine-assisted TCPP nanofibers on graphene.

Fig. 3.26A shows the UV-vis spectra of monomeric TCPP molecules, free-standing TCPP aggregates and GNPs@TCPP nanofibers. The absorption spectrum of the TCPP monomer shows a strong peak at 414 nm, namely a Soret absorption, as a result of a transition from \(a_{1u}(\pi)\) to \(e_g^*(\pi)\), and four weak peaks ranging from 500 - 700 nm, which are ascribed to Q bands of the \(a_{2u}(\pi)\) to \(e_g^*(\pi)\) transition \(^{135,248}\). Free-standing TCPP aggregates reveal a Soret absorption peak at 417 nm and the four weak absorption peaks of Q bands in the TCPP monomer are replaced by a strong peak at 666 nm. The distinct bathochromic and hypsochromic shifts by 3 nm in Soret band of the TCPP confirm aggregation formation in comparison with monomeric TCPP indicates that most of the TCPP building blocks form J-type supramolecular assemblies with induction of arginine \(^{136,241,250}\). Similarly, the UV-vis spectrum of GNPs@TCPP nanofibers also show a Soret peak at approximately 420 nm and one strong peak at 666 nm (along with three relatively weak peaks) in Q-band region. The presence of graphene in this case is responsible for larger bathochromic and hypsochromic shifts, which is about 6 nm. A broad peak at around 350 nm, which is attributed to the characteristic absorbance of graphene, is also observed \(^{249}\). The change in the Q-band region is evident in four weak peaks in the absorbance of monomeric TCPP changing to one strong peak and three relatively weak peaks (inset in Fig. 3.26A) in the absorbance spectrum of free-standing TCPP aggregates and GNPs@TCPP nanofibers This suggests well-defined J-type assemblies of TCPP monomers on the GNPs surface.
The optical properties of TCPP nanofibers on GNPs were further investigated by photoluminescence (Fig. 3.26B). The fluorescence spectrum of TCPP in aqueous solution shows one characteristic emission peak at 669 nm. Interestingly, the photoluminescence spectrum of free-standing TCPP nanobelts and GNPs@TCPP nanofibers show relatively weak and broad emission peaks at approximately 730 and 686 nm, respectively. These significant decreases in the emission peaks are likely due to the coupling from the spatial packing of the TCPP porphyrins and the quenching effect of graphene, suggesting an efficient photoinduced process of electron injection from TCPP to GNPs.

Figure 3.26: (A) and inset of (A) UV-vis absorption spectra and (B) Photoluminescence (PL) spectra of monomeric TCPP molecules (black line), free-standing TCPP nanobelts (red line) and GNPs@TCPP fibers (blue line).

Fig.3.27 exhibits XRD patterns of monomeric porphyrin molecules and GNPs@porphyrin nanofibers. There are no peaks observed in the XRD pattern of monomeric TCPP (black line), indicating the non-crystalline nature of the TCPP monomers. However, the XRD pattern of GNPs@TCPP nanofibers (red line) show several characteristic diffraction peaks of both graphene and TCPP aggregates, while a strong peak at around 26° and a weak peak at 55° are assigned to the graphitic nature of graphene, and other weak diffractions peaks are indexed for TCPP nanofibers. These results indicate that assembled TCPP aggregates are crystalline in nature, which
may be due to aromatic π-π stacking between the porphyrin molecules. Fourier transform infrared (FTIR) and Raman spectra of monomeric TCPP and GNPs@TCPP nanofibers also reveal characteristic bands for both GNPs and porphyrin components (Fig. 3.28 and 3.29).

**Figure 3.27:** XRD patterns of monomeric TCPP molecule and GNPs@TCPP nanofibers.

TCPP porphyrin aggregates have been demonstrated to have photocatalytic properties in many biological energy transduction processes in plants and algae. It has also been confirmed that TCPP aggregates only exhibit photocatalytic properties under visible light. Thus, in this work, we assess the photocatalytic degradation of Rhodamine B (RhB) and methyl orange (MO) dyes by using GNPs@TCPP nanofibers as a photocatalyst in comparison with GNPs and free standing TCPP aggregates. The decreases in the absorption peak at 553 and 464 nm of RhB and MO, respectively, as function of time are monitored to evaluate the photocatalytic performance. Fig. 3.30A and C display the C/C₀ vs. time plot of RhB and MO under different photocatalytic reaction conditions, where C₀ is the initial concentration of dyes and C is the concentration at time t. It is clear in both cases of
**Figure 3.28:** FTIR spectra of monomeric TCPP molecules (black line) and GNP@TCPNP nanofibers (blue line)

**Figure 3.29:** Raman spectra of monomeric TCPP molecules (black line) and GNP@TCPNP nanofibers (red line)
RhB and MO that with the blank experiment (no photocatalysts), negligible dye degradation could be observed, suggesting that the self-sensitized photodegradation of dyes does not occur under these conditions. When GNP s were used as photocatalyst, while a decrease in RhB concentration of approximately 25% was observed, there is an insignificant decrease in the concentration of MO. This is likely due to good adsorption affinity of graphene toward RhB rather than MO \(^{136}\). When using free standing TCPP aggregate photocatalysts, the concentration of RhB and MO are decreased by 90% and 30% respectively after 180 minutes of irradiation time under simulated sunlight. This result demonstrates that the free standing TCPP aggregates display photocatalytic activity toward RhB and MO under visible light irradiation.

![Figure 3.30](image-url)

**Figure 3.30:** (A), (C) Photocatalytic performance and (B), (D) kinetic simulation curve for RhB and methyl orange degradation, respectively, of a) control without catalyst, b) GNP s, c) free standing TCPP nanobelts, d) GNP s@TCPP nanofibers.
Interestingly, the photocatalytic performance increases significantly when GNPs@TCPP nanofibers are used. While RhB is completely degraded after 150 minutes, MO degradation also reaches 80% after 180 minutes. These results indicate that GNPs@TCPP nanofibers exhibit enhanced photocatalytic activity in comparison with GNPs and free standing TCPP aggregates. The photocatalytic activity of GNPs@TCPP nanofibers toward dyes in the dark condition was also tested (Fig. 3.31), which show virtually no photocatalytic activity in this condition, the small decrease in dyes concentration is ascribed to adsorption of dyes by GNPs.

![Figure 3.31: Photocatalytic performance of GNPs@TCPP nanofibers toward Rhdomine B and Methyl orange in the dark condition.](image)

The kinetics of the photocatalytic reaction of RhB and MO by GNPs@TCPP nanofibers are also determined through the plot of ln \( (A_t/A_0) \) vs. time, where \( A_t \) is the peak intensity at time \( t \), and \( A_0 \) is the intensity at time zero (Figure 3.30B and D). From these plots, the degradation rate constant of RhB and MO by GNPs@TCPP nanofibers as a photocatalyst is calculated to be 15.8 X 10^{-3} and 6.5 X 10^{-3} min^{-1}, respectively.
It is well-known that J-type porphyrin assemblies can be used as organic semiconductors to harvest light and generate electron-hole pairs under light irradiation. Moreover, previous studies demonstrated that graphene could be used as a support and promoter to improve charge separation, by the suppressing the recombination of electron-hole pairs generated from irradiation of the porphyrins, increasing the lifetime of the charge carriers. Graphene also plays an important role in enhancing the efficiency of dye adsorption, as it facilitates the interfacial charge transfer to the adsorbed agent. Based on this literature, a possible mechanism for the enhanced photocatalytic activity of the GNPs@TCPP nanofibers photocatalyst toward dyes is proposed as illustrated in Fig. 3.32. When a

![Figure 3.32: The possible mechanism of the GNPs@TCPP nanofibers photocatalyst for dye degradation.](image)

GNPs@TCPP nanofiber is irradiated with visible light, electrons from valence band (VB) of TCPP crystals cross the band gap to the conduction band (CB), resulting the generation of e⁻/h⁺ pairs. The generated electron in the CB may move freely to the graphene sheets, consequently, the generated electron-hole pairs are effectively separated and recombination energy is significantly minimized. Dye molecules are oxidized to degraded products on the surface of TCPP nanofibers by active species such as ‘OH formed by reaction between photogenerated holes with H₂O or OH⁻.
On the other side, oxygen in H$_2$O is reduced on the graphene sheet by the electrons generated from TCPP nanofibers under visible irradiation to form $O_3^-$ radicals $^{268}$.

### 3.12 Conclusions

In summary, we have successfully synthesized GNPs@TCPP nanofiber composites by arginine-mediated self-assembly of monomeric molecules on graphene. The resulting TCPP nanofibers are 50-200 nm in diameter with approximately 5 µm in length, being densely and uniformly distributed on the surface of graphene. The GNPs@TCPP nanofiber composite showed enhanced photocatalytic performance compared to free standing TCPP aggregates under visible light irradiation, with RhB completely degraded after 150 minutes. A possible photocatalytic pathway has also been proposed. This study introduces a new promising material, which is a timely contribution to organic/graphene hybrid nanocatalysts, especially useful for applications environmental remediation.
Chapter IV

Fabrication of a TiO$_2$@porphyrin nanofiber hybrid material: A highly efficient photocatalyst under simulated sunlight irradiation

This chapter reports on the fabrication of a TiO$_2$@porphyrin hybrid material by surfactant-assisted co-assembly of monomeric porphyrin molecules with TiO$_2$ nanoparticles. SEM, XPS, XRD, FTIR, UV-vis and fluorescence spectroscopy were employed to characterize the TiO$_2$@TCPP hybrid material. This material exhibits efficient photocatalytic performance under simulated sunlight, due to synergistic photocatalytic activities of the porphyrin aggregates in visible light and TiO$_2$ particles in the UV region. A plausible mechanism for photocatalytic degradation is also proposed and discussed.
4.1 Introduction

Amongst the many candidates for photocatalysts, anatase (TiO$_2$) is the most promising for industrial use due to its efficient photoactivity, non-toxicity, superior stability and low cost.\textsuperscript{269-270} It is also widely used to both the oxidatively or reductively degrade environmental pollutants in air or water in the presence of UV light.\textsuperscript{271-275} The commonly reported mechanism upon UV irradiation of TiO$_2$ is the generation of electron-hole (e$^-$/h$^+$) pairs which diffuse to the TiO$_2$ surface to react with OH groups forming OH radicals (OH'). These OH radicals is considered as the oxidizing agents that degrade the target pollutants.\textsuperscript{273, 276}

The creation of supramolecular nanoassemblies is a powerful technique for the fabrication of nanostructure materials with tunable morphologies.\textsuperscript{224-228} Among numerous organic-based supramolecular nanoassemblies, $\pi$-conjugated porphyrins have been attracting great attention as organic building blocks for the construction of solid-state soft materials.\textsuperscript{234-239} Various assembly protocols have been successfully employed to form nanostructured porphyrins, including ionic self-assembly,\textsuperscript{240} surfactant-assisted self assembly (SAS),\textsuperscript{241} reprecipitation,\textsuperscript{242-243} etc. Owning to the unique planar geometry, well-understood Soret-band in visible region and the inherent capability to mimic biological processes, porphyrin assemblies have many potential applications such as photoelectronics, optical devices, sensors, and solar energy conversion.\textsuperscript{153, 236, 244-245} Most recently, self-assembled porphyrin nanostructures have been used for visible-light photocatalysis.\textsuperscript{96, 135, 246} Mandal \textit{et al.} fabricated a range of morphologies of assembled structures (spheres, rods, flakes, and flowers) of meso-tetra(4-carboxyphenyl) porphyrin (TCPP) and used them for the photodegradation of the model pollutant Rhodamine B (RhB) under visible light irradiation.\textsuperscript{209} Visible-light photocatalytic performance of various hierarchically structured porphyrin nanocrystals such as nanosheets, octahedral, and microspheres were also investigated.\textsuperscript{96}

Conjugated $\pi$-electron donor-bridge-acceptor structures of TiO$_2$/porphyrin systems have been extensively studied for various applications such as dye-sensitized solar cells,\textsuperscript{150-152} and photochemical solar cells.\textsuperscript{153-154} Recently, these dye-sensitized systems have also been considered as an alternative material for visible-light
Shabana et al. demonstrated that self-assembled monolayers of TCPP on anatase coated-cotton fabric exhibit efficient photocatalytic activity for the degradation of methylene blue and coffee stains. In another study, porphyrin-sensitized TiO$_2$ was successfully studied for photocatalytic degradation of acid chrome blue K. However, both of these studies only investigated the visible light-sensitized property of monomeric porphyrin molecules to enable UV-activated TiO$_2$ photocatalyst having photocatalytic activity under visible light.

To the best of our knowledge, this is first example of the fabrication of a TiO$_2$@porphyrin nanocrystal composite for photocatalysis under sunlight irradiation. We have used freebase-tetracarboxy-porphyrin (H$_2$TCP), for fabrication of TiO$_2$@TCPP hybrid materials by direct self assembly of the monomeric TCPP molecules with the assistance of CTAB surfactant and TiO$_2$ anatase nanocrystalline. Typically, TiO$_2$ powder were suspended in a solution of TCPP monomer in NaOH by sonication. The TCPP-adsorbed TiO$_2$ suspension was then added dropwise in a host solution of CTAB in HCl under vigorous stirring to form the TiO$_2$@TCPP aggregates. The photocatalytic performance of the resulting TiO$_2$/TCPP nanofiber hybrid material was evaluated by the degradation of RhB under sunlight conditions.

4.2 Materials and Methods

Materials

All chemicals were used as received without any further purification. Cetyltrimethylammonium bromide (CTAB), and TiCl$_4$ in HCl were obtained from Sigma Aldrich. Chemicals such as dry acetone, concentrated sulphuric acid (98%), propionic acid, tetrahydrofuran (THF), sodium hydroxide (NaOH), potassium hydroxide (KOH) and ethanol and were purchased from Ajax Finechem.

Synthesis of TiO$_2$ nanoparticles

A synthetic protocol for preparation of TiO$_2$ anatase nanostructured particles was adopted from previous work. Typically, 3ml TiCl$_4$ was slowly added dropwise to 30 ml ethanol at room temperature. A light yellow solution was obtained and gelatinized for 2 days to form a sol gel. Then, the sol-gel solution was dried at 80°C for 6 hours.
The dried gel precursor was calcined at 500°C with a heating rate of 5°C/min for 3 hours to obtain the desired TiO$_2$ powder.

**Synthesis of TiO$_2$@TCPP nanofibers hybrid materials**

TiO$_2$@TCPP nanofibers were fabricated by a typical surfactant-assisted acid-base neutralization strategy. First, 8 mg of TCPP was dissolved in 1 mL of 0.2 M NaOH solution. Then, 1 mg of TiO$_2$ powder were dispersed in this TCPP solution by sonication for 30 minutes. This is assigned as the guest solution. The host solution was prepared by dissolving 70 mg CTAB in 19 mL of 0.01 M HCl solution. Subsequently, the guest solution was added dropwise into the host solution under vigorous stirring at room temperature in the dark for 1 hour. Free standing TCPP nanorods were also fabricated using a similar strategy without addition of TiO$_2$, for comparative purposes.

**Photocatalytic investigation**

Photocatalytic performance of the TiO$_2$@TCPP nanofiber hybrid material was evaluated by the degradation of RhB in aqueous solution. In a typical photodegradation measurement, 0.1 mg of hybrid material was dispersed in a 20 mL aqueous solution of RhB dye with a concentration of 5 mg L$^{-1}$. The dispersion was stirred in the dark for 30 minutes to establish an adsorption/desorption equilibrium before irradiation. The sunlight source for the photocatalytic reaction was a 1500 W air cooled Xenon lamp. At appointed times, 1.5 mL of dispersion aliquots were taken out and centrifuged to remove photocatalyst. The photocatalytic performance of the as-fabricated samples for RhB degradation were evaluated by recording the real-time absorptivity of RhB at a wavelength of 553 nm.

**Characterization**

The crystal structures and elemental compositions of samples were studied by scanning electron microscopy (SEM) using an FEI Verios 460L (operating under HV and Stage bias condition of 1 KeV, using stage bias and Circular Backscatter Detector for low conductive samples). X-ray photoelectron measurements (XPS) were carried out using a K-Alpha XPS instrument using monochromatic Al as the X-Ray source. The Ti 2p core level spectrum was recorded with an overall resolution of 0.1 eV. The
core level spectrum was background corrected using Shirley algorithm and chemically distinct species were resolved using a nonlinear least squares fitting procedure using C as reference. Fourier transform infrared (FTIR) was performed on a PerkinElmer D100 spectrometer in attenuated total reflectance mode. A BrukerAXS D8 Discover instrument with a general area detector diffraction system (GADDS) using a Cu Kα source was utilized to obtain XRD patterns. Ultraviolet-visible (UV-vis) measurements of samples in solution (dissolved in dimethylformamide-DMF) and in solid state were carried out using a Cary 50 Bio spectrophotometer with a cell of 1 cm path length. A UV-vis spectrophotometer was also employed to investigate the photocatalytic performance for Rodhamine B degradation. Fluorescence emission spectra were recorded on a Horiba Jobin Yvon FluoroMax®-4–Spectrofluorometer. All experiments were performed in a quartz cell with a 1 cm path length with a 420 nm excitation wavelength. All the solutions were prepared in a similar manner to that described for the UV–vis study.

4.3 Results and Discussion

The morphologies of TiO₂ nanoparticles, and self-assembled TCPP porphyrin without TiO₂ nanoparticles was investigated by scanning electron microscopy (SEM) as illustrated in Fig. 4.1. It can be clearly seen that without TiO₂, monomeric TCPP molecules assemble to form nanorod structures 70 - 90 nm in width and 300 - 500 nm in length with the assistance of CTAB surfactant (Fig. 4.1A). SEM image of as-prepared TiO₂ is also shown in Fig. 4.1B, which indicate that TiO₂ has particle nanostructure morphology with the size distribution in range of 15 - 30 nm (Fig. 4.2).

Illustrated in Fig. 4.3 is the morphology of TiO₂@TCP aggregates obtained from CTAB and TiO₂-assisted self-assembly from monomeric TCPP molecules. It clearly shows the formation of aggregated TCPP nanofibers with a width of approximately 100 nm and a length of several µm. Interestingly, as can be seen in the higher resolution SEM image and TEM images (Fig. 4.3B-D), TiO₂ retains a particle-like nanostructure and is well-integrated into TCPP nanofiber network. The aggregation of porphyrin molecules to form nanofibers with the assistance of TiO₂ may be ascribed to the facile absorption capability of carboxyl groups on the porphyrin on the TiO₂
Therefore when assembly occurs in the CTAB host solution, TiO$_2$-absorbed TCPP monomers aggregated to form a long fiber structure instead of a rod morphology as is the case for free standing TCPP self-assembly (Fig. 4.1A).

Figure 4.1: SEM images of (A) assembled TCPP nanorods without TiO$_2$ powders and (B) TiO$_2$ anatase nanoparticles.

Figure 4.2: Size distribution of prepared TiO$_2$ anatase nanoparticles

The adsorption of porphyrin onto the TiO$_2$ surface was confirmed by XPS. Fig. 4.4A shows the Ti 2p core level of both the TiO$_2$ and TiO$_2$@TCPP composite. The Ti 2p core level of TiO$_2$ has two signals at 458.61 and 464.44 eV, which is attributed to the binding energies of Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$, respectively. However, these Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$ binding energies in
TiO$_2$@TCPP are shifted to lower binding energies at 458.2 and 463.86 eV respectively. These lower binding energy shifts suggest that Ti is accepting electron density from carbonyl groups of the porphyrin, decreasing the binding energy of Ti core level.\textsuperscript{156} The adsorption nature of carbonyl-group porphyrin on the TiO$_2$ surface can be ascribed to the weak chemisorption.\textsuperscript{279} The O 1s XPS spectrum of TiO$_2$@TCPP aggregates also indicates the formation of hybrid materials through a chemisorption mechanism (Fig. 4.4B). The binding energy in the O 1s spectrum of TiO$_2$ shows a main signal at 530 eV, which is consistent with O-Ti-O binding. However, the binding energy of O 1s shifts to lower energy at 529.7 eV after formation of TiO$_2$@TCPP composite, which is in agreement with previous discussion that O-Ti-O group is receiving electron

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.3.png}
\caption{(A),(B) SEM images and (C), (D) TEM images of as-prepared TiO$_2$@TCPP nanofiber hybrid material.}
\end{figure}
from carbonyl groups of porphyrin, therefore decreasing binding energy of both Ti 2p and O 1s core level. Moreover, by losing electrons in combination with TiO$_2$, the binding energies of O 1s core level of carbonyl groups in porphyrin shift to higher energy as can be clearly seen in Fig. 3B.

Figure 4.5A shows the FTIR spectra of monomeric TCPP molecules, TiO$_2$ nanoparticles and TiO$_2$@TCPP nanofiber hybrid material. It is clear that the FTIR spectrum of the hybrid reveals characteristic bands for both TiO$_2$ and porphyrins components. The crystallinity of TiO$_2$, TCPP monomers and the TiO$_2$@TCPP aggregates was determined by XRD as depicted in Fig. 4.5B. The XRD pattern of TCPP monomers (black line) show no diffraction peaks, indicating the non-crystalline nature of monomeric TCPP molecules. Peak positions and widths in the X-ray diffraction (XRD) pattern (red line) of the as-prepared TiO$_2$ particles confirm the synthesis of pure anatase nanocrystalline TiO$_2$. In the XRD pattern of TiO$_2$@TCPP nanofibers (blue line), apart from peak positions which are well-assigned to anatase TiO$_2$ nanoparticles, the appearance of peaks at about 16° and 17.5° are attributable to the crystalline nature of aggregated TCPP nanofibers, which may due to aromatic π-π stacking between the porphyrin molecules.
Figure 4.5: (A) FTIR spectra and (B) XRD patterns of monomeric TCPP molecules, anatase TiO\textsubscript{2} and TiO\textsubscript{2}@TCPP nanofiber hybrid material.

Optical properties of the samples were investigated by UV-vis and Fluorescence spectroscopy (Fig. 4.6). Illustrated in Fig. 4.6A are the UV-vis spectra of monomeric TCPP molecules and the TiO\textsubscript{2}@TCPP nanofiber hybrid material. The UV-vis spectrum of pristine TiO\textsubscript{2} nanoparticles shows broad peaks at around 400 nm. The UV-vis spectrum of monomeric TCPP molecules show one strong Soret absorption peak at 416 nm as a result of a transition from a\textsubscript{1u} (\pi) to e\textsuperscript{\ast}g(\pi), and four weak peaks in range of from 500 - 700 nm which are attributed to Q bands of the a\textsubscript{2u} (\pi) to e\textsuperscript{\ast}g(\pi) transition.\textsuperscript{248, 257} After self-assembly with the assistance of the surfactant and TiO\textsubscript{2}, the UV-vis spectrum displays characteristic absorption peaks of both TiO\textsubscript{2} and porphyrin nanofibers. While the peak at around 400 nm is ascribed to TiO\textsubscript{2} nanoparticles, the strong absorption peak at 431 nm with a shoulder at around 445 nm, and four weak peaks in range of 500 - 700 nm are ascribed to Soret band and Q bands of aggregated TCPP crystals, respectively. In comparison with the Soret band of TCPP monomers, there are distinct bathochromic and hypsochromic shifts by 15 nm from 416 nm to 431 nm indicating that most of the TCPP building blocks form J-aggregates during supramolecular assembly with the assistance of CTAB surfactant and TiO\textsubscript{2}.\textsuperscript{136, 241, 250} The red-shift in the Q bands
also suggest well-defined J-type assemblies of TCPP monomers in conjunction with TiO\textsubscript{2} nanostructured particles. The fluorescence properties of the monomeric TCPP molecules and TiO\textsubscript{2}@TCPP hybrid materials were investigated by photoluminescence spectra (Fig. 4.6B). The fluorescence spectrum of TCPP molecules in DMF solution shows two characteristic emission peaks at 655 and 714 nm. However, in the fluorescence spectrum of TiO\textsubscript{2}@TCPP, we observed two emission peaks at 658 and 721 nm. These red shifts in the emission peaks are likely due to the coupling from the spatial packing of the TCPP porphyrins.\textsuperscript{96}

![Figure 4.6: A) UV-vis absorption spectra and (B) Photoluminescence (PL) spectra of monomeric TCPP molecules (black line) and TiO\textsubscript{2}@TCPP nanofiber hybrid material (red line).](image)

It is well-known that TiO\textsubscript{2} nanoparticles have a band gap energy of 3.2 eV, and have been employed as a photocatalyst under UV irradiation for many applications.\textsuperscript{280} Furthermore, porphyrin aggregates have a molecular structure that is comparable to photoactive molecules such as chlorophyll, which show photocatalytic properties in many biological energy transduction processes in plants and algae.\textsuperscript{251-252} The band gap energy of free standing TCPP nanorods and aggregated TCPP nanofibers with TiO\textsubscript{2} can be calculated from the UV-visible spectrum in Fig. 4.6A to be ca. 2.88 and 2.55 eV, respectively, which
indicates that the photocatalysis can be performed under visible light, and the introduction of TiO₂ may tune the band gap energy of the porphyrin aggregates. Based on this calculated band-gap energy, it may suggest that the as-prepared TiO₂@TCPP nanofiber hybrid material can be employed as a photocatalyst under sunlight irradiation (both UV and Visible lights). Thus, in this work we evaluated the photocatalytic performance of TiO₂@TCPP composite in comparison with TiO₂ nanoparticles and free standing TCPP nanorods for the degradation of RhB dye under sunlight irradiation. The decrease in the absorption peak of 553 nm of dye as a function of time is monitored to assess the photocatalytic performance. Fig. 4.7A shows the C/C₀ vs. time plot of RhB where C₀ is the initial concentration of RhB and C is the concentration at time t. The plot of ln (Aₜ/A₀) vs. time was also drawn to determine the kinetics of the photocatalytic reaction, where Aₜ is the peak intensity at time t, and A₀ is the intensity at time zero (Fig. 4.7B). For the blank experiment without photocatalyst, negligible RhB degradation could be observed, suggesting that the self-sensitized photodegradation of RhB does not occur readily under these conditions. When free standing TiO₂ nanoparticles and TCPP aggregates are used as photocatalysts, a decrease in RhB concentration of 23% and 50% were observed, respectively. While the decrease in RhB concentration with TiO₂ is likely due to photodegradation of RhB molecules under UV irradiation in sunlight, RhB degradation with free standing TCPP aggregates reveal photocatalytic activity under visible irradiation. However the photocatalytic performance increases significantly when the TiO₂@TCPP nanofiber composite is used, and RhB degradation reaches 78%, with a rate constant of ca. 7.1 X 10⁻³ min⁻¹.

These results indicate that TiO₂@TCPP nanofiber hybrid material can efficiently harvest a wide range of light energies under sunlight conditions for photocatalytic degradation of RhB pollutants.
It has been well demonstrated that for the J-type assembly of π-conjugated organic dyes, that electronic delocalization spans over the aggregated molecules as a result of the strong intermolecular π–π interactions,235, 241 which gives J-aggregated porphyrins photosemiconductor properties. Thus, J-type porphyrin assemblies can serve as organic semiconductors, which can harvest light, especially in the visible range, to generate electron-hole pairs under irradiation.235, 250, 254–255 It also is known that porphyrin aggregates may increase charge separation due to exciton-coupled charge transfer processes in J-type porphyrin aggregate/TiO₂ hybrid materials.152, 281 This synergistic effect of porphyrin aggregates, along with high photocatalytic performance of TiO₂ under UV irradiation could make the TiO₂@TCPP nanofiber hybrid material an efficient photocatalyst under sunlight conditions. Based on the well-documented understanding and above discussions, we propose a plausible mechanism for the enhanced photocatalytic activity of the TiO₂@TCPP nanofiber hybrid material as shown in Fig. 4.8. When TiO₂@TCPP nanofibers are irradiated under sunlight conditions, TCPP nanofibers absorb photon energy from visible light to generate e⁻/h⁺ pairs, by

**Figure 4.7:** (A) Photocatalytic performance for RhB degradation and (B) kinetic simulation curve of a) control without catalyst, b) TiO₂, c) free standing TCPP nanorods, d) TiO₂@TCPP nanofiber hybrid material.
electrons jumping from the valence band (VB) to the conduction band (CB). While one portion of generated electrons in TCPP fibers will be transferred to the conduction band of TiO$_2$, (Verma 2012) the remaining electrons will participate in the reduction of O$_2$ to ‘O$_2^-$’. On the other hand, TiO$_2$ can also harvest light energy in the UV region to generate e$^-$/h$^+$ pairs. These electrons associated with electrons ejected from TCPP nanofibers also reduce the oxygen in H$_2$O. RhB molecules are oxidatively degraded on the surfaces of both TiO$_2$ and TCPP fibers by the holes generated from sunlight illumination of the TiO$_2$@TCPP nanofiber hybrid material.

Figure 4.8: The plausible mechanism of GNPs-supported photocatalyst for Rhdamine B degradation.

4.4 Conclusions

In summary, we have successfully fabricated a TiO$_2$@TCPP nanofiber hybrid material by CTAB surfactant-assisted co-assembly of monomeric TCPP molecules with TiO$_2$ nanoparticles. The as-prepared TiO$_2$@porphyrin composite shows good integration of TiO$_2$ particles with a diameter of 15-30 nm with aggregated porphyrin nanofiber with a width of 70-90 nm and length
of several μm. The TiO$_2$@TCPP hybrid material exhibits efficient photocatalytic performance under sunlight conditions due to synergistic photocatalytic activities of both porphyrin aggregates in visible light and TiO$_2$ particles in UV light. The mechanism for photocatalytic degradation is also proposed and discussed. This work will certainly contribute more insight into the fabrication of hybrid materials, which can harvest a wide range of photon energies from sunlight for photocatalysis, provides a possible solution for environment problems where degradation of organic contaminants in an efficient process is necessary.
Chapter V

Fabrication of a Graphene@TiO$_2$@Porphyrin Hybrid Material and Its Photocatalytic Properties under Simulated Sunlight Irradiation

This chapter presents the fabrication of a nanostructured graphene@TiO$_2$@porphyrin composite was achieved via surfactant-assisted self-assembly. The obtained nanostructures were fully characterized by UV-vis, fluorescence emission spectroscopy, SEM, XRD and FTIR techniques. The applications of three components (graphene@TiO$_2$@porphyrin) based nanostructure in photocatalytic pollutant degradation Rhodamine B is reported, where TiO$_2$ and porphyrin aggregates are shown to be activated for UV and visible light respectively, resulting in a high performing composite. The possible photocatalytic mechanism of RhB degradation by graphene@TiO$_2$@porphyrins composite is discussed.
5.1 Introduction

Graphene have received considerable attention as a platform for studies concerning photocatalytic activity due to favourable properties imparted by its 2D geometry and large surface area. Graphene-based materials have shown excellent charge transfer properties, and have also been used as a scaffold for inorganic semiconductors. For example, a graphene-based nanohybrid has been employed for photocatalytic applications under visible-light irradiation.

Recently, anatase (TiO$_2$) has emerged as a promising material for applications in environmental pollutants degradation *via* oxidative or reductive methods in the presence of UV light, as its displays efficient photoactivity, non-toxicity, high stability and low cost. The mechanistic pathways for pollutant degradation have been discussed in the literature. UV radiation incident on TiO$_2$ generates electron-hole ($e^-/h^+$) pairs, which diffuse to the TiO$_2$ surface and react with OH functional groups yielding OH radical ions. This OH radical ion is involved in the degradation of the target pollutant *via* oxidation.

Porphyrians exhibit many desirable properties such as optical, catalytic and electronic activity. They have been employed to fabricate functional nanomaterials such as nanowires, nanorods, nanotubes and nanoparticles with diverse applications in fields such as photo electronics, optical devices, sensors, and solar energy conversion. The fabrication of nanostructures have been achieved *via* non-covalent interactions such as hydrogen bonding, van der Waals interactions, aromatic $\pi$-$\pi$ stacking, and coordination bonds. The nanostructures produced from porphyrins often exhibit superior properties than their discrete parent molecules. In recent years researchers have used self-assembled nanostructures of porphyrins for photodegradation of pollutants under visible-light irradiation. Therefore, it is of continued interest to fabricate porphyrin nanostructures via self-assembly, and explore its utility in photocatalytic applications.

Recently we have shown that the nanostructures obtained from TiO$_2$@porphyrin and graphene@porphyrin nanohybrid materials are efficient catalysts for
photocatalytic applications under sunlight conditions. In this paper, we report the fabrication of a nanohybrid using graphene/TiO$_2$/self-assembled porphyrin and its use as promising photocatalyst for degradation of Rhodamine B (RhB) under simulated sunlight with excellent stability. The graphene@TiO$_2$@ porphyrin material provides new opportunities as a new class of photocatalyst based on a three component nanohybrid structure.

5.2 Materials and methods

Materials

All chemicals were received from Sigma-Aldrich, (Bengaluru, Karnataka, India) and used without any further purification. Graphene nanoplates were purchased from VNgraphene. Solvents e.g. acetone, propionic acid, tetrahydrofuran (THF), N,N’-dimethylformamide (DMF), sodium hydroxide (NaOH), potassium hydroxide (KOH) and ethanol and were purchased from Ajax Finechem.

Synthesis of TiO$_2$ nanoparticles

A synthetic protocol for preparation of TiO$_2$ anatase nanostructured particles was adopted from previous work. At room temperature, TiCl$_4$ (3mL) was slowly added dropwise to 30 mL ethanol. The obtained yellow solution was gelatinized for 2 days to form a sol-gel. The sol-gel solution was dried at 80°C for 6 h. This was in turn subjected to calcination at 500 °C with a heating rate of 5 °C/min for 3 h to yield the desired product as a TiO$_2$ powder.

Synthesis of graphene@TiO$_2$@TCPP hybrid materials

Graphene@TiO$_2$@ porphyrin hybrid materials were fabricated by a typical one-spot surfactant-assisted acid-base neutralization strategy. Firstly, 8 mg of TCPP was dissolved in 1 mL of 0.2 M NaOH solution. Then 0.1 mg of graphene nanoplates and 1mg of TiO$_2$ were dispersed in TCPP solution by sonication for 30 minutes and stirred for 1h. This is assigned as a guest solution. The host solution was prepared by dissolving 70 mg CTAB in 19 mL of 0.01 M HCl solution. Subsequently, the guest solution was added drop-wise into the host solution under vigorous stirring at room temperature in the dark for 30 minutes. Certain amounts of solution were taken out at
appointed times to investigate the changing morphologies of the TCPP aggregates. Free standing TCPP nanorods were also fabricated using a similar strategy without the addition of GNPs, for comparative purposes.

**Photocatalytic investigation**

The Photocatalytic performance of graphene@TiO$_2$@porphyrin hybrid materials was evaluated by the degradation of RhB in aqueous solution. In a typical photodegradation measurement, 0.1 mg of as-prepared hybrid material was dispersed in 20 mL of an aqueous solution of RhB dye with a concentration of 5 mg L$^{-1}$. The dispersion was stirred in the dark for 30 minutes to establish an adsorption/desorption equilibrium before irradiation. The simulated sunlight source for the photocatalytic reaction was a 1500 W air cooled Xenon lamp. At the appointed time, 3.5 mL of aliquots of dispersion were taken out and centrifuged to remove photocatalyst. The photocatalytic performance of the as-fabricated samples for RhB degradation was evaluated by recording real-time UV-vis absorption spectra of RhB at a wavelength of 553 nm.

**Characterization**

Scanning electron microscopy (SEM) was undertaken using a FEI Verios 460L (operating under HV at 1 KeV, using stage bias and Circular Backscatter Detector for low conductive samples) to study the morphology and elemental composition of samples. TEM images were obtained on a JEOL 1010 TEM instrument operated at an accelerating voltage of 100 kV. Fourier transform infrared (FTIR) was performed on a PerkinElmer D100 spectrometer in attenuated total reflectance mode. A K-Alpha XPS instrument using monochromatic Al as the X-Ray source was used to collect X-ray photoelectron (XPS) spectra. The Ti 2p core level spectrum was recorded with an overall resolution of 0.1 eV. The core level spectrum was background corrected using the Shirley algorithm and chemically distinct species were resolved using a nonlinear least squares fitting procedure using C as a reference. Ultraviolet-visible (UV-vis) measurements of samples in solution (dissolved in DMF) and in solid state were carried out using a Cary 50 Bio spectrophotometer with a cell of 1 cm path length. A UV-vis spectrophotometer was also employed to investigate the photocatalytic
performance by Rodhamine B degradation. Fluorescence emission spectra were recorded on a Horiba Jobin Yvon FluoroMax®-4–Spectrofluorometer. All experiments were performed in a quartz cell with a 1 cm path length with a 420 nm excitation wavelength. All the solutions were prepared in a similar manner to that in the UV–vis study.

5.3 Results and Discussion

UV-vis absorption and fluorescence experiments were undertaken to investigate the optical properties of the porphyrin and the hybrid material consisting of graphene@TiO$_2$@porphyrin. As shown in Figure 5.1, the UV-vis spectrum of the tetrakis (4-carboxyphenyl) porphyrin (TCPP) molecule exhibits a strong Soret band at 416 nm, along with four Q bands in the 500 nm to 700 nm wavelength range, which are assigned to the transitions from $a_{1u}$ ($\pi$) and $a_{2u}$ ($\pi$) to $e^*_g(\pi)$, respectively.$^{248, 257}$ Upon fabrication of the graphene@TiO$_2$@porphyrin hybrid material, an absorption peak appears at 431 nm, with a shoulder peak at 400 nm and 445 nm as shown in Fig. 5.1A. While the peak at around 400 nm is assigned to TiO$_2$ nanoparticles, the strong absorption peak at 431 nm with a shoulder at around 445 nm, and four intensity-increased peaks in range of 500 - 700 nm are attributed to the Soret band and Q bands of aggregated TCPP crystals, respectively. It is of note that a distinct bathochromic and hypsochromic shift is observed of 15 nm from 416 nm to 431 nm in the Soret band of TCPP monomers and aggregated TCPP, respectively, indicating that most of the TCPP building blocks form J-aggregates during supramolecular assembly with the assistance of CTAB surfactant, GNPs and TiO$_2$.$^{136, 241, 250}$ The formation of TCPP nano aggregates in the hybrid material was further examined by employing fluorescence emission spectroscopy measurements. TCPP monomer exhibits two characteristic peaks at 655 nm and 714 nm upon excitation at 420 nm (Fig. 5.1B). The excitation of graphene@TiO$_2$@porphyrin hybrid material shows that the emission peak shifted from 655, 714 nm to 658, 721 nm, respectively. These red shifts in the emission peaks are likely due to coupling derived from the spatial packing of the TCPP porphyrins.$^{96}$
Figure 5.1: A) UV-vis absorption spectra and (B) Photoluminescence (PL) spectra of monomeric TCPP molecules (black line) and TCPP-TiO2-GNPs (red line).

To better understand the hybrid material formation, the morphologies of TiO2, GNPs and graphene@TiO2@ porphyrin were evaluated by field emission scanning electron microscopy (FE-SEM). As shown in Fig. 5.2A and Fig. 5.3, a size distribution in the range of 15-30 nm was achieved for TiO2. In Fig. 5.2B it is seen that the graphene nanoplates are several tens of micrometers in diameter with a thickness of about 10-20 nm.247

Figure 5.2: SEM images of (A) TiO2 and (B) graphene nanoplates.

The morphology and distribution of TCPP nano-aggregates and TiO2 in the hybrid graphene@TiO2@ porphyrin nanomaterial was observed by FE-SEM and transmission electron microscopy (TEM). As shown in Fig. 5.4A, B, Fig. 5.5 and 5.6, TCPP nanorods and TiO2 nanoparticles were successfully formed
Figure 5.3: (A) TEM image and (B) Size distribution of prepared TiO$_2$ anatase nanoparticles

on the surface of GNPs. The nanostructure of the TCPP is a rod morphology with an average diameter of 50-60 nm, and several hundreds of nanometers in length. As shown in TEM images in Figure 3C and D, the TiO$_2$@GNPs nanostructure retains its morphology and is well-integrated with TCPP nanorods. This is ascribed to TCPP aggregation on graphene@TiO$_2$ nanostructure surface via interaction of carboxyl functional groups of TCPP with the TiO$_2$ surface, which is embedded into graphene nanoplates.

The nature of the adsorption of the TCPP porphyrin onto the hybrid TiO$_2$@GNPs surface was determined by using XPS spectroscopy. Fig. 5.7A shows the deconvoluted C1s spectrum of graphene@TiO$_2$@ porphyrin, which could be divided into 4 peaks, the main peak at 284.3 eV corresponded to C=C bonds, the peaks at 286.0 eV, 287.5 e, and 288.9 eV was attributed to C=N, C–N and O–C=O bonds, respectively. The Ti 2p core level of both TiO$_2$ and the hybrid nanomaterial graphene@TiO$_2$@ porphyrin is shown in black and red lines respectively in Fig. 5.7B. Two signals at 458.1 and 464.44 eV were
Figure 5.4: A) and (B) SEM images and (C) and (D) TEM images of TCPP @TiO$_2$@GNPs composite.

Figure 5.5: SEM images of Graphene@TiO$_2$@porphyrin formed via CTAB-assisted co-assembly observed for the Ti 2p core level of TiO$_2$ due to the binding energies of Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$ respectively. For graphene@TiO$_2$@ porphyrin, a decrease in
intensity of Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$ binding energy was observed. The signals at 458.1 eV shifted to 458.2 eV and the signal at 464.4 eV significantly

Figure 5.6: EDS mapping of Graphene@TiO$_2$@porphyrin formed via CTAB-assisted co-assembly

Figure 5.7: (A) C 1s core level of graphene@TiO$_2$@porphyrin, (B) The binding energy of Ti 2p core level in TiO$_2$ (black line) and graphene@TiO$_2$@porphyrin hybrid material (red line).
diminishes. This change in binding energy was attributed to the acceptance of electron density by Ti from carbonyl group of the TCPP, which causes a decrease in binding energy of the Ti core of the nanostructure TiO$_2$@GNPs.\textsuperscript{156} This change can be assigned to weak chemisorptions.\textsuperscript{279}

FT-IR spectra experiments were performed to investigate the non-covalent interaction of TCPP on the nanostructured graphene@TiO$_2$. FT-IR spectra of TCPP, TiO$_2$ and graphene@TiO$_2$@ porphyrin hybrid material are shown in Figure 5.8. The FT-IR spectra (black line) of TCPP showed strong bands at 1725 cm$^{-1}$ (C=O stretching) and 1400 cm$^{-1}$ (C-O stretching) due to carboxyl groups. The binding interaction between TCPP with TiO$_2$@GNPs in the nanohybrid showed changes in peak position and intensity. The peak intensities at 1725 cm$^{-1}$ and 1400 cm$^{-1}$ significantly decreased. This change was due to the binding of the –COOH group of TCPP to the TiO$_2$@GNPs surface. Furthermore, the peak for TiO$_2$ also exists for graphene@TiO$_2$@ porphyrin (blue line), confirming the presence of TCPP and TiO$_2$ on the graphene surface.

\textbf{Figure 5.8:} FTIR spectra of monomeric TCPP molecules, anatase TiO$_2$ and TCPP-TiO$_2$-GNPs composite.

In the previous study, we demonstrated that TiO$_2$@TCPP nano-aggregates showed a synergistic photocatalytic effect toward RhB degradation under visible light
irradiation.\textsuperscript{288} We also showed that graphene can act as an ideal support and promoter material for enhancing the photocatalysis of TCPP aggregates.\textsuperscript{210} Thus, in this work we have incorporated TiO$_2$@TCPP nano-aggregates onto the graphene surface to evaluate the photocatalytic performance of graphene@TiO$_2$@porphyrin in comparison with GNPs, free standing TCPP and TiO$_2$ nanoparticles, for the degradation of RhB dye. The photocatalytic activity was evaluated by monitoring the decrease of the absorption peak at 553 nm. Fig. 5.9 shows the plot of ln ($A_t/A_0$) vs. time, which was used to determine the kinetics of the photocatalytic reaction, where $A_t$ is the peak intensity at time $t$, and $A_0$ is the intensity at time zero. It is obvious that negligible RhB degradation could be observed with the control conditions (without photocatalyst), suggesting that the self-sensitized photodegradation of RhB does not occur under these conditions. When free standing GNPs, TiO$_2$, and TCPP aggregates are used as photocatalysts, a decrease in RhB concentration with rate constants of ca. 1.7, 2.2 and 3.9 X 10$^{-3}$ were observed, respectively. However

\textbf{Figure 5.9: RhB photodegradation under simulated sunlight irradiation.}

the photocatalytic performance increases significantly when the graphene@TiO$_2$@porphyrin hybrid material is employed, RhB degradation reaches a rate constant of ca. 9.4 X 10$^{-3}$ min$^{-1}$. In comparison with the light sources, the
graphene@TiO$_2$@porphyrin shows higher photocatalytic activity when irradiated with simulated sunlight than with visible light (Fig. 5.10). This result further confirmed the synergistic photocatalytic activities of both TiO$_2$ and TCPP aggregates.

**Figure 5.10:** RhB photodegradation of graphene@TiO$_2$@porphyrin hybrid material as photocatalyst toward RhB dye under simulated sunlight irradiation (blue line) and visible light (black line)

It is well-known that porphyrin aggregates have a similar molecular structure to chlorophyll, which shows photocatalytic properties in many biological processes of plants and algae. Furthermore, the photocatalytic activity of TCPP aggregates of various morphologies were also well-studied previously, which demonstrated that TCPP aggregates can be employed as a photocatalyst under visible light conditions. On the other hand, TiO$_2$ nanoparticles, with band gap energy of 3.2 eV have been employed as a photocatalyst under UV irradiation for many applications. It is also known that porphyrin aggregates may increase charge separation due to exciton-coupled charge transfer processes in J-type porphyrin aggregate/TiO$_2$ hybrid materials. Graphene may improve the charge separation by suppressing the recombination of electron-hole pairs generated from irradiation of the porphyrins and TiO$_2$ under visible and UV light respectively, and hence serve to increase the lifetime of the charge carriers. Graphene also plays an important role in enhancing the
efficiency of RhB adsorption and the interfacial charge transfer to the absorbed agent.\textsuperscript{246,257}

Based on the well-documented understanding, the energy levels of each component in the hybrid materials (Fig. 5.11) and above discussions, we propose a possible mechanism for enhanced photocatalytic activity of the graphene@TiO$_2$@porphyrin hybrid material as shown in Fig. 5.12. When graphene@TiO$_2$@porphyrin hybrid material is irradiated with simulated sunlight conditions, TCPP nanorods absorb photon energy from visible light to generate e$^-$/h$^+$ pairs by electrons jumping from the valence band (VB) to the conduction band (CB),\textsuperscript{216} TiO$_2$ nanoparticles also harvest light energy in the UV region to generate e$^-$/h$^+$ pairs.\textsuperscript{282} The self-photosensitization of RhB also occurs at the wavelength of 550 nm. The generated electrons then proceed to the graphene sheets, thus increasing the e$^-$/h$^+$ charge separation. The oxidation reaction of RhB molecules to RhB$^+$ products by holes occurs on the surface of both TCPP nanorods and TiO$_2$. The oxygen in H$_2$O is reduced on the graphene sheet by the electrons generated from simulated sunlight illumination of TCPP nanorods and TiO$_2$ nanoparticles.\textsuperscript{210,288}

![Figure 5.11: Energy levels of TiO$_2$, porphyrin (TCPP) and graphene](image_url)
Figure 5.12: Proposed mechanism of photocatalytic activity by graphene@TiO$_2$@TCPP composites.

Figure 5.13: The recyclability of graphene@TiO$_2$@porphyrin hybrid material as photocatalyst toward RhB degradation

The recyclability of the graphene@TiO$_2$@porphyrin hybrid material was also evaluated as shown in Fig.5.13. The photocatalyst after first cycles of RhB degradation was centrifuged and dried at 60°C for 6 hours, then used for next cycle. This process was repeated for five cycles. The result shows an
insignificant decrease of RhB degradation efficiency (less than 7%) after 5 cycles, suggesting that the graphene@TiO$_2$@porphyrin is relatively durable for dye degradation.

5.4 Conclusions

In summary, we have successfully synthesized a graphene@TiO$_2@$ porphyrin hybrid material by CTAB surfactant and graphene-assisted co-assembly of monomeric TCPP molecules with TiO$_2$ nanoparticles. The resultant graphene@TiO$_2@$ porphyrin composite shows the good integration of TiO$_2$ particles, with a diameter of 15-30 nm and aggregated porphyrin nanorods with 50-60 nm width and several hundreds of nanometers in length on the graphene surface. The graphene@TiO$_2@$ porphyrin hybrid material exhibits enhanced photocatalytic performance compared to free standing TCPP aggregates, TiO$_2$ and GNPs. The mechanism for photocatalytic degradation is also proposed and discussed. This work will certainly contribute more insight into the fabrication of hybrid materials, which can efficiently harvest a wide range of photon energies from sunlight for photocatalysis, providing a possible solution for degradation of pollutants in the environment.
Chapter VI

Conclusions

This chapter provides the summary of the work presented in this thesis and recommendations for the future endeavours of the potential avenues
6.1 Summary of the work

The main objective of this PhD project was to fabricate porphyrin-based nanomaterials for applications in photocatalysis. During the course of the candidature, the author has successfully developed a range of porphyrin-based nanomaterials by using “dissolution-reprecipitation” and the self-assembly method such as: CuTCPP nanosheets, TCPP porphyrin nanobelts, graphene@TCPP nanorods and nanofibre hybrid materials, TiO$_2$@TCPP nanofibre composites and graphene@TiO$_2$@TCPP nanorods composites. The photocatalytic activity of the obtained materials for degradations of dyes pollutants such as RhB and MO, was investigated in detail. The plausible photocatalytic mechanism of dyes degradation by the resultant composites was proposed and discussed. Furthermore, during the candidature, the author also proposed a new method for mass production of graphene nanoplates from natural graphite. The detailed outcomes and significance of each section of the thesis are summarized below:

- A new and facile synthetic route for growing the porphyrin-based Cu TCPP nanosheets with a high specific surface area was developed for the first time. Through the various material analysis techniques, the MOFs were confirmed to have Cu-centered TCPP ligands that were participated to generate the structure of binuclear Cu$_2$(COO)$_4$ paddle wheels. It was proved that control of morphology could be exerted in dissolution/precipitation processes for precise control of nanostuctures, and this was done for the first time with a porphyrin Cu species. Importantly, copper based porphyrin nanostructures are important for nanoelectronics, and morphology is critical for control of applications.

- The author has successfully fabricated porphyrin nanobelts by the self-assembly of monomeric TCPP with arginine for the first time. The mechanism of porphyrin nanobelt formation was discussed. The obtained nanobelts show well-defined and ordered structure with a diameter of about 30 nm and a length of several micrometres. TCPP nanobelts exhibited efficient photocatalytic performance under sunlight conditions with a maximum RhB degradation up to 90% after 3h. The obtained
nanobelts are a promising class of new materials, easily fabricated under mild conditions that are promising candidates for applications in environmental catalysis.

- A new and efficient method of mass production of graphene nanoplatelets with later size of ~10-20 nm thick from natural graphite was successfully developed. The method described is very simple and avoids toxic reagents for the production of defect free and few-layered GNPs. Importantly, no chemical oxidation of graphite occurs when sodium persulfate/sulphuric acid is used for mass production of GNPs. These advances in bulk processing of graphene are always important because of the large number important technological applications that graphene may be used in.

- Well-dispered TCPP nanorods on the surface of graphene was synthesized by surfactant-assisted self-assembly of TCPP monomers adsorbed on graphene. The resulted TCPP nanorods with average diameter of 50 nm and the length of 200 nm are uniformly distributed on the surface of graphene nanoplates. The prepared graphene-supported TCPP nanorods showed enhanced photocatalytic performance compared to free standing TCPP aggregates under visible light irradiation, due to the improved charge separation and charge transfer with introduction of graphene nanoplates. The photocatalytic mechanism is also discussed and the mechanism of action warrants further investigation. This increased our understanding of the synergetic properties between graphene and porphyrin hybrid nanostructures, with possible real world applications. Once the mechanism and mode of self assembly is even better understood: a concise contribution to the understanding of such synergy will be available.

- The author also successfully synthesized GNPs@TCPP nanofiber composites by arginine-mediated self-assembly of monomeric molecules on graphene for the first time. The resulting TCPP nanofibers are 50-200 nm in diameter with approximately 5 µm in length, being densely and uniformly distributed on the surface of graphene. The GNPs@TCPP nanofiber composite showed enhanced photocatalytic performance compared to free standing TCPP aggregates under
visible light irradiation, with RhB completely degraded after 150 minutes. A possible photocatalytic pathway has also been proposed and discussed.

- A TiO$_2$@TCPP nanofiber hybrid material was fabricated by CTAB surfactant-assisted co-assembly of monomeric TCPP molecules with TiO$_2$ nanoparticles. The as-prepared TiO$_2$@porphyrin composite shows good integration of TiO$_2$ particles with a diameter of 15-30 nm with aggregated porphyrin nanofiber with a width of 70-90 nm and length of several µm. The TiO$_2$@TCPP hybrid material exhibits efficient photocatalytic performance under sunlight conditions due to synergistic photocatalytic activities of both porphyrin aggregates in visible light and TiO$_2$ particles in UV light. The mechanism for photocatalytic degradation was also proposed and discussed. Even though porphyrin have been employed as dye-sensitizer to enhance photocatalytic activity of TiO$_2$, however this is first time porphyrin has been used as an independent photocatalyst in composite with TiO$_2$. This is a step towards better control of such composites and the posible future applications, not just for a model dye, but for general environmental applications, such as a broader range of pollutants.

- Finally, the author has successfully synthesized a graphene@TiO$_2$@ porphyrin hybrid material for the first time by CTAB surfactant and graphene-assisted co-assembly of monomeric TCPP molecules with TiO$_2$ nanoparticles. The resultant graphene@TiO$_2$@ porphyrin composite shows the good integration of TiO$_2$ particles, with a diameter of 15-30 nm and aggregated porphyrin nanorods with 50-60 nm width and several hundreds of nanometers in length on the graphene surface. The graphene@TiO$_2$@ porphyrin hybrid material exhibits enhanced photocatalytic performance compared to free standing TCPP aggregates, TiO$_2$ and GNPs. The mechanism for photocatalytic degradation was also proposed and discussed, which provide deeper insight about the synergy effects of three complementary materials in photocatalysis performance under sunlight irradiation.
The work achieved from the thesis will certainly contribute more insight into the fabrication of organic semiconducting materials and organic/inorganic hybrid nanomaterials by the simple method of self-assembly. The porphyrin nanomaterials were mainly formed by J-aggregates supramolecular assemblies with the assistance of surfactants. The formation of nanostructure enables porphyrin monomers to take on exciting properties, which can efficiently harvest a wide range of photon energies from sunlight for photocatalysis, providing a possible solution for degradation of pollutants in the environment. It is a direct demonstration that controlled assembly and new nanostructures have pleasing photophysical properties.

6.2 Recommendations for future work

During the PhD candidature, the author has taken part in several fields of research, and come up with some ideas for future research listed below:

- In the thesis we showed the effective photocatalytic performance of assembled TCPP porphyrin nanostructures, therefore it is reasonable to expect that other porphyrin derivatives, with engineered electron donor properties would lead to a new nanomaterials with further enhanced photocatalytic activity. So in the future, the candidate would like to fabricate several porphyrin-based nanomaterials from other porphyrin derivatives via self-assembly. For example, design of naphthalene diimide-bearing porphyrins to increase the stability of the nanostructure, or filling the porphyrin core with metal ions to enhance the the electron donor properties of the compounds would be viable strategies. These nanomaterials will be assessed for the photocatalytic activity toward degradations of toxic substance such as: dyes, organic compound…

- Similar to TiO₂, other inorganic materials such as ZnO, Cu₂O and MnO have been used as photocatalysts for degradation of pollutants in the UV region. Therefore, in the future, the candidate would like to incorporate inorganic semiconductors such as ZnO, Cu₂O and MnO with assembled porphyrin and graphene for enhanced photocatalysis under a wide range of sunlight irradiation conditions.
• It has been demonstrated that self-assembly was one of the best approaches to fabricate nanomaterials from organic compounds. Therefore, the candidate will employ self-assembly strategies to develop a range of new supramolecular nanostructures from organic compounds, particularly with the tetraphenylethylene derivatives such as water-soluble tetraphenylethylene bearing four sulfonate groups as a sodium salt. The supramolecular nanostructures from these derivatives can be obtained from self-assembly in either solvent mixtures (solvophobic effect) or the assistance of surfactants and ionic compounds.

• Since graphene was successfully employed as a support substrate for enhanced photocatalytic performance of nanomaterials, in the next stage the candidate also would like to study oxide mixtures (Fe\textsubscript{2}O\textsubscript{3}, CuO, MgO) on the surface of graphene to form a composites for the adsorption of heavy metal ions (Pb\textsuperscript{2+}, As\textsuperscript{3+}, and As\textsuperscript{5+}). The incorporation of porphyrin nanomaterials with these composites would make it more effective for heavy metal treatment because along with high adsorpting properties, the hybrid materials could also reduce metal ions to less toxic species.

• The candidate will also study the use of graphene nanoplates as an additive for electrodes to enhance the life time and electrochemical properties of lead-acid and Li-ion batteries.
Chapter VII

References


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