Multi-dimensional micro-/nano TiO₂ reactor spheres for simultaneous organic degradation and heavy metal recovery

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**Multi-Dimensional Micro-/Nano TiO₂ Reactor
Spheres for Simultaneous Organic Degradation and
Heavy Metal Recovery**

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School of Civil and Environmental Engineering

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Spheres for Simultaneous Organic Degradation and
Heavy Metal Recovery**

Ang Koon Keong Jeremy

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ABSTRACT

The intricate link between water and energy has raised the need for a pragmatic approach towards absolving the cycle for sustainable clean water purification. Therefore, significant attention has been drawn towards advanced materials which harness solar energy for effective water purification, and are also able to manage pollutants including pathogens, organics and heavy metals. This thesis explores the feasibility of fabricating titanium dioxide (TiO_2)-based materials and its derivatives through sustainable synthesis approaches for the simultaneous degradation of organics and heavy metal recovery.

In a preliminary study, TiO_2 hollow spheres were fabricated using carbonaceous spheres as templates to investigate the structural morphology and photocatalytic oxidation of organic pollutants as well as changes to flux performance with and without photoinduced superhydrophilicity. The study demonstrated the formation of 300 nm Hierarchical TiO_2 Hollow Spheres (HTHS) composed of 13.79 nm nanoparticulates. The HTHS revealed increased UV-absorbance which suggest light scattering by the hollow morphology which resulted in enhanced organic degradation. The flux evaluation observed increased flux due to superhydrophilicity for both HTHS and P25 nanoparticulate. The P25 demonstrated higher magnitude of flux increment due to higher surface to fluid contact. However, the advantage of larger micro-structures is the pragmatic recovery of material and prevention of release out of the treatment process.

Subsequently, improvements were made to design a novel synthesis process as well as to modify the TiO_2 based spheres. The synthesis method considered a green synthesis pathway which applied minimal additives and involved a 2-step process. Firstly, the highly-concentrated metal nitrate solution penetrated the pores of the carbonaceous spheres followed by a solvothermal treatment in Ti-glycerolate during which Ion Exchange occurs. The morphology of the spheres includes micro spheres consisting of hierarchical, multi-shell hollow spheres assembled by nanoparticulates.

The succeeding study reports the novel synthesis of multi-dimensional hierarchical hollow heterojunctioned carbonaceous copper oxide (CuO)/ TiO₂ spheres (HHHS) synthesized by the penetration of copper (Cu) ions through diffusion. The HHHS of 1.5 μm revealed carbonaceous TiO₂ hierarchical thorns assembled by compact 20 nm nanoparticles and micro/nanostructured mesoporous hollow shells, consisting of heterojunctioned CuO/ CuTi₃O₈/ TiO₂ assembled by 20 to 30 nm nanoparticulates. Experimental results revealed enhanced rate of degradation by 67% compared to the TiO₂ counterpart. The HHHS initiated pollutant degradation when pollutants passed through channels of hierarchical thorn-like structures 20 nm nanoparticulates. Thereafter, the heterojunction shell filtered and adsorbed the pollutants/intermediates using the mesoporous bimodal pore distribution of 4 nm to 30 nm with an enlarged effective surface area of 30.6 m²/g. The charge and pollutant transfer were both aided by the mesoporous shell which heterojunctions mitigated the recombination of electron-hole pair while the superhydrophilicity of the surface enhanced fluid transfer. The enhanced charge separation and transfer were attributed to the mesoporous shell consisting of triple heterojunction of CuO/ CuTi₃O₈/ TiO₂ and a staggering band structure of 1.65/ 2.8/ 3.1 eV, respectively. The generation of reactive oxygen species (ROS) maintained the porosity of the shell structure and the inner hollow sphere minimized the internal volume of the sphere. This reduced the transverse distance for ROS or intermediates, thereby maximizing their interaction.

To further understand the synthesis approach, the use of Fe ions was applied at varying penetration duration to synthesize Hierarchical, Multi-Shell, Micro-/Nano, Fe-doped TiO₂ Hollow Sphere (HMS). The bactericidal capability of the material was also studied. The novel Ion Exchange approach established in this study demonstrated the penetration of Ti into the pores of the carbonaceous spheres which was otherwise usually hydrolysed due to the functional groups. The experimental results revealed that lower concentration of Fe prompted an outward diffusion of Fe ions which created voids within the pores. These voids in turn draw in Ti ions via diffusion, and the solvothermal pressure, aided the overall diffusion into the pores of the carbonaceous spheres. Furthermore, the balance of concentration at the sphere's surface created multi-shell of similar

shell morphology. The reduced compaction of metal ions within the pores of the spheres resulted in porous shells as larger amounts of glycerolate were oxidized prior to the crystallization of the metal ions, permitting larger pore size and specific surface area. Conversely, compacted pores reduced pore size and specific surface area. The morphology of the HMS revealed agglomeration of 20 nm nanoparticulates and uniform dispersion of Fe-doped TiO_2 with an enhanced visible light absorbance bandgap reduction to 2.7 eV. The bactericidal capability of the HMS revealed 40% physical lysis of bacteria under dark conditions due to the hierarchical thorn like structure and 70% bactericidal capability under visible light in 1 h. The visible absorbance of the HMS was aided by the TiO_2 - $\text{Fe}^{3+}/\text{Fe}^{2+}$ alignment which allowed the migration of electrons from the TiO_2 to Fe^{3+} of the conduction and converted it to Fe^{2+} which also mitigated the recombination of electron-hole pair. The initial physical lysis and the subsequent degradation of the bacteria wall or expose RNA/DNA through the generation of reactive oxygen species.

The simultaneous recovery of heavy metal and enhanced pollutant degradation was investigated using the 1.5V photoelectrocatalysis configuration and the previously fabricated HMS for clean water production. The cathode consisted of reduced graphene oxide (rGO) onto a flexible indium tin oxide (ITO)/ polyethylene terephthalate (PET) thin film using electrodeposition. The fabrication of the anode applies a novel low-temperature binding of TiO_2 onto flexible thin film using graphene oxide (GO). The GO-HMS was prepared by sonication of GO and HMS. Subsequently, the mixture was dried atop the cathode to fabricate the anode. The binding of the GO-HMS was due to the GO and the interface of the rGO Cathode film. The photoelectrocatalysis configuration demonstrated enhanced degradation of Cu-Azo complex dye by 20% and concurrently recovered 68% Cu metal by reducing Cu^{2+} over a period of 1 h. The experimental mechanism illustrated the extraction of GO-HMS photoexcited electrons by the anode which mitigated the recombination of electron-hole pair, and enabled the stable formation of holes. In addition, the band alignment of the three-tier TiO_2 - $\text{Fe}^{3+}/\text{Fe}^{2+}$ -GO interface offered high carrier mobility and facilitated the overall transfer of electrons. The excited TiO_2 electron first migrated into the lower band structure of the Fe^{3+} which

converted to Fe^{2+} and was subsequently released into the GO. The formation of holes enabled the production of hydroxyl radical ($\text{OH}\bullet$) for the degradation of the Cu-Azo complex which concurrently allowed the extraction of Cu^{2+} ions. The resupply of electrons towards the cathode recovered Cu through the reduction of Cu^{2+} ions into Cu(s). The formation of 1 micron cubic structure was observed for samples which contain as low as 30 Cu ppm. The build-up into larger micro-rods was attributed to the conductive nature that allowed electrons to concentrate onto the surface of conductive Cu(s) and led to the nucleation of Cu ions. This outward growth of metal reduced the required metal to surface ratio needed for recovery. The lack of reducing agents such as the Cu^{2+} resulted in the recombination of cathode electrons which disrupted the $\text{OH}\bullet$ to form hydroxide (OH^-). Therefore, the photoelectrocatalysis configuration demonstrated the combination of an intrinsic modification of TiO_2 and the extrinsic employment of electrons to enhance photocatalysis while recovering heavy metals.

In summary, the thesis explored the novel synthesis method to design and enabled the fabrication of modifiable TiO_2 micro-/nano-spheres which observed high potential for scalability, as well as practical engineering applications. The TiO_2 micro-/nano-spheres demonstrated enhanced pollutant or bacteria degradation, adsorption, and charge separation and transfer to produce clean water. By synergizing the TiO_2 micro-/nano-spheres into the photoelectrocatalysis configuration, the simultaneous degradation of organics pollutant and recovery of heavy metal attained enhanced performance which could be applied to water treatment facilities to increase the availability of water globally.

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TABLE OF CONTENTS

Abstract.....	i
Acknowledgements.....	v
List of Publications and Patent	vii
Table of Contents.....	viii
List of Tables	xiv
List of Figures	xv
Abbreviations.....	xxiv
Chapter 1.....	27
1. Introduction	27
1.1. Background.....	27
1.2. Scope and Objective.....	29
1.3. Organisation of Report.....	30
2. Literature Review.....	32
2.1. Overview	32
2.2. Water Purification through use of clean energy.....	32
2.3. Overview of Group's Past Research in Water Purification	33
2.3.1. Organic Pollutant Degradation	33
2.3.2. Bacteria Disinfection	35
2.3.1. Heavy Metal Removal	36
2.3.2. TiO ₂ Properties and Photocatalysis Enhancement	36
2.4. The Development of TiO ₂ and its Performance Obstacles in the Field of Water	38
2.4.1. TiO ₂ and its Physiochemical Properties	38
2.4.2. TiO ₂ Water Splitting	39

2.4.3.	TiO ₂ for Water Purification and its Advantages.....	40
2.4.4.	TiO ₂ and its Performance Obstacles	43
2.5.	Significance of Dimensions on Performance Improvement for Water.....	44
2.5.1.	Morphology of Nanomaterials.....	45
2.5.2.	Synthesis of TiO ₂ Hollow Spheres	48
2.5.3.	Scale Up Production of Hierarchical Micro/Nano-Multi-Shell Hollow Spheres	50
2.5.4.	Approaches to Improve the Performance of TiO ₂ Photocatalyst.....	52
2.5.5.	The application of Photogenerated Electron from TiO ₂	63
2.5.6.	Photoelectrocatalysis.....	65
2.5.7.	TiO ₂ based Configuration for Simultaneous Organic Pollutant degradation and Heavy Metal Recovery	66
2.5.8.	Summary and Perspectives on TiO ₂ and Simultaneous Organic Pollutant degradation and Heavy Metal Recovery	67
3.	Methodology	70
3.1.	Material & Synthesis Method	70
3.1.1.	Synthesis of Carbonaceous Spheres	70
3.1.2.	Synthesis of Hierarchical TiO ₂ Hollow Sphere (HTHS) and TiO ₂ Carbon Sphere (TCS).....	70
3.1.3.	Synthesis of Hierarchical Hollow Carbonaceous TiO ₂ Sphere (HHTS)	71
3.1.4.	Synthesis of Cu-Carbonaceous (Cu-C) Sphere	71
3.1.5.	Synthesis of Hierarchical Hollow Heterojunctioned Carbonaceous CuO/TiO ₂ Sphere (HHHS)	72
3.1.6.	Synthesis of Fe-Carbonaceous Sphere (Fe-C sphere)	72
3.1.7.	Synthesis of Hierarchical, Multi-shell, Micro-/Nano, Fe-doped TiO ₂ Hollow Spheres (HMS).....	72

3.1.8.	Synthesis of Graphene Oxide (GO)	73
3.1.9.	Synthesis of GO-HMS solution	73
3.1.10.	Fabrication of Flexible rGO Cathode & HMS Anode	74
3.2.	Material Characterization Methods	75
3.2.1.	Scanning Electron Microscopy (SEM)/ Field Emission Scanning Electron Microscopy (FESEM).....	75
3.2.2.	Energy Dispersive X-ray Spectrometer	76
3.2.3.	X-Ray Diffraction	76
3.2.4.	Transmission Electron Microscopy (TEM)	76
3.2.5.	UV-Visible Absorption Spectrum	77
3.2.6.	N ₂ Adsorption and Desorption Isotherm	77
3.2.7.	Fourier Transform Infrared Spectroscopy (FTIR)	77
3.3.	Application Study	78
3.3.1.	Photocatalytic Oxidation (PCO) using Methylene Blue	78
3.3.2.	Membrane Flux Evaluation	78
3.3.3.	Photocatalytic Oxidation (PCO) using Acid Orange 7	80
3.3.4.	Bactericidal Evaluation.....	81
3.3.5.	Photoelectrocatalysis of Cu-Azo Complex	83
4.	Chapter.....	85
	Introduction.....	85
	Results and Discussion	85
4.1.	Material Characterisation	85
4.1.1.	Synthesis Outline and the Morphological Characterization of HTHS and TCS	85
4.1.2.	Crystal Structure Determination.....	89

4.1.3.	Light Absorption Spectrum	90
4.2.	Water Treatment Performance.....	91
4.2.1.	Photocatalytic Activity Evaluation using Methylene Blue	91
4.2.2.	Membrane Flux Evaluation	93
4.3.	Conclusion	95
5.	Chapter	97
	Introduction.....	97
	Result and Discussion	98
5.1.	Material Characterisation and Synthesis mechanism.....	98
5.1.1.	Morphological Characterization of HHTS	98
5.1.2.	Morphological Characterization of HHHS.....	99
5.1.3.	Explanation of the Synthesis Mechanism through Morphological Evolution.....	103
5.1.4.	Crystal Structure Determination.....	105
5.1.5.	Enhanced Light Adsorption Capability	107
5.1.6.	N ₂ Adsorption and Desorption.....	110
5.2.	Water Treatment Performance and Mechanism.....	112
5.2.1.	Water Treatment Performance Evaluation	112
5.2.2.	Understanding Photocatalytic Mechanism of Micro-/Nanoreactor	115
5.3.	Conclusion	118
6.	Chapter	119
	Introduction.....	119
	Results and discussion.....	120
6.1.	Material Characterization and the Synthesis Mechanism	120
6.1.1.	Morphological Characterization of HMS	120

6.1.2.	Explanation of Synthesis Mechanism through Ion Exchange and Pore Compaction.....	124
6.1.3.	Crystal Structure Determination.....	125
6.1.4.	Enhanced Light Absorption Capability.....	127
6.1.5.	N ₂ Adsorption and Desorption Test.....	128
6.2.	Bactericidal Evaluation and Mechanism	130
6.2.1.	Bactericidal evaluation without visible light irradiation.....	130
6.2.2.	Bactericidal Evaluation using Visible Light Irradiation.....	131
6.2.3.	Bactericidal Mechanisms	132
6.3.	Conclusion	134
7.	Chapter	135
	Introduction.....	135
	Results and discussion.....	135
7.1.	Material Characterization	135
7.1.1.	Morphological Characterization of HMS Anode and rGO Cathode .	135
7.1.2.	FTIR Characterization of HMS Anode and rGO Cathode	137
7.2.	Water Treatment Performance Evaluation.....	138
7.2.1.	Water Treatment Performance Evaluation using Cu-Azo Complex	138
7.2.1.	Water Treatment Performance Evaluation and Mechanism using Azo Dye	143
7.3.	Clean Water Production Mechanism	146
7.4.	Conclusion	148
8.	Chapter	149
8.1.	Conclusion	149
8.2.	Recommendations and Future Work.....	152

9. Chapter	153
9.1. Reference	153
Appendix A	a-1
Appendix B	b-1
Appendix C	c-1
Appendix D	d-1
Appendix E	e-1

LIST OF TABLES

Table 1 Significant Factors and Applicability of TiO_2 photocatalyst.....	68
Table 1 Scherrer Equation estimated grain size of the (101) Anatase Phase of the HTHS and P25.	b-1
Table 2 Scherrer Equation estimated grain size of the (101) Anatase Phase and the (002) CuO phase of the HHHS and HHTS.	c-8
Table 3 Estimated grain size of the 101 Anatase Phase respective HMS using the Scherrer Equation.....	d-3

LIST OF FIGURES

Figure 2.3-1 Membrane flux in dead end filtration device in comparison to particle size (Pan et al., 2008).....	35
Figure 2.3-2 Decomplexation of Cu^{2+} from Cu-EDTA and photocatalytic reduction of Cu^{2+} onto the TiO_2 nanofibers (Lee et al., 2015).....	36
Figure 2.3-3 Illustration of the respective band positions and spatial separation of photogenerated interparticle charges during photocatalytic activation of the heterojunction TiO_2 / SrTiO_3 catalyst. (Ng et al., 2010).....	37
Figure 2.4-1 Relationship between band structure of semiconductor and redox potentials of water splitting (Kudo & Miseki, 2009).....	38
Figure 2.4-2 Photo-induced formation mechanism of electron and hole pair in a TiO_2 semiconductor the presence of water (Chong et al., 2010).	39
Figure 2.4-3 Mechanism of photo-induced hydrophilicity (Fujishima et al., 2000)	42
Figure 2.4-4 The solar energy distribution (Biernat, Malinowski, & Gnat, 2013) ..	43
Figure 2.5-1 Structural dimension of nanostructured TiO_2 (Hussein & Shaheed, 2015)	45
Figure 2.5-2 Light scattering of hierarchical surfaces compared to smooth surfaces (P. Gao, Li, Sun, & Ng, 2014)	46
Figure 2.5-3 Schematic illustration of multi-shell hollow spheres and multiple scattering (Sun Hye Hwang et al., 2014)	47
Figure 2.5-4 Fabrication of the double-shell TiO_2 hollow spheres using a sol-gel and the silica-protected calcination process. (S. Li et al., 2013)	50
Figure 2.5-5 Sequential templating method penetrating highly concentrated metal ions into the pores of the carbonaceous microsphere (Xiaoyong Lai et al., 2011)..	51
Figure 2.5-6 TEM images of carbonaceous microspheres after soaking in a 3 mol/L solution of iron nitrate: a) before heating, and after heating at b) 270 °C, c) 350°C, d) 430 °C, and e) 500 °C (X. Lai et al., 2011).....	52
Figure 2.5-7 Polyhedral representation of the rutile (A) and anatase (B) (Landmann, Rauls, & Schmidt, 2012).....	54
Figure 2.5-8 Fe-doping which results in the formation of Fe^{3+} energy level within the bandgap which allow the migration of charges from TiO_2 and acts as charge	

traps for anti-combination of electron-hole pair (Ali, Tripathi, Ameer, et al., 2017)	56
Figure 2.5-9 C-doped TiO ₂ under UV or visible light irradiation. CB and VB denote the conduction and valence band of the TiO ₂ particle, respectively. The broken line represents the C induced bandgap level that should lie between 1.4 and 1.9 V vs NHE (Yiseul Park et al., 2009).	58
Figure 2.5-10 Electron injection in composite semiconductors (Ni et al., 2007)	59
Figure 2.5-11 Schematic band diagram of the charges transfer between CuO/TiO ₂ heterojunctions (Siew Siang Lee et al., 2013).	60
Figure 2.5-12 Photoinduced injection of dye electron onto the conduction band of TiO ₂ (Ola & Maroto-Valer, 2015).	61
Figure 2.5-13 Photocatalytic activity for GO–TiO ₂ and the electron migration to form O ₂ ^{•-} and subsequently OH [•] for pollutant degradation (J. Liu et al., 2010).	62
Figure 2.5-14 Principle of operation and energy level scheme of the dye-sensitized nanocrystalline solar cell (Grätzel, 2003).	64
Figure 2.5-15 Photoelectrocatalysis configuration for the separation of redox function for pollutant degradation (Garcia-Segura et al., 2013).	66
Figure 3.1-1 (a) Fabrication method of the Flexible Thin Film rGO Cathode layer through electrodeposition, and (b) the HMS Anode fabricated by oven-drying GO-HMS atop the previously fabricated rGO Cathode.	75
Figure 3.3-1 Schematic diagram of the Membrane Flux Evaluation Setup.	79
Figure 3.3-2 Schematic diagram to illustrate the evaluation of the water treatment performance under UV-light and Acid Orange 7 as the probe molecule.	80
Figure 3.3-3 Visible light degradation of E. Coli using Solar Simulator	82
Figure 3.3-4 Experiment setup of the water treatment process with the three configurations namely the (a) 1.5V Power Supply, (b) Loop and (c) Open Circuit setup.	84
Figure 4.1-1 Carbonaceous (C) spheres synthesised via hydrothermal process (a) penetration of Ti into the C spheres, (b) and the solidification of Ti/C spheres, produces Ti-glycolate/ C sphere (TGC). The calcination process (c) produces Ti Hollow Spheres while the (d) carbonization process produces Ti carbon sphere in nitrogen atmosphere.	86

Figure 4.1-2. (a) Carbonaceous (C) Spheres synthesised using glucose in a hydrothermal process, (b) Ti-glycolate / C spheres (TGC) formed after penetration and solidification of Ti via solvothermal treatment. (c & d) Hierarchical TiO₂ Hollow Spheres (HTHS) after calcination at 500°C at a ramping rate of 6 °C/min and holding time of 4 h. (e) The expanded image of (d) revealing the hollow core of the HTHS (f) Titanium Carbon Spheres (TCS) produced using the carbonization of Ti-glycolate / C spheres in nitrogen atmosphere. 87

Figure 4.1-3 The calcination temperature of 500°C was applied for all sphere with changes to other factors. (a) HTHS with 20 h penetration, 4 h solidification duration, calcination ramping rate of 6 °C/min, and a holding time of 4h (b) HTHS with reduced penetration time of 12 h and 2 h solidification time, observed structural dissolution after ramping rate 6 °C/min and holding time of 4h. (c) HTHS of 20 h penetration, 4 h solidification with ramping rate of 6 °C/min and holding time of 1h, (d) HTHS ramping rate of 10 °C/min and a holding time of 1h..... 89

Figure 4.1-4 XRD pattern of Hierarchical TiO₂ Hollow Sphere and P25 Nanoparticles 90

Figure 4.1-5 Light Absorbance Spectrum of HTHS and P25..... 91

Figure 4.2-1 (a) Photocatalytic degradation of MB, rate of degradation for (b) Hierarchical TiO₂ hollow spheres (HTHS) and (c) the P25 nanoparticles using Langmuir-Hinshelwood Kinetics..... 93

Figure 4.2-2 Permeate flux evaluation of UV radiated (HTHS UV and P25 UV) and dark conditioned (HTHS Dark and P25 Dark) using dead end filtration with DI water as the medium and an applied pressure of 5 PSI..... 94

Figure 4.2-3 Illustration of the superhydrophilicity and the water contact surface of HTHS and P25. (a) Cross-sectional view of HTHS (grey) on support membrane (blue) and the larger water channel reducing the influence of superhydrophilicity. (b) Cross-sectional view of P25 nanoparticles (green) on support membrane (blue) and a higher water to P25 nanoparticles contact due to the narrower water channel. 95

Figure 5.1-1. (a) Carbonaceous spheres. (b) dark field FESEM-STEM image of the HHTS with the visible hollow core. (c) The hollow structure of the HHTS spheres

with observable porous support structure and the subsequent growth of the thorn-like hierarchical structure. (d) Schematic diagram of (c). 99

Figure 5.1-2. (a) The encapsulation and synthesis of Ti-glycerolate/ Cu Carbonate Hydroxide Hydrate/ C spheres (TCCS). (b) Schematic diagram illustrating the penetrated Cu ions into the pores of the sphere and the Ti hierarchical structures. (c) The (purple) layer illustrates the interacted Ti-Cu ions, the deeper (blue) remains as Cu Carbonate Hydroxide Hydrate due to the depth of penetration, the (green) reveal the Ti-Cu interaction at the Ti thorns layer. (d) TEM imaging of the Multi-shell Hierarchical Structure of the HHHS revealing the inner sphere within the hollow spheres. (e) Schematic diagram of the three-tier make up of the HHHS including the carbonaceous TiO₂ hierarchical thorn structure (grey), the heterojunction surface layer of carbonaceous CuO/TiO₂ (purple) and a CuO inner shell (blue). (f) The enlarged image of the heterojunction layer is made up of a porous inner layer (purple) and the TiO₂/CuO nanoparticles due to the outward diffusion of the Cu-ions. (g) The nanoparticulate interior morphology (purple) of the HHHS formed by the CuO, the CuO/TiO₂ heterojunction (green) and the hierarchical surface structure carbonaceous TiO₂. (h) The TEM imaging revealing the grainy 20-30 nm nanoparticulate heterojunctions with the lattice of TiO₂ and CuO and insert of Fig 5.1-2 (h) revealing CuTi₃O₈ and CuO. (i) The TEM image of the hierarchical thorn made of compact 20 nm nanocrystals. The EDX mapping of the (j) Ti elements and (k) Cu elements displaying the element composition at the shell (purple), the diffusion of Cu away from the shell (green), and the Ti dominated thorns (yellow). 102

Figure 5.1-3. Schematic diagram to illustrate the synthesis process of the Hierarchical Hollow Heterojunctioned Carbonaceous CuO/TiO₂ Spheres. a) Carbonaceous spheres obtained via hydrothermal synthesis of glucose undergo b) penetration of Cu²⁺ through diffusion. c) The cross-section view of Cu ions penetrated the pores of carbonaceous spheres forming Cu Carbonate Hydroxide Hydrate spheres (Cu-C spheres). The Cu-C spheres undergo solvothermal process to d) obtain the growth of Ti nanocrystals on the surface of the Spheres and the interaction between the Cu and Ti to form heterojunctions. e) Cross-section view showing the growth of the interconnected Ti-glycerolate hierarchical surface and CuO-C Spheres (TCCS) which undergo calcination to obtain f) multi-shell

Hierarchical Hollow Heterojunctioned Carbonaceous CuO/TiO ₂ Spheres, the cross-section reveals the contraction and formation of the inner shells after the removal of the carbonaceous core.	105
Figure 5.1-4. (a) XRD pattern of the synthesized HHHS revealing anatase TiO ₂ and CuO while the HHTS matches anatase TiO ₂ . (b) the shifting of the 101 phase of the HHHS and HHTS compared to P25 as the reference material.	107
Figure 5.1-5. (a) UV-vis absorbance spectra of HHHS, HHTS and P25 and the insert depicting the corresponding Kubelka-Munk function which estimated the band gap changes of the materials. (b) Schematic illustration of light scattering between the hierarchical structure.	109
Figure 5.1-6. Nitrogen adsorption BET isotherm curve of (a) HHHS and (b) HHTS	111
Figure 5.1-7. BJH pore size distributions of HHHS, HHTS and P25.....	112
Figure 5.2-1. (a) Relationship of pollutant adsorption (%) within 1 h of dark adsorption against the Effective Surface Area (m ² /g). (b) Photocatalytic degradation of AO7 in the presence of the HHHS, HHTS, P25	113
Figure 5.2-2. Rate of degradation of AO7 for the HHHS, HHTS, P25	115
Figure 5.2-3. Schematic diagram for the proposed mechanism of the pollutant degradation pathway through HHHS under-photon irradiation. The hierarchical thorns act as water channels which generate ROS for the degradation of pollutant before encountering the mesopores for adsorption and degradation. The mechanism of degradation is illustrated for the hierarchical water channels and the interface between the hierarchical thorns and the mesoporous shell. The inner hollow sphere guides the flow of water and generates an interior region containing ROS and reduces the transverse from the pollutant dominated mesopores for enhanced pollutant degradation.	117
Figure 6.1-1 FESEM imaging of (a) morphology of the Fe-C sphere (6 h) with nanoparticulate surface. (b) HMS-6 revealing the hierarchical surface thorns and the insert showing the 20 nm nanoparticulates which assembled to form the HMS...	121
Figure 6.1-2. Fabrication of (a) HMS-6 and the corresponding EDX elemental mapping of (b) Ti and (c) Fe, (d) HMS-24 and the corresponding EDX elemental	

mapping of (e) Ti and (f) Fe, and (g) HMS-48 and the corresponding EDX elemental mapping of (h) Ti and (i) Fe.....	122
Figure 6.1-3. (a) Fe-C spheres and the corresponding (b) EDX analysis of low Fe content. (c) The FESEM imaging of HMS-1 with the hierarchical thorn like structure and nanoparticulate inner sphere. (d) The corresponding EDX analysis revealing the formation of Ti dominated inner shell revealing the inter-diffusion of Ti-glycerolate and Fe, while Fe element remains undetectable.....	124
Figure 6.1-4. Ion exchange synthesis process between Fe ions (orange) and Ti-glycerolate (blue) (a) HMS-6 (6 h Fe penetrated sphere) undergo uncompact ion exchange which result in (b) uncompact pores and calcination process creates void as glycerol oxidises to fabricate (c) nanoparticulate inner shell. (d) HMS-24 (24 h Fe penetrated sphere) undergo compact ion exchange which result in (e) compact pores. The calcination process generates lesser void due to higher metal ions content as glycerol oxidises to fabricate (f) smooth inner shell due to the quick convergence of ions.	125
Figure 6.1-5. XRD pattern of HMS-6, HMS-24 and HMS-48 revealing anatase TiO ₂ phases and the rutile phase in HMS-24.....	127
Figure 6.1-6. (a) UV-vis absorbance spectrum of HMS-6 and HMS-48 and (b) the corresponding Kubelka-Munk function revealing the estimated bandgap reduction with increased Fe-doping concentration.	128
Figure 6.1-7. The N ₂ adsorption-desorption isotherms of (a) HMS-6, (c) HMS-24 and (e) HMS-48, and the respective pore size distribution (b) HMS-6, (d) HMS-24 and (e) HMS-48.	130
Figure 6.2-1. Cell viability due to physical bacterial lysis using HMS-6 compared to a test with no photocatalyst.....	131
Figure 6.2-2. Cell Viability of HMS and Photolysis (without HMS) after 1h of visible light irradiation.	132
Figure 6.2-3. The Fe-doped TiO ₂ resulted in the formation of Fe ³⁺ which trap charges at the conduction band (CB) through the conversion to Fe ²⁺ and the hole at the valence band (VB) converting Fe ³⁺ to Fe ⁴⁺ . The band of the Fe ³⁺ mitigates recombination of electron-hole by trapping and releasing charges via the redox reaction with water. The HMS thorns of ~300 nm enable piercing and attachment	

onto the E. Coli. The cell membrane lysis allows for the access of $\text{OH}^\bullet$ to enter and degrade the RNA/DNA causing cell death.	133
Figure 7.1-1. (a) Flexible ITO/PET thin film support, (b) electrodeposited rGO Cathode by reducing GO onto the ITO/PET under 3V for 5 mins, (c) synthesized GO-HMS through sonication of GO and HMS solution for 90 mins, (d) Fabricated HMS Anode by drying GO-HMS atop the rGO Cathode.	136
Figure 7.1-2. FTIR (a) Transmittance of GO-HMS, HMS and GO, (b) expanded image of (a) and the changes in GO-HMS at (c) Absorbance of rGO Cathode, HMS Anode and the difference in absorbance pattern between the cathode and anode, and (d) the expanded image of (c) with the changes at 877, 1150 and 1250 1710.	138
Figure 7.2-1 (a) The change in concentration for the three configurations. (b) The corresponding rate of degradation. (c) The recovery of mg copper per cm^2 cathode surface area.	140
Figure 7.2-2. FESEM imaging of reduced Cu particles in (a) 10 mmol/L Cu solution and (b) 30 mg/L Cu solution. (c) No observable Cu content from the Loop configuration after 1h. The corresponding EDX analysis of Cu (d) 10 mmol/L Cu solution and (e) 30 mg/L Cu solution. (f) The Loop rGO Cathode with no observed Cu content. The uniform dispersion of Oxygen (O) element (g) 10 mmol/L Cu solution, (h) 30 mg/L Cu solution, (i) Loop configuration. The sum spectrum (j) 10 mmol/L Cu solution, (k) 30 mg/L Cu solution, (l) Loop configuration.	142
Figure 7.2-3. (a) The change in decolourisation of the azo dye under the alternating configuration of Open Circuit (OC) and Power Supply (PS) and (b) its corresponding rate constant of degradation taken from the first 40 mins.	144
Figure 7.2-4. (a) The mechanism of photocatalysis under the (a) Open Circuit Configuration compared to the (b) Power Supply Configuration for the degradation of Azo dye (AO7).	145
Figure 7.3-1. The (1) PCO which occurs at the anode initiating the excitation of electrons and (2) transfer towards the power supply due to the potential difference. (3) The generation of electrons from the power supply and the (4) electrochemical reduction which occurs at the cathode which reduce Cu^{2+} to Cu^+ and the recovery of Cu(s)	146

Figure 7.3-2 Illustration of the photoelectrocatalysis mechanism which extracted electrons to promote stable oxidative sites for the generation of $\text{OH}^\bullet$ for the degradation of Cu-Azo Complex. The specific utilization of the reintroduced electrons for the recovery of Cu ions attracted by the negative (-ve) charge promoted the reduction of Cu^{2+} to Cu(s) for the subsequent formation of Cu nucleation sites. The utilization of electrons prevented the reverse reaction of the $\text{OH}^\bullet$ to OH^- .	148
Figure 1 HTHS XRD indexing to Anatase TiO_2	b-1
Figure 2 Individual data of the PCO of (a) HTHS and (b) P25.	B-2
Figure 3 Individual data of the permeate flux of (a) UV HTHS, (b) Dark HTHS, (c) UV P25 and (d) Dark P25.	b-2
Figure 4 FESEM image of HHHS.	c-1
Figure 5 TEM image of inner sphere shown by the darker solid sphere within the round hollow shell.	c-2
Figure 6 EDX analysis of HHHS	c-3
Figure 7 HHHS XRD indexing to Anatase TiO_2 , CuO & CuTi_3O_8 .	c-4
Figure 8 HHHS Individual XRD indexing to Anatase TiO_2 .	c-4
Figure 9 HHHS Individual XRD indexing to CuO.	c-5
Figure 10 HHHS Individual XRD indexing to CuTi_3O_8	c-5
Figure 11 HHTS XRD indexing to Anatase TiO_2	c-6
Figure 12 Carbonaceous Spheres XRD pattern	c-6
Figure 13 Cu-C spheres XRD indexing to Copper Carbonate Hydroxide Hydrate	c-7
Figure 14 Kubelka-Munk function reflecting HHTS Carbonaceous TiO_2 with ~3.1 eV, the shift in the eV of the HHHS due to possible hypothetical CuTi_3O_8 with an ~2.8 eV and the presence of CuO with ~1.65 eV.	c-7
Figure 15 HMS-6 XRD indexing to Anatase TiO_2	d-1
Figure 16 HMS-24 XRD indexing to Anatase and Rutile TiO_2	d-1
Figure 17 HMS-48 XRD indexing to Anatase TiO_2 .	d-1
Figure 18 TGA of HMS-48 and the weight reduction at 260 °C which reveal the oxidation of glycerolate and the carbonaceous spheres at 300 °C.	d-2
Figure 19 Individual plot of Dark experiment (a) blank with no catalyst, (b) with HMS-6.	d-2

Figure 20 Individual plot of visible light bacteria degradation (a) Photolysis, (b) HMS-6, (c) HMS-24 and (d) HMS-48.....	d-3
Figure 21 Cathode after copper recovery (left to right) power supply, loop and open circuit.	e-1
Figure 22 (a) Degradation of 30 mg/L Cu Azo Complex after 1h. (b) Rate of Degradation of 30 mg/L Cu Azo Complex after 1h.	e-1
Figure 23 Cyclic Voltammetry of (a) Cu Azo Complex and (b) Azo Dye, using HMS Anode and rGO Cathode.	e-2
Figure 24 Rate of degradation of the Azo Dye for 40 mins in alternation of the Open Circuit and Power Supply Configuration.....	e-2
Figure 25 Electrochemical oxidation of azo dye decolourisation at the anode (a) with and (b) without TiO_2 under dark for a period of 1h.....	e-3

ABBREVIATIONS

Acid Orange 7	AO7
Absorbance	A
Absorption Coefficient	k
Angstrom	Å
Band Gap Energy	E _G
Barrette Joynere Halenda	BJH
Brunauer–Emmett–Teller	BET
Centimetre	cm
Colony Forming Units	CFU
Conduction Band	CB
Conduction Band Electron	e ⁻ _{CB}
Cu-Carbonaceous	Cu-C
Degree Celsius	°C
P25 nanoparticles	P25
Distilled Water	DI Water
Dye Sensitised Solar Cells	DSSCs
Electron Volts	eV
Ethylenediaminetetraacetic Acid	EDTA
Energy Dispersive X-ray Spectrometer	EDX
Escherichia Coli	<i>E. coli</i>
Fe-Carbonaceous Sphere	Fe-C sphere
Field Emission Scanning Electron Microscopy	FESEM
Fourier Transform Infrared Spectrometer	FTIR
Full Width of Half Maximum	FWHM
FWHM	β
Grain diameter	d _c
Graphene Oxide	GO
Hierarchical Hollow Carbonaceous TiO ₂ Sphere	HHTS
Hierarchical Hollow Heterojunctioned Carbonaceous Copper Oxide (CuO)/ TiO ₂ Spheres	HHHS
Hierarchical TiO ₂ Hollow Sphere	HTHS
Hierarchical, Multi-shell, Micro-/Nano, Fe-doped TiO ₂ Hollow Spheres	HMS
Hour	h
Hydroperoxyl Anion	HOO ⁻
Hydroperoxyl Radical	HOO [•]
Hydroxide Ion	OH ⁻

Hydroxyl Radical	OH [•]
Indium Tin Oxide	ITO
Kelvin	K
Kilogram	kg
Kilovolts	kV
Litres	L
Lysogeny broth	LB
Manganese oxide octahedral molecular sieve	K-OMS-2
Methylene Blue	MB
Metre	m
Micrometre	μm
Milligram	mg
Milliwatt	mW
Millilitres	ml
Minute	min
Moles	mol
Nanometre	nm
Negative	-ve
Normal Hydrogen Electrode	NHE
Organic Pollutants	OR
Polyethersulfone	PES
Photocatalytic Oxidation	PCO
Photoelectrochemical cells	PEC
Photon Energy	hν
Polyethylene Terephthalate	PET
Pound per Square Inch	PSI
Reactive Oxygen Species	ROS
Reduced Graphene Oxide	rGO
Reflectance	R
Revolutions per minute	rpm
Scanning Electron Microscopy	SEM
Seconds	s
Superoxide Radical	O ₂ ^{•-}
Tetraethyl Orthosilicate	TEOS
Theta	θ
TiO ₂ Carbon Sphere	TCS
Ti-glycerolate/ Cu Carbonate Hydroxide Hydrate/ Carbonaceous Spheres	TCCS
Titanium Butoxide	TBOT

Titanium Dioxide	TiO ₂
Trapped Electron	e ⁻ _{TR}
Trapped Hole	h ⁺ _{TR}
Ultraviolet	UV
UV-Visible	UV-Vis
Valence Band Hole	h ⁺ _{VB}
Volatile organic compounds	VOCs
Volt	V
Watt	W
Wavelength	λ
X-Ray Diffraction	XRD

CHAPTER 1

1. INTRODUCTION

1.1. BACKGROUND

Amidst the global challenges in the current century, sustainable energy, access to clean water as well as climate change have been widely recognized as the most significant issues that need to be resolved (Smalley, 2005). However, complementing solutions to these issues have yet to be found.

The demand for freshwater is increasing as a result of factors such as competing demands of a globally increasing population, increasing agricultural demand as well as inconsistent weather patterns due to climate changes. According to United Nation average projections, it is estimated that the global population will increase by about 2.9 billion between now and 2050 (Rockstrom, 2003). However, the World Health Organization (WHO) reports an estimated global population of 1.1 billion people still have no access to safe drinking water (UNICEF & WHO, 2014). In addition to being essential for human survival, water is also required for industrialization, urbanization and national development. The increase in total water usage is correlated with urbanization and increased living standards (Miletto & Connor, 2014). This demand ranges from food production to manufacturing industries, energy sectors to economic development, environmental, hygiene and many others (Mulder, Hagens, & Fisher, 2010; Varis & Vakkilainen, 2001). Rapid industrialization and urbanization is ongoing in major developing countries especially the Brazil, Russia, India, China and South Africa. Amidst the rise in global population and urbanization, water adequacy will require innovative solutions to provide more sustainable water treatment process.

Energy consumption is another key issue which is deeply intertwined with the generation of water. Countries recover precious water using energy intensive desalination technology. It is estimated that a total of 16000 desalination plants

worldwide have since been constructed (Miletto & Connor, 2014). Hence, energy intensive generation of water is a major challenge in meeting the demand for water. (Vorosmarty, Green, Salisbury, & Lammers, 2000). The reliance fossil fuel is still the leading source of energy worldwide. According to the International Energy Outlook 2016 report ((EIA), 2016), the global consumption of liquid fuel usage stands at 90 million barrel/day in 2012 and is expected to increase to 121 million barrel/day in 2040.

Lastly, the global emissions of greenhouse gases due to the burning of non-renewable energy resources is heavily criticized as the leading factor of climate change. In view of the rapid global growth, the need for shift in the reliance in fossil fuel is imperative to meet the energy concern of the future. In summary, there is intricate interconnectivity between water and energy, energy and climate change, climate change and water. Hence, innovative technologies need to complement the various revolving intricacies and meet social, industrial and economical expectations.

Pollution is also a major issue which needs to be considered when ensuring the availability of clean water. Within water pollutant classification, three types of main pollutants exist - disease-causing pathogens, oxygen demanding organics which deplete dissolved oxygen and causes marine death, and persistent water-soluble inorganics which are non-degradable. The thesis will examine water purification methods which cater to the degradation of organics, the recovery of inorganic metal ions and elimination of bactericidal activity. The aim is to harvest solar energy in tandem with photoelectrocatalysis process for water purification to resolve the intricate links between the challenges of water, energy and climate change.

1.2. SCOPE AND OBJECTIVE

The overall objective for this study is to employ electrons through photoelectrocatalysis to enhance organic degradation while recovering heavy metals. The approach considers a sustainable and scalable synthesis method to fabricate Micro-/Nano Reactor Spheres integrating properties of Hierarchical, Multi-Shell, Hollow, Modifiable Titanium Dioxide (TiO_2) that will bridge the gap between solar energy harnessing and clean water production.

The explicit objectives are as follows:

- (1) To examine the TiO_2 based spherical morphology for its material's application of organic pollutant degradation.
- (2) To develop a novel and sustainable method for scalable production of a reactor type sphere. The sphere incorporates morphological properties such as, Hierarchical, Multi-Shell, Hollow, Micro-/Nano Structure, and Heterojunctioned Copper (II) oxide and TiO_2 which will be examined for its performance in organic pollutant degradation.
- (3) To explore the mechanism of the Ion Exchange approach and widen the applicability using Titanium (Ti) and Iron (Fe) ions. To fabricate Fe-doped TiO_2 Hierarchical, Multi-Shell, Hollow Spheres and examine the material for its bactericidal capability through the physical and photocatalytic lysis of bacteria.
- (4) To investigate photoelectrocatalysis mechanism for the simultaneous enhancement of photocatalytic oxidation process and reduction of heavy metal ions for heavy metal recovery.

1.3. ORGANISATION OF REPORT

The thesis comprises of 9 chapters and 5 appendices. **Chapters 1, 2 and 3** consist of a brief introduction, literature review and experiment methodology respectively

Chapter 4 reports preliminary characterization of Hierarchical TiO₂ Hollow Sphere using the hard template approach in conjunction with the solvothermal synthesis method. The chapter seeks to understanding the spherical morphology and assess the characteristic in light absorbance, and evaluate its photocatalytic oxidation of organics and membrane flux performance.

Chapter 5 reports on the novel multi-dimensional micro-/nano-reactor spheres for water treatment applying the original synthesis approach which further considers sustainable attention to streamline the use of additives. The synthesis process adopts a penetration approach to incorporate micro-/nano heterojunction of CuO/TiO₂, featuring hierarchical and multi-shell hollow spheres without multiple templating steps. The sphere features assembly of 20-30 nm nanoparticulate with a mesoporous shell consisting of bimodal pore distribution and a triple heterojunction shell of CuO/ CuTi₃O₈/TiO₂. The reactor type sphere was assessed on its organic degradation of pollutants.

Chapter 6 further explore the synthesis mechanism using higher stability Fe resulting in the fabrication of Fe-doped TiO₂ spheres integrating micro-/nano, hierarchical, multi-shell hollow. The chapter investigates and ascertains the novel Ion Exchange Approach between the Fe and Ti ions during the synthesis process. The report further studies the metal ion compaction within the pores which determines the surface area and pores size. The Fe-doped spheres was assessed on its bactericidal capability using the physical and photocatalytic lysis of bacteria.

Chapter 7 reports the use of photoelectrocatalysis to simultaneously enhance degradation of organics and the recovery of heavy metals using the Fe-doped TiO₂ spheres. The study demonstrates an innovative, low cost, low temperature binding of TiO₂ onto flexible indium tin oxide/polyethylene terephthalate thin film at room temperature using graphene oxide. The study exhibits the harnessing of electrons at

the cathode for heavy metal recovery while the extracted electrons from the anode aided in the production of oxidative holes and mitigation of electron-hole recombination to enhanced overall organic degradation.

Chapter 8 concludes the experimental details and discussion obtained from the findings of **Chapters 4, 5, 6 and 7**. Furthermore, recommendations and suggestions are also provided for the continuation of future work.

Chapter 9 compiles the list of references applied in this thesis.

2. LITERATURE REVIEW

2.1. OVERVIEW

The literature review explores the use of Titanium Dioxide (TiO_2) in the field of water purification. The review will first give a brief introduction of the group's past research on TiO_2 followed by the mechanism of TiO_2 in generation of electron-hole for the water purification as well as the issues and challenges pertaining to TiO_2 applications. The review then addresses the means to overcome challenges using morphology augmentation, modification to the crystal structure of TiO_2 , and scalable synthesis methods which are adaptable to such modification. The employment of photoexcited electrons in various applications will help understand the aspects and specific role of electron and holes for their respective purposes. Lastly, the review will summarise the key aspects of TiO_2 and its properties which will be catered to photoelectrocatalysis for the degradation of organics, bacteria and heavy metal recovery.

2.2. WATER PURIFICATION THROUGH USE OF CLEAN ENERGY

The need to develop clean energy and low energy water treatment methods has been a growing need in this century (Smalley, 2005). The harvesting of solar energy using TiO_2 promotes the use of clean, free and renewable resources which complements initiatives to counter climate change. (X. Chen & Mao, 2007). Furthermore, the use of TiO_2 is well accepted due to its low cost, inertness and non-toxicity have made it suitable for numerous commercial ingredients such as sunscreens (Zallen & Moret, 2006), paint pigments (Braun, Baidins, & Marganski, 1992), as well as food colouring (Fujishima, Rao, & Tryk, 2000; Pfaff & Reynders, 1999). Research into TiO_2 applications has expanded into wide ranging fields which includes: photocatalytic oxidation of organic pollutant, bacteria disinfection and heavy metal recovery in the field of water purification as well as photocatalytic hydrogen generation, dye sensitised solar cell devices, and lithium ion batteries in the energy sector.

In the field of water treatment, photocatalytic oxidation (PCO) and superhydrophilicity was observed in TiO₂ under UV-irradiation. (Fujishima et al., 2000; Kazuhito, Hiroshi, & Akira, 2005). The rate of organic oxidation determines the performance of photocatalysts, and typically, the higher the surface area of the photocatalyst, the better the photocatalytic performance due to the higher surface adsorption (Lachheb et al., 2002). The complementing property of TiO₂ semiconductor photocatalyst in the field of water treatment is the photo-induced superhydrophilicity. This property increases the material's affinity with water, hence, making it suitable for water related processes. The function of PCO led to the concept of self-cleaning ceramic membranes, which removes the foulant issue for the current membrane technology (Albu, Ghicov, Macak, Hahn, & Schmuki, 2007; H. Choi, Sofranko, & Dionysiou, 2006; Hyeok Choi, Stathatos, & Dionysiou, 2006; Huang, Leal, & Li, 2008; D. D. Sun, Tay, & Tan, 2003; X. Zhang, Du, Lee, Sun, & Leckie, 2008b; X. Zhang, Zhang, Ng, & Sun, 2009).

2.3. OVERVIEW OF GROUP'S PAST RESEARCH IN WATER PURIFICATION

There are generally 3 main components which affect water quality - organic pollutants, the presence of microorganisms and the presence of heavy metals. Our group's past research observed that the morphology of nanostructures provides crucial advantages in the field of water purification. The following sub-topic will briefly introduce the past research done by the group.

2.3.1. ORGANIC POLLUTANT DEGRADATION

The applicability of TiO₂ photocatalysts for organic degradation has been extensively researched in our group. Organic pollutants, including water based organic pollutants found in soil such as humic acid have been investigated. (T. Zhang, Yan, & Sun, 2012; X. Zhang, Du, Lee, Sun, & Leckie, 2008a; X. Zhang, A. J. Du, et al., 2008b; X. Zhang, Zhang, et al., 2009), (Xu, Ng, Zhang, Bai, & Sun, 2011; X. Zhang, D. D. Sun, G. Li, & Y. Wang, 2008), Recalcitrant AO7 dyes generated from textile industries and ethylenediaminetetraacetic acid (EDTA)

usually generated from textile, electroplating and nuclear industries (Lee, Bai, Liu, & Sun, 2015) have also been investigated. The key advantages of photocatalyst are the non-specific targets and anti-foulant capabilities on the material surfaces which aid in maintaining high photocatalytic performance and stability.

Apart from the material, the study of the morphological structure of TiO_2 has also made a significant impact in the field of water treatment. When 0 dimension spheres were used as membranes, higher flux performance was achieved and organics were degraded concurrently. (H. Bai, L. Liu, Z. Liu, & D. D. Sun, 2013; Pan, Zhang, Du, Sun, & Leckie, 2008), 1 dimension nanowires (X. Zhang, A. J. Du, et al., 2008b; X. Zhang, Zhang, et al., 2009) were applied as a membrane layer for the filtration of organics. Both applications rely on the facile approach by laying TiO_2 nanostructures atop supporting membranes to perform microfiltration or ultrafiltration processes. The studies demonstrated easy recovery of the micro/nanostructures as a result of the larger dimension shown in Fig 2.3-1. The properties of high surface area of TiO_2 and the PCO process enable the maintenance of the trans-membrane pressure due to the oxidation of adsorbed organic pollutants. Furthermore, the photostability of TiO_2 was also demonstrated through multiple cycles of usage (S. S. Lee, H. Bai, Z. Liu, & D. D. Sun, 2013; Z. Liu, Sun, Guo, & Leckie, 2007; X. Zhang, Pan, Du, Ng, et al., 2009).

Figure 2.3-1 Membrane flux in dead end filtration device in comparison to particle size (Pan et al., 2008)

2.3.2. BACTERIA DISINFECTION

Apart from organic pollutants, bacteria and microorganisms are some of the main pollutants in water. The inactivation or removal of microorganisms from water is essential to achieve clean potable water (Shannon et al., 2008). Our group's past research has shown that the PCO process enables the inactivation of water borne bacteria and disintegration into carbon dioxide (CO_2) was demonstrated using TiO_2 -iron (III) oxide (Fe_2O_3) ceramic membranes (D. D. Sun et al., 2003), TiO_2 (H. Bai, Z. Liu, L. Liu, & D. D. Sun, 2013) and TiO_2 /Cadmium Sulphide (CdS) spheres (P. Gao, Liu, Zhang, Sun, & Ng, 2012). In addition, the surface morphology of the photocatalyst provides an added advantage if it possesses hierarchical rod/thorn like structures which is correlated to the physical lysis of bacteria, as the bactericidal effect was observed in the absence of UV-irradiation (H. Bai, Z. Liu, et al., 2013).

2.3.1. HEAVY METAL REMOVAL

Inorganics such as heavy metal ions make up the final type of pollutant. The general difference for heavy metal is purely removal based treatment. TiO_2 was used as the adsorbent material for inorganics such as Cadmium ions (Du, Sun, & Leckie, 2011) and copper (Cu) ions (Xu, Ng, Du, Liu, & Sun, 2011). Further research also explored the decomplexation of Cu^{2+} from Cu-EDTA which underwent photocatalytic reduction onto TiO_2 nanofibers shown in Fig 2.3-2. The adsorbed Cu was used as the raw material for the fabrication of copper(II) oxide (CuO)/ TiO_2 nanofibers (Lee et al., 2015).

Figure 2.3-2 Decomplexation of Cu^{2+} from Cu-EDTA and photocatalytic reduction of Cu^{2+} onto the TiO_2 nanofibers (Lee et al., 2015)

2.3.2. TiO_2 PROPERTIES AND PHOTOCATALYSIS ENHANCEMENT

As TiO_2 is only receptive to ultraviolet light, other metal oxides were used in conjunction with TiO_2 to increase the light absorbance. Photocatalytic enhancement

of the oxidation of organics to produce clean water was assessed. The heterojunction of metal with TiO_2 tends to result in higher photocatalytic performance as shown in Fig 2.3-3. The use of strontium titanate (SrTiO_3)/ TiO_2 heterojunction has been reported to mitigate electron-hole recombination as the higher band position of SrTiO_3 allows for the migration of electrons to the TiO_2 conduction band which acts to trap electrons (Ng, Xu, Zhang, Yang, & Sun, 2010), Manganese oxide octahedral molecular sieve heterojunction K-OMS-2/ TiO_2 / Fe_3O_4 reported the migration of TiO_2 electron to K-OMS-2 which reduced O_2 (T. Zhang et al., 2012). Similarly, in CuO/TiO_2 , the conduction band of CuO acts as electron traps for the recombination of TiO_2 electrons (S. S. Lee et al., 2013; Siew Siang Lee, Hongwei Bai, Zhaoyang Liu, & Darren Delai Sun, 2013).

Figure 2.3-3 Illustration of the respective band positions and spatial separation of photogenerated interparticle charges during photocatalytic activation of the heterojunction $\text{TiO}_2/\text{SrTiO}_3$ catalyst. (Ng et al., 2010)

2.4. THE DEVELOPMENT OF TiO₂ AND ITS PERFORMANCE OBSTACLES IN THE FIELD OF WATER

2.4.1. TiO₂ AND ITS PHYSIOCHEMICAL PROPERTIES

The use of TiO₂ as a white pigment has been ongoing since the 1920s (Bichowsky, 1929). The advantageous characteristics of TiO₂ includes its inertness, non-toxicity, high refractive index and high surface area (X. Chen & Mao, 2007). The photosensitization effect of TiO₂ which splits water (H₂O) into hydrogen (H₂) and oxygen (O₂) under UV-irradiation has since garnered great research interest (Fujishima & Honda, 1972). TiO₂ and other metal oxides absorb various wavelengths of light due to their inherent bandgaps shown in Fig 2.4-1. The bandgaps portray the conduction band edge and valence band edge of the various metal oxides. The wider the bandgap, the higher the photoreactivity and photostability of the compound. However, the drawback is that TiO₂ absorbs only UV radiation, due to the wide bandgap structure of 3.0 to 3.2 electron volts (eV) (Fujishima et al., 2000; Kudo & Miseki, 2009). To achieve water splitting, the conduction band edge needs to be more negative than H⁺/H₂ and the valence band edge must be more positive than O₂/H₂O redox potential. Hence, TiO₂ is regarded to be thermodynamical for water splitting (X. Chen & Mao, 2007).

Figure 2.4-1 Relationship between band structure of semiconductor and redox potentials of water splitting (Kudo & Miseki, 2009)

2.4.2. TiO₂ WATER SPLITTING

The bandgap position of TiO₂ complement the water splitting process. The water medium plays the role of an electron scavenger. H⁺ is reduced by the electrons to form hydrogen (H₂) and H₂O is oxidized by the holes to form O₂. Water splitting into H₂ and O₂ requires the standard Gibbs free energy change ΔG^0 of 237 kJ/mol or 1.23 eV, as shown in Equation (1). Henceforth, the band gap energy (E_G) of the photocatalyst should be >1.23 eV (<1000nm) (X. Chen, Shen, Guo, & Mao, 2010; Turner, 1999).

The illustration in Figure 2.4.-2, portrays the eV of TiO₂ at 3.2. The level of the valence band of TiO₂ is more positive than the redox potential of O₂/H₂O (1.23 V), while the level of the conduction band of TiO₂ is more negative than the redox potential of H⁺/H₂ (0 V vs. NHE) which allows water splitting and hydrogen generation to proceed (Chong, Jin, Chow, & Saint, 2010).

Figure 2.4-2 Photo-induced formation mechanism of electron and hole pair in a TiO₂ semiconductor the presence of water (Chong et al., 2010).

2.4.3. TiO₂ FOR WATER PURIFICATION AND ITS ADVANTAGES

The advantage of TiO₂ in the field of water purification lies in its ability to impart complementing functions for water based processes under the influence of UV-irradiation. Other advantages of TiO₂ include, its inherent band gap position relative to water, photostability, superhydrophilicity (Fujishima et al., 2000; Kazuhito et al., 2005) the ability to adsorb inorganic metal ions (Du et al., 2011; Xu, Ng, Du, et al., 2011), photocatalytic reduction of adsorbed metal ions (Lee et al., 2015) as well as degradation of organic pollutants and bacteria which is attributed to the production of hydroxyl radicals (OH[•]) (Chong et al., 2010; Gaya & Abdullah, 2008).

2.4.3.1. Water Chemistry of TiO₂ and the Photocatalytic Degradation of Organic Pollutants

The absorption of impinging UV photons with energies higher than titanium dioxide band gap of >3.2 eV leads to a series of chain reactions shown in Equations 1.1 to 1.11. (Chong et al., 2010; Gaya & Abdullah, 2008). The denotations of the reaction are as follows with $h\nu$ being UV-light, e^-_{CB} is the electron in the conduction band, e^-_{TR} is the trapped electron, h^+_{VB} is the hole in the valence band, h^+_{TR} is the trapped hole, $(O_2)_{ads}$ is the oxygen adsorbed, $O_2^{\bullet -}$ is the superoxide radical, OH^- is the hydroxide ion, $OH^{\bullet}$ is the hydroxyl radical, OR is the organic pollutants, $HOO^{\bullet}$ is the hydroperoxyl radical, HOO^- is the hydroperoxyl anion, and H_2O_2 is hydrogen peroxide.

The primary photoreactions Equations (1.1) – (1.11) indicate the critical role of the electron–hole pair or charge carriers in photooxidative degradation of pollutants. Equations (1.1) to (1.3) describe the photoexcitation and trapping of electrons and holes. These trapped electrons and hole carriers are usually surface bounded on the TiO₂ photocatalyst and do not recombine immediately after photon excitation (Furube, Asahi, Masuhara, Yamashita, & Anpo, 2001). The elementary surface mechanistic process was postulated for the photocatalytic degradation of organic compounds using TiO₂. However, in the absence of electron scavengers (Eq. (1.4)), recombination proceeds in nanoseconds with simultaneous dissipation of heat energy (Serpone, Lawless, Khairutdinov, & Pelizzetti, 1995). This suggests that the electron scavengers and surface trapped holes and electrons work to mitigate the recombination of the photoexcited electron and hole. Hydroxide (OH⁻) is oxidized to hydroxyl radicals (OH[•]) in the hole (Eq. (1.6)). The OH[•] plays a key role in the degradation of pollutants (Eq. (1.7)). The holes can also oxidise pollutants adsorbed on the surface of the TiO₂ (Eq. (1.8)). The presence of abundant atmospheric O₂ (Eq. (1.5)) is mainly attributed to the functioning electron scavenger and the initial formation of superoxides ions (O₂^{•-}). Superoxide ions can further protonate to form the hydroperoxyl radicals (HOO[•]) (Eq. (1.9)) and subsequently H₂O₂ (Eq. (1.11)), in which, the hydroperoxyl radical acts as a co-scavenger in the photochemical process. The co-existence of both species may further mitigate the recombination of the photocatalysis.

Essentially, the photochemical reactions are attributed to the presence of both water and oxygen and the subsequent formation of hydroxyl radicals (OH[•]), holes

(h^+), superoxide ions (O_2^-) and hydroperoxyl radicals ($HOO^\bullet$). These are highly reactive intermediates that will act concurrently to oxidize large variety of organic pollutants including volatile organic compounds (VOCs) and bioaerosols (Fujishima et al., 2000; Jacoby et al., 1996; Sleiman, Conchon, Ferronato, & Chovelon, 2007).

2.4.3.2. Photo-induced Superhydrophilicity

Apart from PCO, TiO_2 was also observed for photo-induced superhydrophilic properties (Fujishima et al., 2000; Kazuhito et al., 2005). Due to the reduction of $Ti(IV)$ cations to the $Ti(III)$ state by electrons and the oxidation of the O^{2-} anions by the generated holes leading to O_2 atoms ejection from the process. Vacancies are created and occupied by water molecules as shown in Fig. 2.4-3. The subsequent occupation of water molecules transforms the reactive surface of TiO_2 into a superhydrophilic material due to adsorbed hydroxyl groups (Fujishima et al., 2000; Machida, Norimoto, Watanabe, Hashimoto, & Fujishima, 1999; Sakai, Wang, Fujishima, Watanabe, & Hashimoto, 1998; Stevens, Priest, Sedev, & Ralston, 2003; R. Wang et al., 1997).

Figure 2.4-3 Mechanism of photo-induced hydrophilicity (Fujishima et al., 2000)

2.4.4. TiO₂ AND ITS PERFORMANCE OBSTACLES

To potentially apply the capability of the TiO₂ nanomaterials, there are several key challenges affecting the productivity of the photocatalyst.

- (1) Fig 2.4-4 presents the solar spectrum. UV-light, and accounts for less than 5 % percent of solar light.
- (2) TiO₂ photocatalyst activation is limited to UV-light
- (3) The recombination of the photogenerated electron hole pairs which releases energy in the form of heat or photons.
- (4) Morphology suitability of the TiO₂ structure
- (5) Difficulty in the recollection of nano sized materials
- (6) Scalability of TiO₂ materials

Figure 2.4-4 The solar energy distribution (Biernat, Malinowski, & Gnat, 2013)

2.5. SIGNIFICANCE OF DIMENSIONS ON PERFORMANCE IMPROVEMENT FOR WATER

Fig 2.5-1 illustrates the structural morphology of 0-dimension nanomaterials, 1-dimension wires or fibres, 2-dimensional nanosheets and 3-dimensional interconnected structures. 0-dimension nanomaterials having a size less than approximately 50 nm usually have high specific surface area resulting in higher rate of degradation of organic pollutants. However, due to the small size, the nanomaterial suffers drawbacks due to the inability to sufficiently scatter or reflect sunlight (Sun Hye Hwang, Juyoung Yun, & Jyongsik Jang, 2014; Joshi et al., 2010). Furthermore, the nano size makes it unpractical for recovery of the material. 1-dimensional structures such as nanowires or nanofibers have been widely researched as membrane filters. The length enables easy recovery and results in a scaffolding layer when placed atop a supporting membrane. The long but thin diameter enables short charge transverse distance in the photocatalyst, reducing the chance of recombination (H. Bai, L. Liu, et al., 2013; X. Zhang, A. J. Du, et al., 2008b; X. Zhang, Zhang, et al., 2009). 2-dimensional nanosheets are uncommon in the field of water treatment due to the morphology of the structure. Its high adhesion would hinder the flux of water and recovery process of the material (Hussein & Shaheed, 2015). The morphology is more commonly applied in the field of energy due to high capability of lithium storage (Cheng, Hu, Huang, & Jiang, 2014; Leng, Chen, & Xue, 2014).

3-dimensional interconnected structure is the least researched of all the dimensions. Large spheres assembled through the agglomeration of nanoparticles can be regarded as 3-dimensional interconnected structures as the nanoparticles are interconnected and mesopores are formed due to the interconnectivity. Mesoporous spheres assembled through nanoparticles agglomeration demonstrated increased surface porosity due to enhanced pollutant adsorption and degradation by the mesoporous spheres (BET specific surface area of 168 m²/g). Furthermore, the structure enhanced UV absorption due to light trapping which improved overall efficiency (Z. Liu et al., 2007). Similar characteristics were also observed from the synthesis of hierarchical porous TiO₂ hollow microspheres (Zhaoyang Liu, Bai, &

Sun, 2011). In the application of membrane flux, the large and controllable spherical particle size prevents the blockage of the membrane pores, allowing constant flux while purifying water. The material's recovery and water channels through the stacking of spheres ensure high and constant flux which aid in filtration process or recovery of material (Pan et al., 2008).

Figure 2.5-1 Structural dimension of nanostructured TiO₂ (Hussein & Shaheed, 2015)

2.5.1. MORPHOLOGY OF NANOMATERIALS

2.5.1.1. 1-Dimension Hierarchical Surface Structures

The presence of 1-dimensional hierarchical structures with and without heterojunctions, showed improved photocatalytic performance in the rate of pollutant degradation, correlated to the improved light scattering between the hierarchical structure of the spheres (H. Bai, L. Liu, et al., 2013; Bai, Liu, & Sun, 2012; Ng, Wang, & Sun, 2011; Pan et al., 2008; X. Zhang, Pan, Du, Xu, & Sun, 2009), wires (Hongwei Bai et al., 2012; T. Zhang et al., 2012; X. Zhang, Pan, Du,

Xu, et al., 2009). The comparison between the light scattering of the hierarchical nanothorn TiO_2 sub-microsphere and circular microsphere is illustrated in Fig 2.5-2 (P. Gao & Sun, 2014). The presence of rod like hierarchical structures on spherical surfaces achieve bactericidal capability in the absence of light irradiation (H. Bai, Z. Liu, et al., 2013).

Figure 2.5-2 Light scattering of hierarchical surfaces compared to smooth surfaces (P. Gao, Li, Sun, & Ng, 2014)

2.5.1.2. Hollow and Multi-Shell Hollow Structure

Hollow structures have attracted much attention in the field of energy generation especially DSSCs and LIB with potential applications in water purification. The large spherical size created water channels while demonstrating degradation of water borne pollutants so as to not hinder the interaction of the water, pollutant and photocatalyst (Pan et al., 2008). The light weight hollow morphology reduced the total material mass as well as the transport time to enhance overall performance

(Lai, Halpert, & Wang, 2012; Sadoughi et al., 2013). Additionally, they exhibit enhanced light harvesting capability, owing to the hollow structure and enhanced surface-to-volume ratio (Sun Hye Hwang et al., 2014; S. Li, Chen, Zheng, Li, & Huang, 2013; Zhaoyang Liu et al., 2011; Z. Liu et al., 2007; Lv, Xiao, Zhu, & Li, 2014), and simultaneously increased the diffractions on the hollow spheres and the reflections on the shell structure (Lai et al., 2012; J. Yu & Zhang, 2010). However, the architectural structure of single shell hollow sphere acquires low area density and reduced the per-area efficiency (S. C. Yang et al., 2008).

The multi-shelled hollow spheres are simply a maximisation of the space within the hollow sphere. The additional shells increased surface area which improved light scattering within the shell. This resulted in stronger optical confinement and enhanced photocatalytic activity illustrated in Fig 2.5-3 (Sun Hye Hwang et al., 2014; S. Li et al., 2013; H. C. Zeng, 2011). The introduction of multi-shell hollow spheres further enhanced the overall performance as packing density and light harvesting increased (M. Chen, Ye, Zhou, & Wu, 2013). Furthermore, the thin shell and large surface resulted in the shortening of Li^+ diffusion distance and active surfaces for the electrolyte and electrode (G. Zhang, Wu, Song, Paik, & Lou, 2014).

Figure 2.5-3 Schematic illustration of multi-shell hollow spheres and multiple scattering (Sun Hye Hwang et al., 2014)

In summary, the application of a hierarchical form of hollow spheres is highly relevant in both fields of water purification as the morphological structure

complements the treatment functions. Furthermore, the redox reactions are mainly surface bound reaction with the liquid medium, structural morphology and surface area greatly contributes to the overall photocatalytic activity. Additionally, the recombination chances when electron migration from the bulk to the surface is affected by the travel distance (Schneider et al., 2014). Hence, the large enough spherical size facilitates recovery of nanomaterials, while 0 dimensional nanostructures shorten the transverse distance of charge carrier to greatly enhance the photocatalysis. However, to potentially apply the spherical structure, direct fabrication will be required for pragmatic scalability.

2.5.2. SYNTHESIS OF TiO₂ HOLLOW SPHERES

TiO₂ Hollow Spheres are generally synthesized using three distinct synthetic methods - hard template which used rigid solid materials, soft template which used liquid droplets or micelles and template free methods which self-assemble into desired structures. The hard and soft template increase cost but provide uniformity in size and shape, while the template free methods is limited to the materials' ability to self-assemble and is limited to other forms of photocatalyst modification (J. Hu, Chen, Fang, & Wu, 2011; Lai et al., 2012; J. Wang, Bai, Wu, Yin, & Zhang, 2009).

2.5.2.1. Soft Template/Micelle Method

The soft template method involves the formation of aggregated surfactant molecules in an aqueous media, with high enough concentration of the surfactant that exceeds the critical micelle concentration (Rossmannith et al., 2008).

The parameters such as water/surfactant ratio, water/titanium precursor ratio, ammonia concentration, feed rate, and reaction temperature were significant in controlling TiO₂ nanoparticle size and size distribution (Kim, Kim, & Kim, 2005). The main drawback for the micelle method is the large amount of adsorbed surfactant required on the surface of nanoparticles and the further separation and removal of some solvents from products that leads to high production cost (Capek, 2004).

2.5.2.2. Template Free Method

The various methods to synthesize TiO_2 hollow spheres through the template free approach were demonstrated in recent years (Jia, Yang, Chen, & Wang, 2015; Kang, Yin, Li, Li, & Mu, 2012; Ke, Chen, Su, & Kuang, 2013; Shang, Jiao, & Chen, 2012). Double shell TiO_2 hollow spheres were synthesised using a simple mixture of Ti_4F , sucrose and water (X. Wu, G. Q. Lu, & L. Wang, 2011). However, the lack of optimisation of the sphere's packing density, further development of multi-shell hollow spheres and the difficulty in controlling sphere size limits the application of the product. Lai and co-workers postulated that the niche assembly methods and the difficulty in generalization was possibly causing it to be unsuitable for scalability and low cost production (Lai et al., 2012).

2.5.2.3. Hard Template Method

Hard template methods have been widely adopted for hollow structure material since size, shape and structure are controllable. The hard templates are usually fabricated using organic materials such as carbon (C) or silicon oxide (SiO_2). The surface of the templates is usually coated with metal oxide precursor to form a metal ion surface with an organic template core. The subsequent removal of the template results in the formation of a hollow structure (Z. Li et al., 2009). Typically, multi-shell spheres require multiple recoating of organic atop the formed hollow shells to create a second shell as shown in Figure 2.5-4 (Sun Hye Hwang et al., 2014; S. Li et al., 2013). The modification to create hollow microspheres as templates was reported to create double shelled TiO_2 hollow spheres (T. Chen, Du, Zhang, & Fan, 2013; Schäfer et al., 2014).

Figure 2.5-4 Fabrication of the double-shell TiO₂ hollow spheres using a sol-gel and the silica-protected calcination process. (S. Li et al., 2013)

2.5.3. SCALE UP PRODUCTION OF HIERARCHICAL MICRO/NANO-MULTI-SHELL HOLLOW SPHERES

Due to the water crisis and the global shift towards sustainable solar energy, factors such as material's abundance, low cost (Bavykin, Friedrich, & Walsh, 2006) and the simplistic synthesis of the desired morphology will be required to ensure pragmatic scalability for engineering applications.

In recent years, an alternative form of synthesis of multi-shell hollow spheres was reported. The report demonstrated the penetration of highly concentrated iron and nickel ions into carbonaceous spheres. Post calcination of the spheres generated multi-shell hollow spheres at different temperature stages (X. Lai et al., 2011). Through this method of synthesis, further development has been carried out on metal oxides such as, Cr₂O₃ (H. Sun, Wang, Chu, Ma, & Wang, 2015), ZnO (Dong et al., 2012; X. Zeng, Yang, Shi, Li, & Gao, 2014), Cu₂S (Xiong & Zeng, 2012), CoMn₂O₄, ZnMn₂O₄, ZnCo₂O₄ and NiCo₂O₄ (G. Zhang & Lou, 2014), all of which have shown enhanced capability in their respective field. However, the use of TiO₂

was not applied due to the hydrolysis of the Ti precursor solution (G. Zhang et al., 2014) atop the carbonaceous spheres due to the functional groups (X. Sun & Y. Li, 2004).

The sequential templating approach reported by X. Lai et al. (2011) is a one-step synthesis of multi-shell hollow spheres, up to quadruple shells of Fe_2O_3 , NiO , Co_3O_4 , CuO . The method illustrated in Fig 2.5-5 forces highly concentrated metal ions to penetrate the pores of carbonaceous spheres via diffusion. The calcination of the spheres at increasing temperature produces multi-shell hollow spheres.

Figure 2.5-5 Sequential templating method penetrating highly concentrated metal ions into the pores of the carbonaceous microsphere (Xiaoyong Lai et al., 2011)

At various temperature intervals shown in Fig 2.5-6, the reduction of the carbonaceous sphere was observed. The oxidation of the carbonaceous spheres reduces sphere size and enables the metal ions to converge and form hollow shells. Remaining metal ions will converge as the concentration in the carbonaceous pores is enough to form more hollow shells leading to multi-shell formation. The prerequisite factors include the large penetration of the metal ions within the carbonaceous sphere and the matching of the rate of metal oxide shell formation with the rate of carbonaceous microsphere disintegration (X. Lai et al., 2011). Further studies reported other factors, including the adjustment of penetration time and the diameter of carbonaceous sphere (G. Zhang & Lou, 2014). Size of the

multi-shells hollow spheres was uniform and product scalability was demonstrated through this synthesis method.

Figure 2.5-6 TEM images of carbonaceous microspheres after soaking in a 3 mol/L solution of iron nitrate: a) before heating, and after heating at b) 270 °C, c) 350°C, d) 430 °C, and e) 500 °C (X. Lai et al., 2011).

2.5.4. APPROACHES TO IMPROVE THE PERFORMANCE OF TiO₂ PHOTOCATALYST

Apart from the structural morphology and surface porosity, the approaches to improve photocatalytic performance of TiO₂ were generally done through the modification of optical properties, as the wide bandgap of TiO₂ is only receptive to ultraviolet light.

The introduction of impurities into the crystal structure through doping or surface modification through the application of semiconductor composite were the main approaches to deal with the wide bandgap. Furthermore, the impurities aid in the mitigation of electron-hole recombination due to the presence of unequal band structure which creates charge traps. The various techniques include: metal ion, anion doping, semiconductor composite, dye sensitization, and more recently graphene oxide composite.

2.5.4.1. Lattice Structure of TiO₂ Photocatalyst

The crystal structures of TiO₂ are commonly found in four crystalline polymorph forms namely, orthorhombic brookite, monoclinic TiO₂ (B), tetragonal rutile and tetragonal anatase.

The anatase and rutile crystal structure of TiO₂ is predominantly of great research interest due to it being the photocatalytically effective among the various

counterparts. The two phases have a common primary structural unit, the TiO_6 octahedron where each Ti^{4+} is surrounded by 6 O_2^- ions shown in Figure 2.5-7. In the case of the anatase phase, more distortion can be seen compared to the rutile phase, making it more unsymmetrical. The Ti-Ti distances in anatase are larger, whereas the Ti-O distances are shorter than those in rutile. In the rutile structure, each octahedron is in contact with 10 neighbour octahedrons (two sharing edge oxygen pairs and eight sharing corner oxygen atoms), while, in the anatase structure, each octahedron is in contact with eight neighbours (four sharing an edge and four sharing a corner). These differences in lattice structures cause different mass densities and electronic band structures between the two forms of TiO_2 (X. Chen & Mao, 2007). This difference in structure is caused by the stacking arrangement of the octahedron. With the inherent difference in bond length and stacking arrangement for these two phases, the Ti-O bond strength, bond coupling, physical and chemical/ photochemical properties are also expected to consequently differ (L. Liu & Chen, 2014).

Figure 2.5-7 Polyhedral representation of the rutile (A) and anatase (B) (Landmann, Rauls, & Schmidt, 2012)

The phase transformation from anatase to rutile can occur if input of energy, typically above 700°C, is provided to allow the formation of a more symmetrical structure. (Andronic, Perniu, & Duta, 2013; Hongwei Bai et al., 2012; H. Bai, Z. Liu, et al., 2013; X. Chen & Mao, 2007; Siew Siang Lee et al., 2013; Ranade et al., 2002; Pu Xu et al., 2010). This stratification of lattice structure reduces the total active sites and increases the crystallinity of the structure; which consequently alters the band gap of the material (Kudo & Miseki, 2009).

The band gap of anatase and rutile were reported to be of dissimilar values with the anatase being 3.2 eV (387nm) and the rutile 3.0 eV (413 nm) (Hanaor & Sorrell, 2010). The difference between the band gap of the anatase and rutile phases was mainly due to the differences in the conduction band levels, and results in photocatalytic effectiveness between anatase and rutile crystals (Tomita et al.,

2006). This difference in band gap and absorption onset has been ascribed to the difference in lattice structure, including the bond length and TiO_6 stacking, which causes different orbital coupling between the oxygen 2p and titanium 3d orbital (X. Chen & Mao, 2007).

Due to the dissimilar bandgap between anatase and rutile, TiO_2 with a hybrid of anatase and rutile structures was reported to outperform the individual polymorphs (G. Li & Gray, 2007). The application of anatase with rutile content has been commercially used in the formation of P25 nanoparticles. The migration of conduction electrons from the rutile structure to the anatase with a lower band gap of ~ 0.4 eV, acted as electron traps to mitigate the recombination of electron hole pairs (Scanlon et al., 2013).

2.5.4.2. Doping of TiO_2 Photocatalyst

Doping of TiO_2 photocatalyst with other elements narrows its electronic and optical properties. The Ti or the O_2 component can be substituted with other elements to alter the material's optical properties. An optimal amount of transition metal ions doped into TiO_2 can introduce charge traps or capture centres resulting in the production of defects sites and thereby decrease in the electron-hole recombination (Sajjad, Leghari, Chen, & Zhang, 2010; Wenjiao Wang, Zhang, Chen, Anpo, & He, 2010; Xing et al., 2013; Y. Yang & Tian, 2012; Yuan, Zhang, Anpo, & He, 2010). The modification via the use of the doping method modifies the entire bulk material, making the material into a composite while the sensitisation method only modifies the surface properties of the bulk material.

2.5.4.2.1. Metal Doping

Generally, doping of metal creates additional electronic states near the conduction and valence bands of TiO_2 . The doping with Cr^{3+} resulted in visible light absorption to the conduction band (CB) of TiO_2 (Zhu et al., 2006). The doping of TiO_2 with cerium ions resulted in decreased recombination rates of the electron and holes, while the presence of Ce dopant ions generated additional electronic states in the

bandgap of TiO_2 above the valence band by capturing the photoformed holes (N. Yan, Zhu, Zhang, Zhao, & Liu, 2012). Visible-light absorption of Ti^{3+} doped TiO_2 has been shown (Lu, Linsebigler, & Yates, 1994; Sasikala et al., 2009). However, the instability of surficial Ti^{3+} centres and oxygen defects on TiO_2 in air results in easy oxidation of the Ti^{3+} centres into Ti^{4+} by the oxygen dissolved in water (Nakamura et al., 2000; Zuo et al., 2010). The Fe^{3+} doping creates electronic states below and above the conduction band and valence band of TiO_2 as shown in Fig 2.5-8. This allowed for the trapping of charges which migrated from TiO_2 onto the Fe^{3+} , preventing recombination. The trapped charges will be released via the reduction of oxygen species or oxidation of hydroxide due to the unstable Fe^{2+} and Fe^{4+} (Ali, Tripathi, Azam, et al., 2017).

Figure 2.5-8 Fe-doping which results in the formation of Fe^{3+} energy level within the bandgap which allow the migration of charges from TiO_2 and acts as charge traps for anti-combination of electron-hole pair (Ali, Tripathi, Ameer, et al., 2017)

2.5.4.2.2. Non-metal Doping

Doping with non-metals such as nitrogen (N), sulphur (S), carbon (C), phosphorus (P) has been reported to shift absorption of the TiO₂ material towards the visible light region (Asahi, Morikawa, Ohwaki, Aoki, & Taga, 2001; Ohno et al., 2004; Okada, Yamada, Jin, Tazawa, & Yoshimura, 2003; Umebayashi, Yamaki, Itoh, & Asai, 2002; J. K. Zhou et al., 2008). Much of dopants are C or N due to their similar atomic radius with the O atom, while the ionic radius of S is too large to fit into the lattice. The doping of N revealed a mixing of *p* states of N and 2*p* states of O. This mixing was found to shift the valence band edge upwards, reducing the band gap (Asahi et al., 2001).

The doping of non-metal C received great attention (B. Lavand & S. Malghe, 2015; Hongwei Bai et al., 2013; Khan, Al-Shahry, & Ingler, 2002; P. Xu et al., 2010; Zabek, Eberl, & Kisch, 2009) and is easily achieved via carbon-based additives. A direct solvothermal method involving acetone, in which the carbon adsorbed onto the TiO₂ nanocrystal during calcination forming carbonate bonds was recently proposed (B. Liu et al., 2014). Carbon contained in titanium alkoxide precursor was incorporated into the lattice of TiO₂ via controlled calcination (Y. Park et al., 2009). Doping of carbon by calcining oleylamine wrapped TiO₂ nanosheets was obtained via thermal decomposition in air (Y. J. Yang et al., 2015). However, doping with C and P too deep into the material hinders the transfer of photo-induced charge to the surface (Asahi et al., 2001). Nonetheless, the doping of carbon into the lattice of the TiO₂ demonstrated red shift into the visible light region, narrowing the bandgap TiO₂. Furthermore, C is less likely to form recombination sites and enhances the photocatalytic ability of the metal oxide (Asahi et al., 2001).

Figure 2.5-9 C-doped TiO₂ under UV or visible light irradiation. CB and VB denote the conduction and valence band of the TiO₂ particle, respectively. The broken line represents the C induced bandgap level that should lie between 1.4 and 1.9 V vs NHE (Yiseul Park et al., 2009).

2.5.4.3. Semiconductor composites

The combination of two different metal oxides are generally termed heterojunction. TiO₂ heterojunctions results in different band gap which serves to improve the visible light absorbance portrayed in Fig 2.5-10 (Ni, Leung, Leung, & Sumathy, 2007). The species with smaller bandgap will adsorb visible light while TiO₂ absorbs UV-light. The species with a higher or more negative conduction band level (CB) will be able to inject electrons to the lower conduction band of TiO₂, and hence, trapping electrons and mitigating recombination.

Figure 2.5-10 Electron injection in composite semiconductors (Ni et al., 2007)

The surface growth of zinc oxide on TiO_2 nanotube (H. Y. Yang et al., 2009) and the deposition of copper oxide on TiO_2 surface, has also shown increased photocatalytic hydrogen generation (S. Xu & D. D. Sun, 2009). The growth of heterojunction SrTiO_3 on base material TiO_2 nanowires reported higher pollutant degradation efficiency. The two semi-conductors of unequal bandgap aid in facilitating interfacial electron transfer by separation of photogenerated charges at heterojunctions interfaces and act as potential traps for the photo-generated electrons, increasing the reaction lifetimes of electron hole pair (Ng et al., 2010).

Metal oxides can form a type of heterojunction, known as p-n heterojunction. The n-type semiconductor possesses excess electrons while the p-type possess excess holes (Brito & Zanoni, 2016; Kohl, 1977). TiO_2 is generally an intrinsic n-type metal oxide (Forro et al., 1994). In combination with extrinsic p-type metal oxide like CuO , it forms p-n heterojunctions which enhance the overall charge transfer as shown in Fig 2.5-11 (S. S. Lee et al., 2013; Siew Siang Lee et al., 2013). Through the synergy of the p-n CuO/TiO_2 heterojunction, the charge transfer and separation of photogenerated charge carriers are enhanced and inhibits photocorrosion as well as electron-hole recombination (Q. Q. Hu et al., 2016; S. S. Lee et al., 2013; X. C. Zhang & Tang, 2012).

Figure 2.5-11 Schematic band diagram of the charges transfer between CuO/TiO_2 heterojunctions (Siew Siang Lee et al., 2013).

2.5.4.4. Dye Sensitization

Organic dyes have been widely employed as sensitizers for TiO_2 nanomaterial to improve its optical properties, especially in dye-sensitized solar cells (DSSCs) (Grätzel, 2003). However, the usage of dye requires an electron donor to prevent the degradation of the dye due to the injection of electrons into the conduction band of TiO_2 as shown in Fig 2.5-12.

Figure 2.5-12 Photoinduced injection of dye electron onto the conduction band of TiO₂ (Ola & Maroto-Valer, 2015).

In the presence of TiO₂, Acid Orange 7 (AO7), found largely in textile industries as an organic pollutant, was sensitive to degradation by visible light. The initial injection of electrons into the conduction band of TiO₂ and the subsequent production of oxygen radicals was believed to result in the oxidative degradation of AO7 (X. Zhang, D. D. Sun, et al., 2008). This made dye sensitization inapplicable for water treatment process. The degradation of organic dyes under the influence of light sources and TiO₂ is as follows.

2.5.4.5. Graphene Oxide

Graphene oxide (GO) has emerged as one of the promising materials for photocatalysts, due to high mobility of charge carriers, large specific surface area, flexible structure, high transparency, and good electrical and thermal conduction (Xiang, Yu, & Jaroniec, 2012). The application of GO and TiO_2 has been widely researched as an electron acceptor to mitigate electron-hole recombination. It is illustrated in Fig 2.5-13 that electrons on the GO react with adsorbed O_2 to form $\text{O}_2^{\cdot-}$ and subsequently $\text{OH}^{\cdot}$ (J. Liu et al., 2010). The use of GO has been observed to extend photo-receptivity of photocatalysis to the visible light region. The GO- TiO_2 composite can be easily prepared using ultrasonication of GO and TiO_2 solution to achieve binding of TiO_2 and carboxyl groups of GO (P. Gao et al., 2014; P. Gao & Sun, 2013). Furthermore, GO- TiO_2 has enhanced bactericidal activity under solar irradiation compared to pure TiO_2 (P. Gao et al., 2014; J. C. Yu et al., 2005). Other report showed that graphene remained stable after photoinactivation of the bacteria (Akhavan & Ghaderi, 2009)

Figure 2.5-13 Photocatalytic activity for GO- TiO_2 and the electron migration to form $\text{O}_2^{\cdot-}$ and subsequently $\text{OH}^{\cdot}$ for pollutant degradation (J. Liu et al., 2010).

2.5.5. THE APPLICATION OF PHOTOGENERATED ELECTRON FROM TiO_2

The applications of photogenerated electrons from TiO_2 have been widely researched in various functions including dye sensitised solar cells, hydrogen generation, and photochemical cells.

2.5.5.1. Dye Sensitised Solar Cells (DSSCs)

The introduction of dye sensitised solar cells (DSSCs) shown in Figure 2.5-14 has been proposed by Prof. Michael and team in 1991 (O'Regan & Grätzel, 1991). The photo-excitation of the dye caused the migration of electrons onto the conduction band of the TiO_2 . The electron transfers onto the anode which is then drawn towards the cathode, resulting in an electron flow to generate electricity. The dye molecule is regenerated by the electron donation from the electrolyte as the mediator. The electrolyte is regenerated at the counter electrode by electrons passing through the load which allows for the continuous generation of current. The open-circuit voltage of the solar cell corresponds to the difference between the redox potential of the mediator and the Fermi level electron of the solid and the redox potential of the electrolyte. The device generates electric power from light without undergoing any permanent chemical transformation (Grätzel, 2003).

Figure 2.5-14 Principle of operation and energy level scheme of the dye-sensitized nanocrystalline solar cell (Grätzel, 2003).

2.5.5.2. Hydrogen Generation

The generation of hydrogen by TiO_2 photocatalysis has been the fundamental mechanism of water splitting (X. Chen et al., 2010; Fujishima & Honda, 1972). The concept of water splitting is the application of electrons to reduce H^+ into H_2 and holes in the conduction band to oxidise H_2O into O_2 . To enhance the overall H_2 generation, the incorporation of composites such as, CuO onto the surface of TiO_2 nanoparticles (Xu, Ng, Zhang, Bai, & Sun, 2010; S. Xu & D. D. Sun, 2009) or fabrication of $\text{SrTiO}_3/\text{TiO}_2$ nanofibers heterostructures (Hongwei Bai et al., 2012) was developed and has demonstrated improvement of photocatalytic process due to the heterogeneous structure. However, the use of Cu-EDTA for the generation of hydrogen reported a lowering of H_2 generation as the reduction of Cu^{2+} onto the TiO_2 nanofiber takes place (Lee et al., 2015).

2.5.6. PHOTOELECTROCATALYSIS

The combination of PCO and photoelectrochemical cells (PECs) to configure photoelectrocatalysis has been researched to further develop water treatment methods shown in Fig 2.5-15 (Garcia-Segura & Brillas, 2017; Garcia-Segura, Dosta, Guilemany, & Brillas, 2013). The photoelectrocatalysis usually consists of a TiO_2 anode which generates electrons to the cathode where the reduction process take place, facilitated by connecting salt bridge. The anodes are typically grown through a Ti sheet to synthesize a TiO_2 hierarchical nanostructured array (C. Liu et al., 2017). The reduction cathode has been demonstrated to generate reactive oxygen species which enhanced organic degradation if oxygen is diffused around the cathode (Garcia-Segura et al., 2013; Juang et al., 2016). The degradation of organics such as phenol and EDTA with the reduction of Cr(VI) to Cr(III) has been demonstrated using PECs, with the anode providing the oxidation process while the cathode initiates the reduction process (Q. Wang et al., 2016; Q. Wang et al., 2017). The degradation function demonstrated the reduction process of O_2 or heavy metal at the cathode and the oxidation of organic pollutant at the anode. However, most anodes and cathodes have been fabricated on hard templates which do not provide flexibility nor light penetration, making it a major drawback for solar applications.

Figure 2.5-15 Photoelectrocatalysis configuration for the separation of redox function for pollutant degradation (Garcia-Segura et al., 2013).

2.5.7. TiO₂ BASED CONFIGURATION FOR SIMULTANEOUS ORGANIC POLLUTANT DEGRADATION AND HEAVY METAL RECOVERY

Generally, the various applications have been used to facilitate the photocatalytic redox process including: photovoltaic cells for electricity generation (Grätzel, 2003), photocatalytic water splitting in a PEC cell setup to produce hydrogen and oxygen (Fujishima & Honda, 1972; Reece et al., 2011) or to degrade organics via a photoelectrocatalysis process (Garcia-Segura & Brillas, 2017), and lastly, through photocatalytic process to concurrently degrade organic wastewater and produce hydrogen (Lee et al., 2015).

The configuration of the photoelectrocatalysis can enable enhanced organic degradation and heavy metal recovery through the specific application of anode and cathode functions. Due to the separation of the redox process, the oxidative anode

plays a function purely for the degradation of organics and bacteria. The cathode can serve as reductive sites for the recovery of heavy metal. It was reported that the co-generation of hydrogen through wastewater produces highly combustible hydrogen gas and requires delicate devices for storage and subsequent usage which was one of the difficulties faced for the application of this design (Chandra & Xu, 2006). Hence, the counter application of the reductive electrons through heavy metal recovery could be directed for heavy metal recovery and preventing hydrogen generation.

2.5.8. SUMMARY AND PERSPECTIVES ON TiO₂ AND SIMULTANEOUS ORGANIC POLLUTANT DEGRADATION AND HEAVY METAL RECOVERY

Our research group and many others have performed significant research to investigate the potential applications for TiO₂. There are several broad applications of TiO₂ in the field of water purification related to organic pollutants, bacteria and heavy metal removal.

The application of TiO₂ in water purification will require modifications. The limiting ultraviolet absorbance will require modifications of the crystal structure either through metal, non-metal doping or the creation of metal oxide heterojunctions. Furthermore, the morphology should include properties such as, micro-/nano structures for recovery of material while also promoting charge transfer and separation, hierarchical surface structures for light scattering and bactericidal capability, and hollow structures which promotes charge transfer, as well as reduce overall material usage and light weight. The synthesis process requires unsophisticated, direct and low-cost methods to achieve scalability but also achieve a combination of all desired requirements.

Lastly, due to the high illuminated surface area needed for solar applications, configuration will require the simplistic binding of TiO₂ onto anode and an adequate cathode material. Furthermore, the use of graphene oxide can aid in the mobility of charge carriers from the anode towards the cathode. The anode and

cathode material needs to be low-cost, easily available as well as allow light penetration. Additionally, flexible and light weight material will further aid in configuration for the water purification process.

The summary of the significant factors of the TiO₂ morphological structure and the configuration to achieve simultaneous Organic Pollutant degradation and Heavy Metal Recovery is shown in Table 1.

Table 1 Significant Factors and Applicability of TiO₂ photocatalyst

Significant Factors of TiO ₂	Applicability
Recovery of material in water medium	Micro structure ensures ease of material recovery.
Morphology of the TiO ₂ structure	<p>Micro-/nano structure promotes water channels for water movement, while the microstructure enables easy recovery of material. The nanostructure reduces charge transfer distance.</p> <p>Hierarchical structure promotes light scattering and bacteria killing capability.</p> <p>Hollow structure promotes short charge transverse distance and internal light harvesting.</p> <p>Multi-shell slight increases total density of TiO₂ without compromises on electron-hole recombination due to the presence of thin shells. Furthermore, light harvesting can also be promoted with multi-shell structure.</p>

The visible light utilisation	Modification of the crystal structure of TiO_2 through metal or non-metal doping as well as heterojunction with other metal oxides.
Scalability of TiO_2 materials	<p>Facile synthesis method to acquire micro-nano structure, hierarchical, hollow, multi-shell, spheres for scalable and practical purposes.</p> <p>Synthesis method must provide flexibility for the modification of TiO_2.</p> <p>Synthesis method must take into consideration green and sustainable approach, using sustainable materials and reduced use of additives.</p>
The utilisation of electron-hole for degradation and heavy metal recovery	<p>Anode and cathode material should be of low-cost, easily available, enable light penetration, flexible and light weight.</p> <p>TiO_2 is easily bound onto the supporting anode.</p> <p>Configure photoelectrocatalysis setup to target electron application for heavy metal reduction and recovery.</p>
Retention time of fluids in photocatalyst	Increased photocatalytic efficiency will reduce the overall pollutant and photocatalyst contact duration.

3. METHODOLOGY

3.1. MATERIAL & SYNTHESIS METHOD

3.1.1. SYNTHESIS OF CARBONACEOUS SPHERES

The carbonaceous spheres were synthesized using a hydrothermal process ((X. Sun & Y. Li, 2004)). 9 g of glucose was dissolved in 100 mL of deionized water, forming a clear glucose solution. The glucose solution was placed into a 120 mL Teflon-lined container at 160 °C for 4 h. The spheres were then washed and centrifuged with absolute ethanol and water in repetition for 3 cycles each. The spheres were then oven-dried at 80 °C for at least 12 h. The final diameter of the carbonaceous spheres was approximately 500 nm, applied in the synthesis of material in the Methodology section 3.1.2.

The synthesis of materials in Methodology sections 3.1.3 to 3.1.7, 80 mL of 1 mol/L glucose solution was sealed in a 120 mL Teflon-lined container (Ang, Juay, Kok, Bai, & Sun, 2017). The mixture was heated at 180 °C for 10 h and subsequently cooled naturally to room temperature. Similar washing techniques were applied for the carbonaceous spheres. The final diameter of the spheres was approximately 1000 nm.

3.1.2. SYNTHESIS OF HIERARCHICAL TiO₂ HOLLOW SPHERE (HTHS) AND TiO₂ CARBON SPHERE (TCS)

150 mg of the above carbonaceous spheres was then added into 100 mL of mono ethylene glycol under stirring and sonicated for 10 mins to provide ample dispersion of the spheres in the solution. 1.7 mL of titanium(IV) butoxide (Sigma Aldrich 97 % reagent grade) was then added to the solution. The solution was then transferred into a 120 mL Teflon sealed stainless steel digestion bomb and kept in an oven at 120 °C for 20 h followed by 4 h at 170 °C. The produced black precipitate was then centrifuged and washed several times with ethanol and DI water and dried in an

oven for 24 h at 80 °C. The black precipitate was further calcinated in a furnace at 500 °C for 4 h at a heating rate of 6 °C/min to produce white TiO₂ hollow spheres. Similar heating condition of 500 °C for 4 h at a heating rate of 6 °C/min under nitrogen conditions was applied to produce carbonized TiO₂ Carbon Spheres (TCS). The changes to the structural formation of HTHS were observed at varying calcination rates and holding periods.

3.1.3. SYNTHESIS OF HIERARCHICAL HOLLOW CARBONACEOUS TiO₂ SPHERE (HHTS)

The HHTS was prepared in accordance to (Ang et al., 2017). 100 mg of the as-prepared carbonaceous spheres was dispersed in 50 mL of absolute ethanol and sonicated for 15 min. Thereafter, 1.4 mL titanium(IV) butoxide and 10 mL glycerol were dissolved in the ethanol mixture and left to mix for 3 h (Tian et al., 2011). The mixture was then transferred into a Teflon-lined stainless-steel autoclave, which was then heated at 180 °C for 24 h. The synthesized material was collected by centrifugation after the autoclave cooled to room temperature, followed by ethanol washing and centrifugation for 3 cycles each. The materials were dried at 80 °C for at least 8 h and the calcination rate was controlled at 500 °C for 2 h at a ramping rate of 2 °C/min.

3.1.4. SYNTHESIS OF CU-CARBONACEOUS (CU-C) SPHERE

The HHTS was prepared in accordance to (Ang et al., 2017). Firstly, 7.25 g of copper(II) nitrate trihydrate (Cu(NO₃)₂·3H₂O) was dissolved in ethanol to form 3 mol/L copper nitrate solution. Next, 200 mg of the synthesized carbonaceous spheres from 3.1.1 was added into the copper nitrate solution and sonicated for 15 min before it was left to age for 6 h under stirring condition at room temperature, to allow for the penetration of Cu ions (X. Lai et al., 2011). The Cu-infused spheres were then separated through centrifugation and washed with ethanol and water in repetition for 3 cycles each. The spheres were dried at 80 °C for 8 h to produce Copper Carbonate Hydroxide Hydrate (Cu-C) spheres (XRD analysis shown in Figure 13 of the Appendix C).

3.1.5. SYNTHESIS OF HIERARCHICAL HOLLOW HETEROJUNCTIONED CARBONACEOUS CuO/TiO_2 SPHERE (HHHS)

The HHHS was prepared in accordance to (Ang et al., 2017). The synthesis approach of the Hierarchical Hollow Heterojunctioned Carbonaceous Copper Oxide (CuO/TiO_2) spheres (HHHS) was similar to that of Hierarchical Hollow Carbonaceous TiO_2 Spheres (HHTS) from 3.1.3 with the addition of the Cu-C spheres mentioned in 3.1.4. 100 mg of the Cu-C spheres was then dispersed into the absolute ethanol- titanium(IV) butoxide - glycerol solution stated in 3.1.3. The mixture was transferred into a Teflon-lined stainless-steel autoclave, and underwent solvothermal process to produce Ti-glycerolate/ Cu Carbonate Hydroxide Hydrate/ Carbonaceous spheres (TCCS). Following that, the TCCS was further separated through centrifugation, washed with ethanol and oven-dried before calcinating at 500 °C for 2 h at a ramping rate of 2 °C/min to produce HHHS.

3.1.6. SYNTHESIS OF FE-CARBONACEOUS SPHERE (FE-C SPHERE)

The Fe-C spheres were prepared with reference to a modified penetration method (Ang et al., 2017; X. Lai et al., 2011). Iron (III) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) was first dissolved in 10 mL ethanol to form 3 mol/L iron nitrate solution. 200 mg of the synthesized carbonaceous spheres was then added into the iron nitrate solution and sonicated for 15 mins. The mixture was left to stir at room temperature for 1, 6, 24 and 48 h. The spheres were separated through centrifugation and washed with ethanol and water in alteration for 3 cycles each. The spheres were oven-dried at 80 °C for at least 8 h to produce Fe-carbonaceous (Fe-C) spheres.

3.1.7. SYNTHESIS OF HIERARCHICAL, MULTI-SHELL, MICRO-/NANO, FE-DOPED TiO_2 HOLLOW SPHERES (HMS)

The synthesis of the Hierarchical, Multi-shell, Micro-/Nano, Fe-doped TiO_2 Hollow Spheres (HMS) was prepared referencing a modified synthesis

solvothermal method (Ang et al., 2017; Tian et al., 2011). 100 mg of the previously fabricated Fe-C spheres were dispersed in 30 mL of absolute ethanol, followed by 2.5 mL of titanium(IV) butoxide and 12.5 mL glycerol. Subsequently, the mixture was sonicated for 15 mins before being left to stir for 3 h. The mixture was then transferred into a Teflon-lined stainless-steel autoclave, which was then heated to 180 °C and kept for 24 h. The autoclave was left to cool naturally to room temperature followed by centrifugation and ethanol wash for 3 cycles. The materials were oven-dried at 80 °C for at least 12 h and calcined at 500 °C for 3 h at a ramping rate of 2 °C/min. The spheres are named based on the iron penetration period of 1, 6, 24 48 h with HMS-1, HMS-6, HMS-24, HMS-48 respectively. However, for the HMS-48, 3 mL of titanium(IV) butoxide and 15 mL of glycerol was used for the synthesis process.

3.1.8. SYNTHESIS OF GRAPHENE OXIDE (GO)

The GO was prepared according to the modified Hummer's method (Hummers & Offeman, 1958) and the procedure was previously described in (P. Gao, Liu, Lee, Zhang, & Sun, 2012; P. Gao & Sun, 2014). Typically, 500 mg of graphite powder and 2 g of sodium nitrate (NaNO_3) were placed into 18 mL of concentrated sulfuric acid. The mixture was stirred for 1h at 5 °C by ice bath. 3 g of potassium permanganate (KMnO_4) was gradually added before continuous stirring for 2h at 5 °C by ice bath. The mixture was heated to 35 °C for 30 mins and 40 mL of DI water was added before heating the mixture up to 100 °C for 15 mins. The mixture was left to cool to room temperature. 70 mL of DI water was added for dilution before 10 mL of hydrogen peroxide (35%) was added. The samples were filtered and washed twice with 400 mL of 5% HCl followed by 200 mL of DI water for 3 cycles. The samples were vacuum dried for at least 5 days.

3.1.9. SYNTHESIS OF GO-HMS SOLUTION

20 mg of the prepared GO was placed in 10 mL of DI water and sonicated for 1 h. 20 mg of HMS-6 was dispersed in 200 μL of 2000 mg/L GO solution and sonicated for 90 mins to fabricate GO-HMS.

3.1.10. FABRICATION OF FLEXIBLE rGO CATHODE & HMS ANODE

The fabrication of the cathode and anode is illustrated in Fig 3.1-1. The transparent indium tin oxide (ITO)/ Polyethylene terephthalate (PET) film was applied as the support structure to fabricate the flexible thin film anode and cathode. A modified electrodeposition method (Guo, Wang, Qian, Wang, & Xia, 2009; A. Liu et al., 2014; Palenzuela et al., 2014; Paredes et al., 2011; Toh, Loh, Kamarudin, & Daud, 2014) was applied to fabricate reduced Graphene Oxide (rGO) layer atop the ITO/PET film. The fabrication of the rGO Cathode applied 50 μ l of 200 mg/L GO solution packed between two ITO/PET films, with the conductive ITO opposite each other. Voltage of 3 V was applied across the film for 5 min. The electrons reduced the GO atop the ITO/PET film on the cathode section of the electrodeposition device, fabricating the rGO Cathode (Palenzuela et al., 2014). The HMS Anode was fabricated using the rGO Cathode as the support structure. The addition of 30 μ l of the previous fabricated GO-HMS was layered and oven-dried for 24 h at 60°C.

Figure 3.1-1 (a) Fabrication method of the Flexible Thin Film rGO Cathode layer through electrodeposition, and (b) the HMS Anode fabricated by oven-drying GO-HMS atop the previously fabricated rGO Cathode.

3.2. MATERIAL CHARACTERIZATION METHODS

3.2.1. SCANNING ELECTRON MICROSCOPY (SEM)/ FIELD EMISSION SCANNING ELECTRON MICROSCOPY (FESEM)

The morphology of the as-fabricated spheres was characterized using scanning electron microscope (SEM, Carl Zeiss AG (Oberkochen, Germany) Evo-50 or the field-emission scanning electron microscope (FESEM, JEOL JSM-7600F). The microscope revealed the surface structure and morphology of the solid samples of size ranging from micro to nanometres working at an accelerated voltage of 3-10 kV and at magnification ranging from $20,000\times$ to $150,000\times$.

3.2.2. ENERGY DISPERSIVE X-RAY SPECTROMETER

The elemental mapping of the fabricated spheres was observed using the energy dispersive X-ray spectrometer (EDX) (Oxford Instrument, X-Max, 80 mm²) attached to the FESEM. The device maps the scanned area of its element make up and tabulates the amount of element within the scanning area.

3.2.3. X-RAY DIFFRACTION

The X-ray diffraction (XRD) analysis was used to examine the physio-chemical makeup of the spherical structures. Powdered solid samples were illuminated with x-rays of a fixed wavelength and the reflected radiation was recorded. The data was analysed for the reflection angle to obtain the inter-atomic spacing as each crystalline solid has its unique characteristic x-ray diffraction pattern. The model used for the analysis of the samples was the Bruker AXS GmbH D8 advanced X-ray diffraction (Karlsruhe, Germany) with monochromated high-intensity Cu_{Kα} radiation ($\lambda = 1.5418 \text{ \AA}$) across a 2θ range of 5–80, step size of 0.0040 and step time of 2 s.

3.2.3.1. Scherrer Equation

The Scherrer Equation (1) was applied to estimate the diameter of the nanoparticle grain size:

$$d_c = \frac{k\lambda}{\beta \cos\theta} \quad (1)$$

Where d_c denotes the grain diameter in nm, k a constant of 0.891, λ the wavelength of the XRD device 0.15418 nm, β denotes the measurement of the XRD peak at full width of the half maximum (FWHM) value at 2θ of the shape pattern.

3.2.4. TRANSMISSION ELECTRON MICROSCOPY (TEM)

The TEM imaging was analysed by JEM-2010 with a point resolution of 1.9 Å, accelerating voltage of 200 kV and magnification of 50 × to 1,200,000 ×. Through

the imaging, the hollow structure morphology and the routine imaging of the atomic columns of the material ranging from micro to nanometres, will be revealed.

3.2.5. UV-VISIBLE ABSORPTION SPECTRUM

The UV-visible spectra of the fabricated samples were measured between 250 to 800 nm using Shimadzu UV-2600 UV-Vis spectrophotometers. The indirect band gap energy (E_G) of the photocatalysts was approximated by employing the Kubelka-Munk function which converts diffusive reflectance measurements into the equivalent absorption coefficients:

$$F(R) = \frac{(1-R)^2}{2R} = \frac{k}{s} = \frac{Ac}{s} \quad (2)$$

Where R is the reflectance, k is the absorption coefficient, s is the scattering coefficient, c is the concentration of the absorbing species, A is the absorbance.

3.2.6. N₂ ADSORPTION AND DESORPTION ISOTHERM

The N₂ adsorption and desorption isotherm was used to measure the porosity of materials at liquid nitrogen temperature (77 K) using a Quadrasorb EVO/ SI system. The Brunauer–Emmett–Teller (BET) model was used to derive the specific surface area of the materials. The samples were degassed at 200 °C for 16 h prior to measurement. The Barrette-Joynere-Halenda (BJH) method was employed to obtain the pore size distribution of the spheres.

3.2.7. FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

The FTIR spectra were recorded in the range of 400-4000 cm⁻¹ at a resolution of 4 cm⁻¹ using PerkinElmer FT-IR Spectrometer Frontier. The GO, HMS and GO-HMS samples applied compressed potassium bromide (KBr) pellets and air as the background scan. The HMS Anode and rGO Cathode thin film was directly measured for their FTIR spectra and applied PET as the background scan.

3.3. APPLICATION STUDY

3.3.1. PHOTOCATALYTIC OXIDATION (PCO) USING METHYLENE BLUE

The Photocatalytic Oxidation (PCO) experiments were carried out for Hierarchical TiO₂ hollow spheres (HTHS) and P25 nanoparticles (P25) in glass container with a magnetic stirrer to maintain homogenization throughout the reaction. UV irradiation from a low-pressure UVP Pen-Ray mercury lamp (model no. 11SC-1L, UVP, LLC, California, USA) was used for the experiment; the energy emission of the UV lamp is centred at 365 nm with a light intensity of 1150 mW/cm².

100 mL of 30 mg/L MB solution was prepared and a baseline sample was taken. 30 mg of the catalyst spheres were then immersed in the MB solution and stirred in the dark for 1h to allow for adsorption-desorption equilibrium of the samples and the initial concentration of the MB solution was taken. The PCO process started once the lamp is lit, the MB samples were taken at 15 min interval via a syringe and filtered using glass syringe filters (0.45 µm) to separate the material for subsequent analysis. The concentration of MB was determined by a UV–visible spectrophotometer (Thermo Scientific Evolution 300) between wavelengths of 400 to 800 nm. The kinetics of the organic pollutant degradation was tabulated using the Langmuir–Hinshelwood model to derive the rate of pollutant degradation in Appendix A.

3.3.2. MEMBRANE FLUX EVALUATION

The investigation of membrane flux through an indirect irradiation method was carried out based on the schematic diagram illustrated in Fig 3.3-1 for the Hierarchical TiO₂ hollow spheres (HTHS), and P25. The HTHS and P25 were first filtered atop a PES microfiltration membrane with a pore size of 0.2 µm and a surface area of $9.62 \times 10^{-4} \text{ m}^2$ as the support membrane. The samples were then irradiated under UV-vis light for a period of 4 h. A low-pressure UVP Pen-Ray mercury lamp (model no. 11SC-1L, UVP, LLC, California, USA) was used for the

experiment; to induce UV-irradiation, the energy emission of the UV lamp is centred at 365 nm with a light intensity of 1150 mW/cm². After that, the membrane permeate flux was tested using a dead-end filtration device under an applied pressure of 5 PSI inserted on the feed as shown in the schematic diagram below. During the test of the membrane flux, no UV-irradiation was provided. The weight of permeate flux was captured obtained in a weighing scale and converted to volume using the water density value of 999.97 kg/m³. The resulting changes in weight were recorded at 2 min intervals. As a control, HTHS and P25 membranes were also evaluated in the absence of UV-irradiation. The samples were kept in the dark for 4 h prior to the membrane flux evaluation.

The flux of each sample was tabulated based on the amount of water filtrated at an interval of 2 mins and an effective membrane surface area of $9.62 \times 10^{-4} \text{ m}^2$.

$$\text{Flux} \left(\frac{\text{L}}{\text{m}^2 \cdot \text{hr}} \right) = \frac{\text{Volume (L)}}{\text{Surface Area (m}^2\text{)} \cdot \text{Time (hr)}}$$

Figure 3.3-1 Schematic diagram of the Membrane Flux Evaluation Setup

3.3.3. PHOTOCATALYTIC OXIDATION (PCO) USING ACID ORANGE

7

The photocatalytic activities of the HHHS, HHTS and conventional P25 photocatalysts were evaluated under UV irradiation (365 nm), using Acid Orange 7 (AO7) ($C_{16}H_{11}N_2NaO_4S$) as the organic probe molecule. The procedure is as shown in Fig 3.3-2. The organic degradation test was carried out in a cylinder containing 10 mg of the respective photocatalysts in 100 mL solution of 10 mg/L AO7. The mixture was kept in the dark for 1 h to achieve dark adsorption equilibrium while keeping the solution homogeneous under stirring condition. The evaluation proceeded with the initial exposure of UV irradiation from a low-pressure UVP Pen-Ray mercury lamp (model no. 11SC-1L, UVP, LLC, California, USA) and samples were taken at intervals of 10 min for a period of 1 h. The results were analysed using the Thermo Scientific™ Evolution 300 UV-Vis Spectrophotometer to observe the decolorization of AO7 at characteristic absorbance wavelength (λ) of 483 nm. The kinetics of the organic pollutant degradation was tabulated using the Langmuir–Hinshelwood model to derive the rate of pollutant degradation in Appendix A.

Figure 3.3-2 Schematic diagram to illustrate the evaluation of the water treatment performance under UV-light and Acid Orange 7 as the probe molecule.

3.3.4. BACTERICIDAL EVALUATION

3.3.4.1. Preparation of Culture Medium Plates

The agar solution was prepared by dissolving 40 g of Tryptone Soya Agar powder (Oxoid, CM0131) with 1 L of DI water. The agar solution was then sterilised for 15 min at 121 °C in an autoclave. The agar solution was cooled to approximately 55 °C and was then transferred into empty Petri dishes and was left to cool in a sterilised biosafety cabinet for 2 h.

3.3.4.2. Cultivation of Microorganisms *Escherichia coli*

E. coli (ATCC® 25922™) was chosen as the model pathogen for the bacteria disinfection experiments. *E. coli* was cultivated in Lysogeny broth (LB) solution prepared by mixing 25 g of Miller Luria-Bertani nutrient powder in 1 L of deionised (DI) water. The mixture was stirred till the powder was fully dissolved before it was sterilized in an autoclave at 121 °C for 15 min and cooled naturally to room temperature. The LB solution was used to cultivate *E. coli* at 37 °C for 18 h in a shaking incubator to ensure cells reach exponential growth. The cells were harvested by centrifugation to remove residual macromolecules. The *E. coli* cells were serially diluted in 0.9% NaCl saline solution to achieve a concentration of 10⁶ colony forming units (CFU) per mL.

3.3.4.3. Anti-bactericidal test without visible light irradiation

10 mg of HMS-6 were first added to 50 mL of diluted bacteria solution and left to stir at 250 rpm. The mixture was left in an enclosed setup. Aliquots were withdrawn at the start of the experiments and subsequently at every 10 min interval for a period of 60 mins. The collected aliquots were immediately spread on LB culture medium plates, with 0.1 µL of sample per plate. Three LB plates were used for each sampling point. The plates were then incubated for a period of 24 h at 37°C. Anti-bactericidal test without visible light irradiation was also carried out without the

addition of photocatalyst. Using the mentioned preparation steps, the bacteria suspension was also left to stir at 250 rpm in an enclosed setup.

3.3.4.4. Anti-bactericidal test with visible light irradiation

The anti-bactericidal test was carried out using a solar simulator with UV-vis light source at 300 W. An UV filter is then attached to block out the UV-light shown in Figure 3.3-3. 10 mg of HMS were first added to 50 mL of diluted bacteria solution and left to stir at 250 rpm. Aliquots were withdrawn at the start of the experiments and subsequently at every 10 min interval for a period of 60 mins. The collected aliquots were immediately spread on LB culture medium plates, with 0.1 μL of sample per plate. Three LB plates were used for each sampling point. The plates were then incubated for a period of 24 h at 37°C.

Figure 3.3-3 Visible light degradation of *E. Coli* using Solar Simulator

3.3.5. PHOTOELECTROCATALYSIS OF CU-AZO COMPLEX

The experiment applied the HMS Anode and rGO Cathode in a Petri dish without salt bridge to assess the activities of the photoelectrocatalysis configuration shown in Fig 3.3-4. In the experiment, three setups were used, namely, the (a) Power Supply setup connected both anode and cathode to a 1.5 V battery through copper tapes, the (b) Loop setup connected both anode and cathode through copper tape without any added potential difference and, the (c) Open Circuit setup isolates the anode and cathode configuring it to a photocatalytic oxidation process. The experiment was performed using the same anode but in the sequence of Power Supply, Loop and Open Circuit for 3 cycles. The experiment used Acid Orange 7 (AO7) ($C_{16}H_{11}N_2NaO_4S$) and copper sulphate Cu-azo dye complex as the organic pollutant and heavy metal source respectively. 10 mg/L AO7 and 10 mmol/L copper sulphate pentahydrate was dissolved in DI water and 80 mL solution was transferred into a Petri dish. Both films of 1 cm in width were submerged 2 cm into the solution and kept in the dark for 1 h to achieve dark adsorption equilibrium under a stirring condition. The evaluation proceeds under the exposure of UV-visible irradiation from a low-pressure UVP Pen-Ray mercury lamp (model no. 11SC-1L, UVP, LLC, California, USA) and samples were taken at intervals of 15 min for a period of 1 h. The results of the decolourization of the Cu-azo dye complex were analysed using Shimadzu UV-1800 spectrophotometer to observe the characteristic absorbance wavelength (λ) of 484 nm. The copper recovery was analysed via the use of PerkinElmer Optima 8300, Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) and PerkinElmer SCIEX, Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), ELAN DRC-e, Axial Field. The samples were prepared by soaking 0.5 cm² cathode material in 1 mol nitric acid for 3 h before further diluting to obtain a 10 mL solution containing 0.0001 mol of nitric acid. The solution was filtered through a 0.45 μ m syringe filter. Additional characterization on the rGO Cathode surface was also performed using FESEM imaging to observe the recovery of Cu(s). Further elemental mapping was performed using Energy Dispersive X-ray Spectrometer (EDX), Oxford Instrument, X-Max, 80 mm² sample was mounted in the FESEM to verify the elemental composition of the recovered Cu.

An additional experiment was applied using the same setup but the pollutant only consisted of AO7 in the sequence of Open Circuit and Power Supply for 3 cycles. The results of the AO7 dye were analysed using Shimadzu UV-1800 at characteristic absorbance wavelength (λ) of 484 nm. The kinetics of the organic pollutant degradation was tabulated using the Langmuir–Hinshelwood model to derive the rate of pollutant degradation, as presented in Appendix A.

Figure 3.3-4 Experiment setup of the water treatment process with the three configurations namely the (a) 1.5V Power Supply, (b) Loop and (c) Open Circuit setup.

4. CHAPTER

INTRODUCTION

The chapter introduces the preliminary understanding of TiO₂ hollow spheres using carbonaceous sphere as template. The synthesis process will fabricate Hierarchical TiO₂ Hollow Sphere (HTHS) which will be evaluated against P25 nanoparticles for its photocatalytic degradation of pollutants as well as changes to flux with and without the influence of UV-irradiation. The fabrication of Ti Carbon Sphere (TCS) is used to aid in the understanding of the synthesis process.

RESULTS AND DISCUSSION

4.1. MATERIAL CHARACTERISATION

4.1.1. SYNTHESIS OUTLINE AND THE MORPHOLOGICAL CHARACTERIZATION OF HTHS AND TCS

In order to achieve Ti based spheres, the adaptation of G. Zhang and Lou (2014) methodology with solvothermal processes was used, as summarised in Fig 4.1-1. Carbonaceous spheres were used as the hard template, synthesised via the hydrothermal treatment of glucose solution (Xiaoming Sun & Yadong Li, 2004). The (a) penetration of Ti ions into the carbonaceous spheres was applied in the form of titanium glycolate solution in an autoclave vessel. The temperature increase allows (b) solidification producing Ti-glycolate/ C Spheres (TGC). The calcination and carbonization of the TGC led to HTHS and TCS, respectively.

Figure 4.1-1 Carbonaceous (C) spheres synthesised via hydrothermal process (a) penetration of Ti into the C spheres, (b) and the solidification of Ti/C spheres, produces Ti-glycolate/ C sphere (TGC). The calcination process (c) produces Ti Hollow Spheres while the (d) carbonization process produces Ti carbon sphere in nitrogen atmosphere.

Firstly, Field Emission Scanning Electron Microscope (FESEM) and Scanning Electron Microscope (SEM) were employed to study the morphology of the spheres. The imaging of the (a) carbonaceous (C) spheres, (b) the intermediate Ti-glycolate/ C spheres (TGC), (c), (d) and (e) the crystalline Hierarchical TiO_2 Hollow Spheres (HTHS) and the (f) Titanium Carbon Spheres (TCS) are shown in Fig 4.1-2. The imaging of (a) the carbonaceous spheres portrays the hard template with smooth surface and uniform diameter of 500 nm. The subsequent introduction of Ti into the C spheres led to the formation of (b) TGC using the solvothermal process. The surface now consists of a uniform layer of Ti structure with the formation of a nanoparticulate surface taking the shape of the C sphere template. The formation of the Ti layer was attributed to the hydrophilic function groups around the surface of the carbonaceous spheres (X. Sun & Y. Li, 2004; G. Zhang et al., 2014). The calcination of TGC produces the HTHS, and changes to the spherical surface reveals a hierarchical surface morphology shown in Fig 4.1-2 (c). Furthermore, a reduction of ~150-200 nm of the spherical diameter was observed. The expanded image of Fig 4.2-1 (e) reveals the hollow interior morphology of the spheres, additionally, there were no changes in spherical size nor surface structure of the carbonized TCS shown in Fig 4.1-2 (f) due to the present carbonaceous sphere. This affirms that the contraction of the HTHS was dependent on the

decomposition of the carbonaceous template, which was attributed to the contraction of C spheres during the calcination process (G. Zhang et al., 2014).

Figure 4.1-2. (a) Carbonaceous (C) Spheres synthesised using glucose in a hydrothermal process, (b) Ti-glycolate / C spheres (TGC) formed after penetration and solidification of Ti via solvothermal treatment. (c & d) Hierarchical TiO₂ Hollow Spheres (HTHS) after calcination at 500°C at a ramping rate of 6 °C/min and holding time of 4 h. (e) The expanded image of (d) revealing the hollow core of the HTHS (f) Titanium Carbon Spheres (TCS) produced using the carbonization of Ti-glycolate / C spheres in nitrogen atmosphere.

To further understand the contraction of the spheres, investigation into the penetration duration, the rate of calcination increment and holding duration was performed. Lowering the penetration duration greatly affected the structural stability of the HTHS as shown in images Fig 4.1-3 (a) and (b). The shortening of penetration duration from 20 h to 12 h and solidification duration from 4 h to 2 h clearly weakened the structural formation of the HTHS, revealing the inability to retain the spherical structure after calcination. The instability of the TiO_2 structure signifies the lack of bonding between the TiO_2 nanoparticles due to the reduced synthesis duration. The contraction of the HTHS was in accordance to the surface of the carbonaceous spheres, which demonstrated the highly functionalised surface of the C spheres.

The changes to the shell surface structure were investigated with regard to changes to its calcination ramping rate and holding time. The results are compared in Fig 4.1-3 (a), (c) & (d). The reduced holding duration from 4 h to 1 h results in smoother spherical surface, as shown in Fig 4.2 (a) and (c) respectively. The similar spherical size of $\sim 300\text{nm}$ indicates that the carbonaceous spheres have already oxidised, which revealed that the hierarchical surface morphology was dependent on the calcination duration. The increase of ramping rate to $10\text{ }^\circ\text{C/min}$ while maintaining a 1 h holding duration, resulted in a reduced size to 300 nm , and rough surface morphology with a less circular structure as shown in Fig 4.1-3 (d). Moreover, structural similarities could be observed between HTHS shown in Fig 4.1-3 (d) and that of $6\text{ }^\circ\text{C/min}$ and 4 h holding duration shown in Fig 4.2 (a). The change in surface morphology could be related to the faster ramping rate which accelerated the oxidation of the carbonaceous spheres, resulting in the rapid contraction of the TiO_2 shell and the less spherical structure.

Overall, the calcination of the Ti-glycolate carbon spheres resulted in the formation of TiO_2 structures with observable reduction in spherical diameter from 500 nm to $\sim 300\text{ nm}$. However, the surface structure of the HTHS was determined by: (1) The penetration/solidification duration of the synthesis process which determined the structural stability of the HTHS. (2) The ramping rate of calcination which controlled the rate of carbonaceous spheres' oxidation. (3) The holding time

of the calcination process which provided more energy, resulting in the changes to surface structure.

Figure 4.1-3 The calcination temperature of 500°C was applied for all sphere with changes to other factors. (a) HTHS with 20 h penetration, 4 h solidification duration, calcination ramping rate of 6 °C/min, and a holding time of 4h (b) HTHS with reduced penetration time of 12 h and 2 h solidification time, observed structural dissolution after ramping rate 6 °C/min and holding time of 4h. (c) HTHS of 20 h penetration, 4 h solidification with ramping rate of 6 °C/min and holding time of 1h, (d) HTHS ramping rate of 10 °C/min and a holding time of 1h.

4.1.2. CRYSTAL STRUCTURE DETERMINATION

The crystal structures of the as-prepared HTHS and P25 nanoparticles were determined using X-ray diffraction (XRD) and the results are shown in Fig 4.1-4. The HTHS and P25 diffraction peaks $2\theta = 25.4^\circ$ (101), 37.9° (004) and 48.1° (200) were indexed to the anatase crystalline phase of TiO_2 via the use of International Centre for Diffraction Data (ICDD 01-086-1157). Moreover, P25 nanoparticles

contained rutile phase and the diffraction peaks of 110, 103 and 211 were indexed to (ICDD 0-021-1276). Using the Scherrer Equation, the grain size for the 101 reflection of the anatase HTHS is approximated at 13.79 nm and the P25 at 20.17 nm. This grain size can be attributed to the nanoparticulate surface structure of the HTHS shown in the FESEM imaging 4.1-2 (c).

Figure 4.1-4 XRD pattern of Hierarchical TiO₂ Hollow Sphere and P25 Nanoparticles

4.1.3. LIGHT ABSORPTION SPECTRUM

The light absorption spectra of the HTHS and P25 are shown in Fig 4.1-5. The TiO₂ content of the HTHS and P25 clearly limits the absorption to the ultraviolet region between 250 to 400 nm. The presence of rutile in P25 with a reduced bandgap of 3 eV would have display larger absorption in the visible light region above 400 nm (Scanlon et al., 2013). However, the HTHS spectrum observed slightly more absorbance in the visible light region. These changes can be attributed to the enhanced light scattering of the hollow spheres (Kang et al., 2012), and the doping of carbon-based material from the titanium-glycolate precursor, resulting in

a slight increase in absorbance in the visible light region (Y. Park et al., 2009; Y. J. Yang et al., 2015).

Figure 4.1-5 Light Absorbance Spectrum of HTHS and P25.

4.2. WATER TREATMENT PERFORMANCE

4.2.1. PHOTOCATALYTIC ACTIVITY EVALUATION USING METHYLENE BLUE

To investigate the photocatalytic activity of HTHS compared to that of P25, methylene blue (MB) was used as the probe molecule. The change in visible light absorption of the MB dye was taken as the rate of dye degradation. The photocatalytic degradation rate of MB in the presence of the various samples is tabulated based on Langmuir-Hinshelwood kinetics (Dung, Van Khoa, & Herrmann, 2005; Gaya & Abdullah, 2008; Mills & Le Hunte, 1997). Results of the photocatalytic oxidative performance of the HTHS and P25 are compared in Fig 4.2-1.

The degradation rate of the MB solution over a period of 45 mins is shown in Fig 4.2-1 (a). The HTHS demonstrated higher photocatalytic activity compared to P25. The calculated rate constant of degradation for the (b) HTHS is 0.05 /min while the (c) P25 is 0.03 /min. Typically, the presence of the rutile phase results in better photocatalytic performance compared to anatase, due to the dual band alignment which allow for the transfer and trapping of electrons from the conduction band which prevented recombination (Scanlon et al., 2013). Hence, the increased rate of degradation for the HTHS can be attributed to the carbon doping into the crystal structure, the smaller particles size as well as the light scattering between particles. The morphology of the HTHS and the light adsorption spectrum, the light scattering between and within the structure might have contributed to enhanced light scattering in the solution. Additionally, the smaller grain size of 13.79 nm from the XRD pattern reduces the transverse distance of the electrons reducing electron-hole recombination (Chong et al., 2010). The doping with the carbon (Y. Park et al., 2009) might have further aided in the formation of higher valence band which traps holes to aid in the oxidation and production of hydroxyl radicals ($\text{OH}^{\bullet}$) while also preventing the recombination of electrons from the conduction band back to the valence band of the TiO_2 .

Figure 4.2-1 (a) Photocatalytic degradation of MB, rate of degradation for (b) Hierarchical TiO_2 hollow spheres (HTHS) and (c) the P25 nanoparticles using Langmuir-Hinshelwood Kinetics.

4.2.2. MEMBRANE FLUX EVALUATION

Next, the membrane flux and the UV-induced superhydrophilicity of the HTHS compared to P25 nanoparticles was investigated using a dead-end filtration setup, DI water was applied as the water medium. The metal oxides were layered atop a support membranes and were either kept in the dark or UV-irradiated for 4 h. The results of flux are tabulated in Fig 4.2-1. The UV-irradiated membranes are denoted by HTHS UV and P25 UV and the dark conditioned membranes are denoted as HTHS Dark and P25 Dark.

Under the dark condition, the flux for HTHS Dark was approximately 75% larger than that of the P25 Dark. Clearly, the flux of membrane is greatly reduced with decreased size of the TiO_2 . The HTHS demonstrated higher membrane flux due to its larger size. This resulted in larger pack density of the HTHS compared to P25

illustrated in Fig 4.2-3. Due to the applied pressure, the compaction of the P25 nanoparticles resulted in narrower void spacers for the transverse of flux.

Figure 4.2-2 Permeate flux evaluation of UV radiated (HTHS UV and P25 UV) and dark conditioned (HTHS Dark and P25 Dark) using dead end filtration with DI water as the medium and an applied pressure of 5 PSI.

The introduction of UV-irradiation demonstrated the effect of UV-induced superhydrophilicity of TiO_2 and the increased in flux is demonstrated for HTHS UV and P25 UV. Nevertheless, the change in flux for HTHS UV is lower compared to P25 UV. The change in flux performance can be attributed to the packing density of the structure, although, the densely packed P25 membrane results in higher resistance compared to the HTHS membrane (Pan et al., 2008). As superhydrophilicity changes the surface properties of TiO_2 from the O to the O-H species (Fujishima et al., 2000), the influence of surface properties will greatly affect the surrounding water. This change in surface property will be more apparent for the closely packed P25 membrane. Moreover, the large water channel within the

HTHS membrane reduced the influence of the surface superhydrophilicity as majority of water does not contact the surface of HTHS compared to the P25 nanoparticles. The initial surge in flux for the HTHS UV might suggest that the expulsion of air bubbles trapped within the hollow structure, created air gaps within the HTHS membrane which reduced the overall resistance and led to the increased flux performance. The gradual reduction in flux indicated that UV-light is required to maintain superhydrophilicity.

Figure 4.2-3 Illustration of the superhydrophilicity and the water contact surface of HTHS and P25. (a) Cross-sectional view of HTHS (grey) on support membrane (blue) and the larger water channel reducing the influence of superhydrophilicity. (b) Cross-sectional view of P25 nanoparticles (green) on support membrane (blue) and a higher water to P25 nanoparticles contact due to the narrower water channel.

4.3. CONCLUSION

HTHS was successfully fabricated using carbonaceous spheres as templates and resulted in hierarchical surface consisting of agglomerations of nanoparticles of 13.79 nm and hollow interior structure. The photocatalytic performance of HTHS demonstrated enhanced pollutants degradation due to the possible doping of carbon through the Ti-glycolate and the hollow interior which caused light scattering. The combination of the properties enabled enhanced photocatalytic performance compared to the P25. The fabricated HTHS was investigated under various

synthesis conditions to observe changes in the structural stability and surface morphology. However, the Ti-precursor was not able to penetrate the carbonaceous sphere to produce multi-shell structure. These properties were dependent on the synthesis duration, the ramping and holding duration of calcination which affected the contraction of the carbonaceous spheres. The flux evaluation demonstrated the superhydrophilicity of TiO_2 and the packing density which was a great factor influencing flux performance. However, owing to the large morphological structure and size, flux was generally independent of superhydrophilic surfaces. Hence, larger materials are generally unaffected by surface changes, however, mesoporous structures will be greatly influenced by the superhydrophilic surfaces.

5. CHAPTER

This Chapter 5 of this thesis is reprinted with permission from *Catalysis Science & Technology* and was invited for cover highlight during the writing of the Thesis:

Koon Keong Jeremy Ang, Jermyn Juay, Yonghao Kok, Hongwei Bai, Darren D. Sun, “Multi-Dimensional Micro-/nano-reactor Spheres for Sustainable Water Treatment”, *Catalysis Science & Technology*, 2017, DOI: 10.1039/C7CY00483D.

INTRODUCTION

To further improve upon morphology, the synthesis process was enhanced to incorporate multi-dimensional properties such as micro-/nano structures consisting of heterojunctioned carbonaceous CuO/TiO₂, hierarchical thorns, and multi-shell hollow spheres.

The novel synthesis approach demonstrated the applicability of carbonaceous spheres hard templates and the use of highly concentrated Cu(NO₃)₂ solution to enable diffusion of ions into the porous structure of the spheres. The Cu-infused sphere was further encapsulated with Ti-glycerolate through a solvothermal process which forms thorn surface morphology. The fabricated sphere integrated the multiple dimensions using the porous interior of the carbonaceous spheres to adsorb metal ions while its functionalized exterior surface enabled the formation of one-dimensional (1D) hierarchical structure.

A novel micron-sized Hierarchical Hollow Heterojunctioned Carbonaceous CuO/TiO₂ Sphere (HHHS) was fabricated. The HHHS consists of carbonaceous TiO₂ thorn and a mesoporous shell interface containing carbonaceous TiO₂, CuTi₃O₈/CuO heterojunctions and an inner core shell assembled by 20-30 nm nanoparticulates. The report will further investigate the synthesis and seeks to introduce a hypothetical structure of CuTi₃O₈ observed within the HHHS.

The chapter will further investigate the degradation mechanism to elucidate the applicability of the hierarchical and micro-/nano-structure of the mesoporous array

for its pollutant adsorption, degradation and transfer throughout the spheres to generate clean water.

RESULT AND DISCUSSION

5.1. MATERIAL CHARACTERISATION AND SYNTHESIS MECHANISM

The fabricated spheres, namely, the multi-shell hollow, hierarchical, and heterojunctions carbonaceous CuO/TiO₂ spheres, are simplified as (HHHS), the hierarchical hollow carbonaceous TiO₂ spheres (HHTS) were fabricated without the addition of copper element. Conventional P25 was applied as the reference material for comparison due to its similar grain size.

5.1.1. MORPHOLOGICAL CHARACTERIZATION OF HHTS

The STEM imaging of the HHTS is shown in Fig 5.1-1 (b). HHTS have a diameter of approximately 3 μm and the hierarchical structure thorn length of approximately 1 μm at each sides of the sphere. The hollow core diameter measuring 1 μm is similar to that of the carbonaceous spheres shown in Fig 5.1-1 (a) and is indicative of typical hard template synthesis of hollow spheres. The hollow interior of the HHTS revealed in Fig 5.1-1 (c) consists of a grainy base layer approximately 50 nm thick, which serves as the support layer for the growth of the thorn-like hierarchical structures. The two-tier morphology structure of the HHTS is further illustrated in Fig 5.1-1 (d). The absence of carbonaceous spheres reported the synthesis of a sphere which was dissolved and recrystallized to form hierarchical spheres (Tian et al., 2011). In the presence of carbonaceous hard template, the nucleation sites are diverted onto the surface of the carbonaceous spheres due to its highly functionalized surface (X. Sun & Y. Li, 2004; X. Sun, Liu, & Li, 2006), which further indicated the surface encapsulation of the carbonaceous spheres surface.

Upon closer inspection of Fig 5.1-1 (c), the interior of the hollow surface reveals a grainy base layer. The difference between the shell and the thorn structure implies

that the reactive functional groups resulted in a grainy layer support structure (yellow layer), which retained an independent morphology to that of the thorn-like hierarchical structure.

Figure 5.1-1. (a) Carbonaceous spheres. (b) dark field FESEM-STEM image of the HHTS with the visible hollow core. (c) The hollow structure of the HHTS spheres with observable porous support structure and the subsequent growth of the thorn-like hierarchical structure. (d) Schematic diagram of (c).

5.1.2. MORPHOLOGICAL CHARACTERIZATION OF HHHS

The fabrication of Hierarchical Hollow Heterojunctioned Carbonaceous CuO/TiO₂ Spheres (HHHS) involves an additional stage of copper penetration via diffusion into the pores of the carbonaceous spheres (X. Lai et al., 2011), resulting

in the formation of Cu Carbonate Hydroxide Hydrate (Cu-C) spheres (indexed to PDF 00-062-0167 in Fig 13 of the Appendix C). This is followed by the encapsulation of 1D Ti-glycerolate (Tian et al., 2011) thorn-like structures, resulting in the formation of Ti-glycerolate/ Cu Carbonate Hydroxide Hydrate /CuO/ Carbonaceous spheres (TCCS), depicted in images Fig 5.1-2 (a) - (c), which illustrates the different tiers of the structure. The schematic diagram illustrates the different tiers of the TCCS, the carbonaceous spheres (red), the Cu Carbonate Hydroxide Hydrate (blue), the mixture between Ti-glycerolate and Cu Carbonate Hydroxide Hydrate (purple) and Ti-glycerolate (grey). The carbonaceous spheres shown in Fig 5.1-1 (a) revealed the conjoining of the spheres which is revealed in Fig 5.1-2 (a). Nonetheless, the hierarchical surface took the shape of the carbonaceous spheres and demonstrated that despite the addition of copper ions within the carbonaceous pores, the encapsulation of the Ti-glycerolate was unhindered. The formation of the HHHS was further revealed in Fig 5 of the Appendix C. The overall diameter of HHHS is approximately 3 μm , with a circular shell of 1 μm and wavy 1D thorn structure of approximately 1 μm at both sides of the sphere. The calcination of the TCCS resulted in the fabrication of the HHHS in the TEM and FESEM image shown in Fig 5.1-2 (d) and 3(g) respectively. The corresponding schematic diagrams Fig 5.1-2 (e) and 3(f) illustrate the various tiers of the structure. The HHHS revealed similar hierarchical surface structure of 3 μm to that of the HHTS. The growth and crystallization of the Ti-glycerolate hierarchical thorns can be observed before and after calcination, revealing straightening of the 1D hierarchical thorn structures in the HHHS. However, the HHHS had a thicker outer hollow shell of 1.2 μm in diameter (purple) and thickness of approximately 200-300 nm made up of nanoparticulate agglomerations measuring 30 nm marked by the green boundary shown in Fig 5.1-2 (g). Furthermore, the diameter of the hollow sphere measures at 850 nm which is 150 nm less than the 1 μm carbonaceous sphere and portrays spherical irregularity. The assembly of Ti-glycerolate is largely determined by the functionalized surface groups shown in the HHTS and the copper ions present diffuse outwards and interact with the Ti-glycerolate surface forming the green boundary layers. Concurrently, the void left by the Cu ions allows for the inward penetration of the

Ti which forms the purple boundary rings which is of 850 nm in diameter. The calcination process oxidized and removed the carbonaceous sphere (red) which led to the contraction and formation of the smaller inner sphere. Due to the deeper penetration of Cu, the inner sphere likely existed as CuO (blue) (X. Lai et al., 2011). The CuO/TiO₂ shell (purple) and the carbonaceous TiO₂ thorn (grey), both remained rigid and unaffected by the contraction. This resulted in the formation of the multi-shell hollow sphere HHHS. The HHHS consists of overlapping lattice structures of the base layer, consisting of 2 lattice fringes shown in the TEM image of Fig 5.1-2 (h). The interplanar spacings are 0.352 nm (d_{101}) and 0.253nm (d_{111}) which are consistent with anatase TiO₂ and CuO respectively (S. S. Lee et al., 2013; Siew Siang Lee et al., 2013). The TEM imaging suggests the presence of CuTi₃O₈ with an interplanar spacing of 0.243 nm. A change in the tone of nanoparticles suggests a change in elements. It has been reported that CuO revealed a lighter tone than TiO₂ in a heterojunction formation (Siew Siang Lee et al., 2013), hence, the change to a darker tone suggests the formation of CuTi₃O₈. The TEM image in Fig 5.1-2 (i) further revealed the crystal makeup of the linear hierarchical thorn (grey) consisting of a 20 nm-sized crystal forming the bulk diameter of 3 μ m.

Further characterisation via EDX analysis was applied to Fig 5.1-2 (g) on a copper grid support which affected the overall composition of Cu element. Fig 5.1-2 (j) and (k) show the elemental mapping of Ti and Cu, with segmentation of the shell (purple), the diffusion of Cu away from the shell (red), and the Ti dominated thorns (yellow). The Cu is largely found near the 100 nm shell (purple) which is the penetrated Ti-Cu, and the outward diffusion of 100-200 nm to the boundary (green). After which, minimal Cu is observed on thorns further away from the shell, which is largely dominated by TiO₂. The Ti-Cu elements typically possess nanoparticulate structure while the hierarchical thorns are largely composed of TiO₂. The elemental mapping of Ti displayed an even distribution throughout the spheres. The Cu elemental map, on the other hand, observed a more circular distribution pattern, signifying majority of the heterojunctions is retained and located at the shell layer.

Figure 5.1-2. (a) The encapsulation and synthesis of Ti-glycerolate/ Cu Carbonate Hydroxide Hydrate/ C spheres (TCCS). (b) Schematic diagram illustrating the penetrated Cu ions into the pores of the sphere and the Ti hierarchial structures. (c) The (purple) layer illustrates the interacted Ti-Cu ions, the deeper (blue) remains as Cu Carbonate Hydroxide Hydrate due to the depth of penetration, the (green) reveal the Ti-Cu interaction at the Ti thorns layer. (d) TEM imaging of the Multi-shell Hierarchial Structure of the HHHS revealing the inner sphere within the hollow spheres. (e) Schematic diagram of the three-tier make up of the HHHS including the carbonaceous TiO₂ hierarchial thorn structure (grey), the heterojunction surface layer of carbonaceous CuO/TiO₂ (purple) and a CuO inner shell (blue). (f) The enlarged image of the heterojunction layer is made up of a porous inner layer (purple) and the TiO₂/CuO nanoparticles due to the outward diffusion of the Cu-ions. (g) The nanoparticulate interior morphology (purple) of the HHHS formed by the CuO, the CuO/TiO₂ heterojunction (green) and the hierarhical surface structure carbonaceous TiO₂. (h) The TEM imaging revealing the grainy 20-30

nm nanoparticulate heterojunctions with the lattice of TiO₂ and CuO and insert of Fig 5.1-2 (h) revealing CuTi₃O₈ and CuO. (i) The TEM image of the hierarchical thorn made of compact 20 nm nanocrystals. The EDX mapping of the (j) Ti elements and (k) Cu elements displaying the element composition at the shell (purple), the diffusion of Cu away from the shell (green), and the Ti dominated thorns (yellow).

5.1.3. EXPLANATION OF THE SYNTHESIS MECHANISM THROUGH MORPHOLOGICAL EVOLUTION

The synthesis process of the HHHS is illustrated in the schematic diagram shown in Fig 5.1-3. The (a) carbonaceous sphere, possessing a highly-functionalized surface and porous structure, was used as the hard template for the (b) diffusion and penetration of Cu²⁺ ions forming bonds (X. Lai et al., 2011; X. Sun & Y. Li, 2004) (c). The subsequent (d) solvothermal treatment resulted in the encapsulation of the Cu-infused spheres with Ti-glycerolate hierarchical structure (e) due to the presence of hydroxyl groups in the glycerol molecules and the surface functional groups of the Cu-infused spheres (P. Shao et al., 2015; Shao, Tian, Shi, Gao, & Cui, 2015). The elemental changes before and after the Cu-infusion were analysed via XRD and is shown in Fig 12 and 13 of the Appendix C indexed to Copper Carbonate Hydroxide Hydrate. This demonstrates the reaction between the copper nitrate solution with the surface functional groups to form copper carbonate hydroxide hydrate compounds after drying. The solvothermal process reported fast nuclei growth within 30 min which resulted in a solidified outer shell and the continual dissolution-recrystallization resulted in the formation of 1D directional thorns (Tian et al., 2011). The observed 30 nm nanoparticulates which made up the thorny structure are primarily attributed to the bonding characteristic of C-O, O-H and C-H between Ti-glycerolate, which creates a steric barrier to hinder the aggregation of primary nanoparticles and redirect the growth of the nanoparticles into the thorn-like structures (P. H. Shao et al., 2015; Tian et al., 2011). It was reported that copper ions provided a kind of cohesive force which is able to attract and hold molecules together (Sauvage, Duplan, & Niess, 2016). This suggests that Cu ions do diffuse out of the pores and the Ti fills the void, allowing for the exchange of Ti and Cu ions within the pores of the carbonaceous spheres which results in the

smaller hollow diameter of 850 nm. The difference between the shell structure of the HHHS and the irregular interior shape reveals penetration of ~75 nm into the 1 μ m carbonaceous sphere. The formation of the 300 nm thick Ti-Cu heterojunction shell shown through the EDX analysis confirmed the heterojunction layer. From the results of BET and BJH analysis between the HHHS and HHTS shown in Fig 5.1-7, different shell structure can be concluded as higher mesoporous formation was observed. This result correlates to the nanoparticulate morphology of the HHHS shell structure (purple) of 5.1-2 (g). The formation of the structure is a result of two simultaneous processes during the calcination process (f), firstly the oxidation of the carbonaceous spheres and secondly the simultaneous crystallization of the metal ions. The penetration synthesis method has reported the reduction of spherical size during calcination, due to the convergence of metal ions within the pores during the calcination process (Lai et al., 2012). Since there is a solidification of the Ti-glycerolate hierarchical structure and Ti-Cu bonds which form within the carbonaceous spheres (purple), the crystallisation of the outer shell will be independent of the carbonaceous template (red) while the carbonaceous spheres shrink during oxidation. The counteracting of metal ion convergence and restricting movement of the metal ions causes the carbonaceous pores to act as templates for the metal ions, creating barriers and limiting the interaction between ions of neighbouring pores. This, in turn, maintains the nucleation and crystal growth of the particles during calcination which shapes the interior of the hollow structure, resulting in a surface agglomeration of nanoparticles. Due to the fast nuclei growth of 30 mins and limited outward diffusion of Cu, it is unlikely that the penetration depth of Ti will penetrate further than Cu which was allowed a period of 6 h. Hence, the more deeply penetrating Cu ions (blue) are dependent on the carbonaceous spheres which shrink and converge to form the inner smaller CuO sphere (X. Lai et al., 2011). The assembly method amplifies the utility of the sacrificial templates and factors in greener methodological approach through the selection of benign solvents such as, ethanol, glycerol, and widely abundant glucose as the sacrificial template to enable a more scalable and sustainable synthesis method. The absence of step (b) and (c) results in the formation of HHTS.

Figure 5.1-3. Schematic diagram to illustrate the synthesis process of the Hierarchical Hollow Heterojunctioned Carbonaceous CuO/TiO₂ Spheres. a) Carbonaceous spheres obtained via hydrothermal synthesis of glucose undergo b) penetration of Cu^{2+} through diffusion. c) The cross-section view of Cu ions penetrated the pores of carbonaceous spheres forming Cu Carbonate Hydroxide Hydrate spheres (Cu-C spheres). The Cu-C spheres undergo solvothermal process to d) obtain the growth of Ti nanocrystals on the surface of the Spheres and the interaction between the Cu and Ti to form heterojunctions. e) Cross-section view showing the growth of the interconnected Ti-glycerolate hierarchical surface and CuO-C Spheres (TCCS) which undergo calcination to obtain f) multi-shell Hierarchical Hollow Heterojunctioned Carbonaceous CuO/TiO₂ Spheres, the cross-section reveals the contraction and formation of the inner shells after the removal of the carbonaceous core.

5.1.4. CRYSTAL STRUCTURE DETERMINATION

The XRD analysis shown in Fig 5.1-4 (a) revealed well-crystallized HHTS classified as the anatase TiO₂ phase based on the diffraction peaks at $2\theta = 25.4^\circ$ (101), 37.9° (004) and 48.1° (200) indexed to the ICDD (PDF 01-086-1157). The XRD patterns for the HHHS observed similar diffraction peaks at $2\theta = 25.4^\circ$ (101), 37.9° (004) and 48.1° (200) which also correspond to the anatase phase of TiO₂. Moreover, additional diffraction peaks are observed at $2\theta = 35.4^\circ$ (002) and 38.8° (111) which were indexed to copper (II) oxide (CuO) through the ICDD (PDF 00-048-1548), in addition to indexing of hypothetical Copper Titanium Oxide CuTi₃O₈

(PDF 01-081-8477) (indexing information provided in Fig 10 of the Appendix C). The unique feature of the CuTi_3O_8 pattern is the peak at 37° which is absent in both anatase TiO_2 and CuO shown in Fig 10 of the Appendix C. The unique peak at 37° relates to the d spacing of 0.243 nm shown in the TEM insert of Fig 5.1-2 (h). Due to the presence of TiO_2 and CuO , the pattern can be assumed to consist of overlapping CuTi_3O_8 , CuO and Anatase TiO_2 spectrum due to the structural similarities. Fig 5.1-4 (b) further analysed the shift in diffraction peaks of the 101 phase of the anatase TiO_2 . The HHTS observed shifts towards higher diffraction angles while the HHHS observed lower diffraction angles shift when compared to P25. The results imply changes to the interplanar spacing due to the tension caused by the addition of impurities of the elements into the lattice of TiO_2 (B. Liu et al., 2014). The shift towards a higher diffraction angle for the HHTS is plausibly due to the formation of carbonaceous TiO_2 as the synthesis material is confined to the elements of Ti, O, H, and C prior to calcination. Moreover, prior to calcination the TCCS possessed Ti-Glycerolate hierarchical structures with C-O and C-H bond structures (Tian et al., 2011) which could have altered the diffraction angle. The introduction of Cu into the HHHS resulted in the counter shift of the diffraction angles. This shift is suspected to be due to the replacement of Ti of $0.68\text{\AA}$ with larger Cu ionic radii of $0.72\text{\AA}$ (Y. Wang et al., 2014) and shown to agree with the substitutional doping of Ti with Cu (B. R. Chen, Nguyen, Wu, Martin, & Koci, 2016; Gonell, Puga, Julián-López, García, & Corma, 2016). Per the Scherrer equation, the estimated crystalline grain size taken from the TiO_2 (101) phase of HHTS is 16.91 nm. The HHHS respective grain size for TiO_2 (101), CuO (002) and CuTi_3O_8 unique peak at 37° was obtained as 26.71 nm, 25.59 and 42.56 nm. The factors for the increase in the grain size of the (101) phase of the TiO_2 after the introduction of Cu element include the substitutional doping of larger Cu for Ti as well as the formation of CuO/TiO_2 or the overlapping of CuTi_3O_8 with the 101 anatase phase might have also resulted in the changes in intensity and peak width and the shift towards the lower diffraction angle.

Figure 5.1-4. (a) XRD pattern of the synthesized HHHS revealing anatase TiO₂ and CuO while the HHTS matches anatase TiO₂. (b) the shifting of the 101 phase of the HHHS and HHTS compared to P25 as the reference material.

5.1.5. ENHANCED LIGHT ADSORPTION CAPABILITY

The optical properties of the HHHS, HHTS and P25 samples were characterized using the UV-vis solid spectrometry and the results are shown in Fig 5.1-5 (a). The respective band gap energies are estimated using the Kubelka-Munk function

plotting $(F(R) h\nu)^2$ against $h\nu$ which is measured in electron volt (eV) shown in the insert of Fig 5.1-5 (a). The light absorption of the samples is illustrated in Fig 5.1-5 (b).

The UV-vis spectrum is analysed via two regions, ultraviolet light from 200 nm to 400 nm and visible light from 400 nm to 800 nm. Similarities in light absorption pattern are observed for both HHHS and HHTS between the 200 and 400 nm regions with a minor peak at 330nm illustrated with black arrows before sloping down. Comparing the HHTS to P25, the observed increase in the UV region suggested light scattering among the TiO_2 hierarchical nanothorns (Tian et al., 2011; X. Zhang, Pan, Du, Xu, et al., 2009). The similarities between the HHTS and HHHS can be attributed to the hierarchical region of the spheres which is dominated by TiO_2 shown in the EDX analysis of Fig 5.1-2 (j). The introduction of CuO within the hollow shell resulted in different absorption values in the visible light region (S. S. Lee et al., 2013; X. C. Zhang & Tang, 2012). For HHTS, the Kubelka-Munk function estimated a bandgap energy reduction to ~ 3.1 eV, which is lower compared to ~ 3.4 eV for P25. Fundamentally, P25 contains rutile phase which will result in a smaller bandgap energy (Scanlon et al., 2013) compared to the anatase HHTS shown in the XRD pattern and should have resulted in higher visible light absorption than the HHTS (J. Yan et al., 2013). The opposing red shift displayed in the anatase HHTS light spectrum can be correlated to the reduction of its bandgap energy, due to inherent changes in the crystal structure. The higher angle shift of the HHTS in the XRD pattern reaffirms the carbon-based bonds revealed through the formation of Ti-glycerolate (Tian et al., 2011) and the plausible formation of carbonaceous TiO_2 , resulting in the red shift and long tail in the visible light spectrum of the HHTS (In, Kean, Orlov, Tikhov, & Lambert, 2009; Lettmann, Hildenbrand, Kisch, Macyk, & Maier, 2001; B. Liu et al., 2014; Y. Park et al., 2009; Shen et al., 2006; Y. J. Yang et al., 2015). The unique light absorption spectrum between 200 nm to 370 nm is observed for both HHHS and HHTS, which suggests that the hierarchical thorns also contain carbonaceous TiO_2 . Due to the various types of metal oxide structures found within HHHS via the XRD analysis, the shift in the eV to ~ 2.8 is not completely representative of the HHHS. The bandgap of CuO is reported to range from 1.2-2.0 (Thi Hiep, Thu Loan, Thi Dieu

Thuy, & Quang Liem, 2013) and could be represented by the continuous downslope of HHHS. If carbonaceous TiO₂ in both HHTS and HHHS exhibits an E_G of ~3.1, reports show a reduction in UV adsorption in Cu doped TiO₂ (Y. Wang et al., 2014; Y. Yan et al., 2016). The findings from XRD analysis and TEM images suggest carbonaceous CuO/CuTi₃O₈/TiO₂ heterojunctions in the HHHS (X. C. Zhang & Tang, 2012). The 2.8 eV bandgap of HHHS might have corresponded to the formation of carbonaceous CuO/TiO₂ heterojunctions or CuTi₃O₈ reported in Fig 5.1-4 of the XRD analysis.

Due to the multiple compositions of CuO, TiO₂ and Cu doped TiO₂ or CuTi₃O₈ within the HHHS, the UV pattern could have reflected multiple compositions which are segmented based on the Figure 14 of Appendix C. The continuous downslope of HHHS towards ~1.65 eV, could be correlated to CuO, which coincide with reports which affirm that the E_G of CuO ranges between 1.2-2.0 eV (Thi Hiep et al., 2013). The presence of carbonaceous TiO₂ in HHHS would have exhibited similar E_G of ~3.1 eV as with the HHTS. Reports reveal that the band gap decreases from 2.872 to 2.794 eV as Cu concentration increases from 0.1% to 10% (wt) in doped TiO₂ (Ganesh et al., 2014). Hence, the E_G of 2.8 eV reported correlates to Cu doped TiO₂ or CuTi₃O₈ (Y. Wang et al., 2014; Y. Yan et al., 2016).

Figure 5.1-5. (a) UV-vis absorbance spectra of HHHS, HHTS and P25 and the insert depicting the corresponding Kubelka-Munk function which estimated

the band gap changes of the materials. (b) Schematic illustration of light scattering between the hierarchical structure.

5.1.6. N₂ ADSORPTION AND DESORPTION

To further examine the porosity characteristics of the samples, the N₂ adsorption & desorption was carried out for both HHHS and HHTS while using conventional P25 nanoparticles as a comparison. The results of the adsorption isotherm shown in Fig 5.1-6 (a) HHHS and (b) HHTS, were used to tabulate the effective surface area and pore size distribution of the samples via BET and BJH analysis respectively. BET analysis tabulated an effective surface area of 30.6 m²/g for HHHS, 14.1 m²/g for HHTS and 50.1 m²/g for the P25 samples. This low surface area of HHHS and HHTS is likely due to the formation of the highly dense nanocrystals packed in the 1D thorn structure revealed in the TEM image of Fig 5.1-2 (i). The N₂ adsorption / desorption isotherm curves of the HHHS in Fig 5.1-6 (a) correspond to the type IV isotherm of the H3 type hysteresis (Cychosz, Guillet-Nicolas, Garcia-Martinez, & Thommes, 2017) according to the International Union of Pure and Applied Chemistry (IUPAC) classification which indicated presence of mesopores (2-50 nm) (Sing et al., 2008), while the HHTS in Fig 5.1-6 (b) shows a type 2 isotherm with a more macroporous adsorbent.

Figure 5.1-6. Nitrogen adsorption BET isotherm curve of (a) HHHS and (b) HHTS

To further illustrate the mesopores, the BJH pore size distributions of the 3 samples are compared in Fig 5.1-7. A bimodal distribution of small mesopores (3-5 nm) and larger mesopores (20-30 nm) within the HHHS is observed whereas HHTS mainly consist of larger mesopores (20-30 nm). The P25 nanoparticles have a range of pore volumes, with the majority between the 20 to 30 nm. The trend of pore distribution for the HHHS also observed larger range of mesopores like that of the HHTS. The results reaffirm the TEM image of the hierarchical thorn which is

densely packed and nonporous. The introduction of the copper ions in the synthesis of the HHHS plays an important role in the formation of a bimodal distribution of pores and the enlargement of the effective surface area. This resulting mesoporous formation is aligned with the addition of copper and further substantiates the agglomeration of porous nanoparticles base layer. In contrast, the absence of the copper ions shown in HHTS resulted in larger mesopores as observed through the FESEM imaging of the interior pore structure of the HHTS in Fig 5.1-7.

Figure 5.1-7. BJH pore size distributions of HHHS, HHTS and P25.

5.2. WATER TREATMENT PERFORMANCE AND MECHANISM

5.2.1. WATER TREATMENT PERFORMANCE EVALUATION

The photocatalytic activity of the HHHS, HHTS and conventional P25 were evaluated by means of discoloration efficiency of acid orange 7 (AO7) as the probe

molecule under the effects of ultraviolet-A (365 nm) light. The P25 nanoparticles were applied due to its similarities in grain size to that of HHHS and HHTS of 20-30 nm. Each sample underwent 60 min of undisturbed dark adsorption of AO7 before the start of the UV-irradiation (indicated in Fig 5.2-1 by the UV off region) to achieve adsorption-desorption equilibrium. The dark adsorption is compared to the relative BET effective surface area to further elucidate the adsorption capabilities of the samples for pollutants of larger molecular structures. The results of the adsorbed pollutants are compared to the relative BET effective surface area of the microspheres shown in Fig 5.2-1 (a). Among the three photocatalysts, the HHHS displays higher adsorption than the HHTS while P25 demonstrated the highest overall adsorption. The key aspect for effective surface area is based on the adsorption of pollutant and the corresponding reactive photocatalytic sites (Herrmann, 1999). The correlated results of the pollutant adsorption of HHHS and HHTS in Fig 5.2-1 (a) indicate that there was no pore blocking of the mesoporous shell as there is no reduction in the amount of pollutant adsorbed. Hence, the adsorption value of the HHHS indicated access of channels and pollutant transfer into the inner pores encapsulated within the spheres.

Figure 5.2-1. (a) Relationship of pollutant adsorption (%) within 1 h of dark adsorption against the Effective Surface Area (m²/g). (b) Photocatalytic degradation of AO7 in the presence of the HHHS, HHTS, P25

After an hour of dark adsorption, the degradation of AO7 proceeded for 60 min under the effects of UV-irradiation shown in Fig 5.2-1 (b). The final pollutant removal of 98%, 84% and 82% was obtained for HHHS, HHTS and P25

respectively. The results of the rate of photocatalytic degradation were determined via the use of pseudo first-order kinetics of the Langmuir-Hinshelwood kinetics tabulated in Fig 5.2-2. The results reveal the rates of degradation for HHHS, HHTS and P25 at 0.057/min, 0.034/min and 0.028/min respectively. The results of the HHTS and P25, clearly show similarities in the overall rate of degradation. The HHTS does demonstrate faster degradation rate in view of its lower adsorption capacity and inferior mesoporous structure and surface area. While the dual anatase, rutile phases of P25 have always been known to enhanced photocatalytic performance (Scanlon et al., 2013), the presence of carbonaceous TiO₂ could have led to an enhanced rate of degradation due to the narrower bandgap structure, good crystallinity and morphology which scatters and harnesses light photons, resulting in higher hydroxyl radical production (Chong et al., 2010). This would indicate that the adsorption of the pollutant is not the primary degradation means to achieve the rate of degradation but is instead, the generation of hydroxyl radicals. The lack of pores and effective surface area suggests electron transfer towards the surface of the hierarchical thorns with the aid of the carbon-TiO₂ bond to achieve higher hydroxyl radical production. HHHS displayed the fastest rate of degradation, which it is clearly due to the heterojunction carbonaceous CuO/TiO₂ outer shell and its highly mesoporous structure. The heterojunctioned CuO/TiO₂ in addition to its small crystal size of 20 - 30nm provides short electron transverse (S. S. Lee et al., 2013; S. P. Xu & D. D. Sun, 2009; X. C. Zhang & Tang, 2012) and the well-placed bandgap structure of carbonaceous-TiO₂ relative to CuO.

CuO synergies mitigate electron-hole recombination through the transfer of electron across the conduction band of the two structures, deterring excited electrons from directly returning to the valence band which dissipates energy into heat (S. S. Lee et al., 2013). Furthermore, its mesoporous structure and adsorption of pollutants, which allow for the scavenging of electrons, provide the necessary uptake of electrons mitigating electron-hole recombination. To understand the pollutant removal pathway, its degradation mechanism will be further elaborated.

Figure 5.2-2. Rate of degradation of AO7 for the HHHS, HHTS, P25

5.2.2. UNDERSTANDING PHOTOCATALYTIC MECHANISM OF MICRO-/NANOREACTOR

The pollutant degradation pathway and the enhanced photocatalytic performance of HHHS are elucidated in Fig 5.2-3. Pollutants move through regions with hierarchical thorns which act as water channels before engaging the porous heterojunction to adsorb pollutants for degradation and subsequent release from the micro-/nano-reactor.

The first region of interaction will be the hierarchical thorns which act as water channels. Upon photon absorption, the TiO₂ thorns promote electrons from the valence band to the conduction band to engage in redox reactions, generating reactive oxygen species (ROS), typically hydroxyl radicals (OH[•]) in the presence of water (Chong et al., 2010). Due to the low porosity of the hierarchical thorns which lacks the capability to capture pollutants, led to a region dominated by ROS. The

ROS region acts to degrade pollutant as it flows through the hierarchical water channels (Hoffmann, Martin, Choi, & Bahnemann, 1995). This manifestation is enhanced by the carbonaceous-TiO₂ in the hierarchical structure with E_g of ~ 3.1 eV which induces light harnessing and scattering, promoting greater capture of photons. Furthermore, the closely packed hierarchical thorns enable ease of charge transfer to the surface of the thorns for a quick and constant generation of OH[•].

The next region of the pollutant pathway is the heterojunctioned outer shell, where the mesoporous structures filter and capture pollutants and are oxidised due to the loss of electrons from carbonaceous CuO/TiO₂ heterojunctions (X. W. Zhang, D. D. Sun, G. T. Li, & Y. Z. Wang, 2008). The region features triple heterojunctions, with the carbonaceous TiO₂ exhibiting the largest bandgap of 3.1 eV, the CuTi₃O₈ region of 2.8 eV, while the smallest bandgap of CuO is reflected at 1.65 eV. Report reveals the conduction band increases from -0.255 to -0.2 eV as Cu concentration increases in doped TiO₂ relative to NHE (Ganesh et al., 2014). Therefore, the correlated position of CuTi₃O₈ would be between that of TiO₂ and CuO which conduction band is positive (Brito & Zanoni, 2016; Fang, Xing, Bonakdarpour, Zhang, & Wilkinson, 2015; S. S. Lee et al., 2013; Thi Hiep et al., 2013). The combination of the p-n heterojunction of p-type CuO and n-type TiO₂ creates a space charge region whereby the electrons will flow from the TiO₂ to CuO from the higher Fermi level to the lower Fermi level (S. S. Lee et al., 2013; Lei et al., 2016). The conduction band of CuTi₃O₈ positioned between both TiO₂ and CuO creates an intermediate pathway in the electron flow, facilitating the charge separation and transfer of electrons, and hence, enhancing photocatalytic performance. In the triple heterojunction of the carbonaceous-TiO₂/CuTi₃O₈/CuO micro-/nano-reactor, allows for the inward transfer of electrons towards the mesoporous heterojunction shell due to the increasing Cu content at the shell region compared to the outer thorny region. The effective electron-hole separation of the heterojunction shell, coupled with the mesoporous shell enables smooth transfer of electron-hole at the active sites. This ease of charge transfer is further accelerated with the aid of the bimodal pore distribution within its shell, enabling proximity of photocatalyst, pollutant and ROS. This inward transfer of electrons creates oxidative sites at the outer region for pollutant degradation which in turn enables a

porous system for the smooth fluid transfer and electron transfer towards the inner core of the hollow sphere. Furthermore, the photoinduced superhydrophilicity of the HHHS would have facilitated in the overall transfer of fluid through the mesoporous shell (Fujishima et al., 2000).

The final region of hollow sphere will contain space dominated with water, intermediates or ROS due to the presence of the smaller shell and possible scattering of light within (S. H. Hwang, J. Yun, & J. Jang, 2014; S. Li et al., 2013; X. Wu, G. Q. Lu, & L. Z. Wang, 2011). Furthermore, the presence of the inner hollow sphere constructs a pathway for the pollutant and restricts the pollutant's displacement from the outer shell, thereby maximizing the rate of interaction with the mesoporous region of the micro-/nano-reactor (Chong et al., 2010). The porous heterojunction will be sandwiched between two regions of ROS films which will supplement pollutant degradation at the interfaces of the heterojunctions at both surfaces for the degradation, adsorption and transfer of both pollutant and water throughout the spheres to produce clean water.

Figure 5.2-3. Schematic diagram for the proposed mechanism of the pollutant degradation pathway through HHHS under-photon irradiation. The hierarchical thorns act as water channels which generate ROS for the degradation of pollutant before encountering the mesopores for adsorption and degradation. The mechanism of degradation is illustrated for the

hierarchical water channels and the interface between the hierarchical thorns and the mesoporous shell. The inner hollow sphere guides the flow of water and generates an interior region containing ROS and reduces the transverse from the pollutant dominated mesopores for enhanced pollutant degradation.

5.3. CONCLUSION

The Hierarchical Hollow Heterojunctioned Carbonaceous CuO/TiO₂ Spheres were successfully fabricated to create a micro-/nano-reactor spheres by adopting various strategies for morphological augmentation and TiO₂ modifications. The multi-dimensional morphology incorporated micro-/nano structure assembled by heterojunctioned carbonaceous CuO/TiO₂, hierarchical thorns, and mesoporous multi-shell hollow spheres. The approach integrated the use of green synthesis, maximizing the use of carbonaceous template, for the successful fabrication of a porous interior shell whilst retaining size to overcome water treatment issues. The HHHS micro-/nano-reactor exhibited enhanced photocatalytic performance attributed to merits of (1) the carbonaceous TiO₂ hierarchical which act as water channels generating ROS for pollutant degradation, (2) the widely dispersed carbonaceous CuO/TiO₂ heterojunctions which narrowed bandgap and enhanced charge separation and transfer, mitigating electron-hole recombination, (3) enhanced by the triple heterojunction interface of carbonaceous TiO₂/CuTi₃O₈/CuO to maintain shell porosity, (4) the superhydrophilic bi-modal mesoporous shell structure to filter pollutant by adsorption and degradation, (5) the photoinduced superhydrophilic surface which facilitated the transfer of fluid through the mesoporous shell, and lastly, (6) the inner shell morphology to guide and channel the pollutants, enabling a degradation, adsorption and transfer of water and pollutants throughout the sphere. In addition, the overall synthesis is not limited to the use of Cu or Ti ions (X. Lai et al., 2011; G. Zhang & Lou, 2014) and could be tailored by different shapes and sizes of the hard template. A wider use of materials could be applied to fabricate other forms of mixed metal oxide spheres with different types and sizes of hierarchical structures to further optimize the architectural structure of the spheres.

6. CHAPTER

INTRODUCTION

Due to the non-uniform dispersion of Cu, the uniform heterojunction or doping throughout the Hierarchical Hollow Heterojunctioned Carbonaceous CuO/TiO₂ Spheres is difficult to be obtained. The use of Fe ions was applied to enhance the synthesis outcome. Furthermore, the change in metal ions will demonstrate the flexibility of the synthesis process to cater to different mixture of metal ion combination.

The chapter will apply the use of Fe ions to fabricate Hierarchical, Multi-shell, Micro-/Nano, Fe-doped TiO₂ (HMS) revealing uniform dispersion of Ti and Fe elements. The synthesis of multi-shell hollow spheres will be investigated with the use of different Fe penetration duration. The chapter further introduces the novel concept of Ion Exchange approach in the pores of the carbonaceous spheres between the Ti and Fe ions. Hence, it demonstrates the synthesis mechanism of the inner sphere and the multi-shell structure. Furthermore, the compaction of ions in the pores of the carbonaceous sphere will illustrate the correlation between the inner sphere morphology and the specific surface area and the resulting pore size distribution. The fabrication of multi-shell TiO₂ sphere using the ion exchange approach will be reported using Ti based precursor which would otherwise be typically hydrolysed on the surface of carbonaceous spheres.

Finally, the photocatalytic performance of HMS will be evaluated. The evaluation of its bactericidal capability will investigate the physical lysis of bacteria using HMS and the generation of hydroxyl radicals (OH[•]) under visible light to understand the bactericidal mechanism of HMS.

RESULTS AND DISCUSSION

6.1. MATERIAL CHARACTERIZATION AND THE SYNTHESIS MECHANISM

6.1.1. MORPHOLOGICAL CHARACTERIZATION OF HMS

The FESEM imaging in Fig 6.1-1 (a) reveals the formation of Fe-C spheres with observable nanoparticulate surface and a diameter of ~ 800 nm. The successful fabrication of the Hierarchical, Multi-shell, Micro-/Nano, Fe-doped TiO_2 Hollow Spheres (HMS) is shown in Fig 6.1-1 (b). The HMS have a spherical diameter of ~ 1.5 μm and surface composed of hierarchical thorns formed by aggregation of 20 nm nanoparticles (the expanded insert of Fig 6.1-1 (b)).

Figure 6.1-1 FESEM imaging of (a) morphology of the Fe-C sphere (6 h) with nanoparticulate surface. (b) HMS-6 revealing the hierarchical surface thorns and the insert showing the 20 nm nanoparticulates which assembled to form the HMS.

The fabricated HMS shown in Fig 6.1-2 with the various penetration duration of 6, 24 and 48 h are denoted and displayed in (a) HMS-6, (d) HMS-24 and (g) HMS-48 respectively. The corresponding EDX mappings are shown to the right of the FESEM images Ti (b), (e) and (h) and Fe (c), (f) and (i).

The FESEM imaging of HMS-6, HMS-24 and HMS-48 reveals the hollow interior diameter of ~ 800 nm and an inner sphere of ~ 500 nm which is consistent with the diameter of Fe-C spheres of ~ 800 nm (Fig 6.1-1 (a)). The reduction of the inner sphere in diameter was attributed to the contraction of the carbonaceous sphere during calcination (Ang et al., 2017; X. Lai et al., 2011; G. Zhang & Lou, 2014). The HMS-6 and HMS-24 reveal the formation of ~ 1.5 μm sphere with a ~ 100 nm outer shell structure, whereas, the HMS-48 which was synthesized with increased Ti-glycerolate content had a slightly thicker outer shell of 200 nm and an increased spherical diameter of ~ 1.7 μm . The EDX analysis revealed that the HMS consists of uniformly distributed Ti and Fe elements demonstrating an outward diffusion of Fe ions. This further established that longer Fe ions penetration duration determined the depth and mass of Fe ions being stored within the pores of

the carbonaceous spheres (X. Lai et al., 2011), and hence, the increased penetration duration correlated with increasing concentration of Fe that will be diffused out. Moreover, the change in surface morphology can be observed with increasing Fe penetration duration in addition to similar surface structure for both the inner shell as well the interior surface of the outer shell. The HMS-6 revealed an inner sphere assembled through the agglomeration of nanoparticulates, whereas the HMS-24 and HMS-48 with increased Fe penetration duration portrayed smoother surface structure.

Figure 6.1-2. Fabrication of (a) HMS-6 and the corresponding EDX elemental mapping of (b) Ti and (c) Fe, (d) HMS-24 and the corresponding EDX elemental mapping of (e) Ti and (f) Fe, and (g) HMS-48 and the corresponding EDX elemental mapping of (h) Ti and (i) Fe.

To further investigate the synthesis mechanism, the Fe-C Spheres were prepared with penetration time of 1h and the corresponding fabricated HMS-1 is shown in Fig 6.1-3 (a) and (c), respectively. The corresponding EDX analysis is displayed to the right as Fig 6.1-3 (b) and (d). The HMS-1 consisted of hierarchical thorn surface structure and an inner sphere morphology assembled by nanoparticulates which is

similar to HMS-6. In addition, the EDX analysis in Fig 6.1-3 (d) clearly revealed the formation of TiO_2 based inner shell and confirmed the penetration of Ti-precursor into the pores of the carbonaceous spheres. The imaging further demonstrated the viability of the synthesis method to fabricate TiO_2 based multi-shell structure without multiple coating method.

Nevertheless, the fabricated HMS-1 revealed through the EDX analysis almost undetectable Fe element but clearly defined Ti inner sphere. The lack of Fe element is due to the doping of Fe into the Ti crystal structure, in addition to the dominating Ti masked the presence of Fe. It was reported that the nucleation of the Ti outer shell would occur within the first 30 mins of the solvothermal process (Tian et al., 2011). Thus, it is unlikely that the Fe ions would be lost into the solution as the ion exchange would have taken place in a short time span. Furthermore, the low concentration of Fe ions might have resulted in a slow diffusion rate. Henceforth, for the mass of Ti penetrated to be large enough to form an inner Ti sphere, the solvothermal pressure might have played a role in the inward diffusion of the Ti ions.

Figure 6.1-3. (a) Fe-C spheres and the corresponding (b) EDX analysis of low Fe content. (c) The FESEM imaging of HMS-1 with the hierarchical thorn like structure and nanoparticulate inner sphere. (d) The corresponding EDX analysis revealing the formation of Ti dominated inner shell revealing the inter-diffusion of Ti-glycerolate and Fe, while Fe element remains undetectable.

6.1.2. EXPLANATION OF SYNTHESIS MECHANISM THROUGH ION EXCHANGE AND PORE COMPACTION

Reports have shown that the formation of the inner sphere was a result of compaction of the metal ions in the pores of the carbonaceous spheres (Lai et al., 2012; X. Lai et al., 2011). Therefore, the inner sphere formation can be illustrated by the compaction of Ti-Fe ions during the Ion Exchange process within the carbonaceous pores shown in Fig 6.1-4 (a) to (c). During the solvothermal process, the Fe ions diffused out of the pores of the spheres due to the low Fe concentration, this in turn led to the inward diffusion of Ti-glycerolate to replace the void in the pores. The inward diffusion was further aided by the pressure created in the solvothermal process. The loosely formed HMS-6 and HMS-1 was a result of unconcentrated Ti-Fe ions within the pores. The weight loss during the calcination process is revealed through the TGA analysis of HMS-48 (shown in Figure 18 of Appendix D). Besides, report revealed that the boiling point of glycerol is 290 °C (Takamura, Fischer, & Morrow, 2012). The initial 10% loss in weight at ~260 °C to 300 °C can be correlated to loss of glycerolate. The carbonaceous spheres which contributed to the main mass of the sphere correlated to the oxidation between 300 °C to 350 °C. Hence, during the calcination process shown in Fig 6.1-4, the oxidation of the glycerolate created voids in the carbonaceous spheres, after which, the carbonaceous spheres oxidized and the metal ions then converges and agglomerates to form the nanoparticulate inner sphere. The highly-compacted Fe ions in HMS-24 Fig 6.1-4 (d) to (f) illustrate a compacted pore scenario. Due to the compacted scenario, in addition to the surface functionalization of the spheres (X. Sun & Y. Li, 2004), two types of Fe ions were compacted within the pores. First, the Fe ions which are bonded with the carbonaceous pores due to the functionalized surface, and the second were the ions held between the functionalized Fe. The non-

functionalized Fe ions enabled the quick release and exchange of the Ti and Fe ions within the pores. Hence, with higher ion compaction, lesser void was created by the oxidation of glycerolate which enabled quicker convergence between the pores to form the round and smooth surfaced inner sphere (Ang et al., 2017; G. Zhang & Lou, 2014). The inner sphere was a result of the contraction of the carbonaceous sphere during calcination (Lai et al., 2012; X. Lai et al., 2011), while the outer shell was independent of the contraction but reflected similar surface structure due to the balance of concentration.

Figure 6.1-4. Ion exchange synthesis process between Fe ions (orange) and Ti-glycerolate (blue) (a) HMS-6 (6 h Fe penetrated sphere) undergo uncompact ion exchange which result in (b) uncompact pores and calcination process creates void as glycerol oxidises to fabricate (c) nanoparticulate inner shell. (d) HMS-24 (24 h Fe penetrated sphere) undergo compact ion exchange which result in (e) compact pores. The calcination process generates lesser void due to higher metal ions content as glycerol oxidises to fabricate (f) smooth inner shell due to the quick convergence of ions.

6.1.3. CRYSTAL STRUCTURE DETERMINATION

The crystal structure was determined for all HMS-6, HMS-24 and HMS-48 via the use of XRD analysis shown in Fig 6.1-5. The XRD pattern revealed well crystallized HMS which are indexed to the anatase phase of TiO_2 based on the diffraction peaks of (101), (004), and (200) via the (ICDD PDF 03-065-5714) and

the rutile phase diffraction peaks of (110), (101), and (111) was indexed to (ICDD PDF 01-089-0553). The XRD patterns were observed to be classified under TiO_2 even with increasing Fe concentration. In addition, no phases of Fe were found within the XRD pattern even though the EDX analysis clearly revealed uniform distribution of Fe within the HMS. Hence, this suggests that the Fe ions were doped into the lattice of the TiO_2 . It was reported that the similar molecular size of Ti (0.68 Å) and Fe (0.64 Å) easily enabled substitutional doping which Fe replaced Ti in the lattice structure of TiO_2 (Sood, Umar, Mehta, & Kansal, 2015). However, the transformation towards the rutile phase was observed for the HMS-24 which was influenced by the increased concentration of Fe-doping in TiO_2 . Reports showed that Fe-doping reduced crystallinity and shifted the transformation of anatase to rutile to lower temperature (Bally, Korobeinikova, Schmid, Lévy, & Bussy, 1998; Hirano, Joji, Inagaki, & Iwata, 2004; Nasralla et al., 2013; Wu, Yang, & van de Krol, 2014). The increased Ti concentration for HMS-48, rebalanced the Fe to Ti ratio, and hence displayed no anatase to rutile phase transformation. Per the Scherrer equation, the estimated grain size of the TiO_2 anatase phase for the HMS-6, HMS-24 and HMS-48 is 17.54 nm, 18.5 nm and 20.17 nm respectively. The increase in grain size was observed to be correlated to the increase in the Fe-doping concentration. The rutile phase for HMS-24 was estimated at 21.44 nm which suggests the anatase transformation into the higher crystallinity structure (Kudo & Miseki, 2009).

Figure 6.1-5. XRD pattern of HMS-6, HMS-24 and HMS-48 revealing anatase TiO₂ phases and the rutile phase in HMS-24.

6.1.4. ENHANCED LIGHT ABSORPTION CAPABILITY

The HMS-6, HMS-24 and HMS-48 were assessed on their optical properties and the results of the UV-visible absorbance measurement are shown in Fig 6.1-6 (a) while the Kubelka-Munk function of the respective band gap energies is shown in Fig 6.1-6 (b). The red shift in the spectrum of the HMS-48 exhibited the highest visible light absorbance followed by the HMS-24 and HMS-6, which is directly correlated to the longer penetration duration and higher Fe content. The Kubelka-Munk function derived from the UV-visible spectrum revealed the lowering of the bandgap from 3.1 eV for HMS-6, 2.9 eV for HMS-24 to 2.7 eV for HMS-48. The band gap reduction can be attributed to the increased Fe-doping concentration (George et al., 2011) shown in the EDX analysis in Fig 6.1-2, even though there is an absence of Fe phases in the XRD pattern in Fig 6.1-5 (Asiltürk, Sayılkan, & Arpaç, 2009; Cui, Wang, Niu, Chen, & Cheng, 2009; Nasralla et al., 2013).

Figure 6.1-6. (a) UV-vis absorbance spectrum of HMS-6 and HMS-48 and (b) the corresponding Kubelka-Munk function revealing the estimated bandgap reduction with increased Fe-doping concentration.

6.1.5. N₂ ADSORPTION AND DESORPTION TEST

The N₂ adsorption-desorption isotherms plot for HMS-6, HMS-24 and HMS-48 are shown in Fig 6.1-7. The BET specific surface area estimated from the adsorption isotherm of the HMS-6, HMS-24 and HMS-48 is 43.165 m²/g, 20.054

m^2/g and $31.029 \text{ m}^2/\text{g}$, respectively. The isotherms for the three HMS corresponded to the type IV isotherm of the H3 type hysteresis based on the IUPAC classification indicative of mesopores of (2-50 nm) (Sing et al., 2008). The BJH pore size distribution revealed a shift towards the lower mesoporous region of 4-10 nm for the HMS-24 and HMS-48 with increasing penetration duration compared to 10-30 nm for the HMS-6. Apart from the pore size, the longer penetrated HMS-48 also observed reduction in its specific surface area by $12.1 \text{ m}^2/\text{g}$ compared to HMS-6. The change clearly correlates to the pore compaction illustrated in Fig 6.1-4. Moreover, a further reduction of the specific surface area of HMS-24 was observed. The reduced surface area affirmed that the transformation towards the rutile phase and increased crystallite size of 21.44 nm tabulated using the Scherrer equation in 6.1.3, increased the crystallinity, and further reduced the specific surface area of the HMS-24 (Kudo & Miseki, 2009; Siew Siang Lee et al., 2013). Nonetheless, the reduced pore distribution and specific surface area affirmed ion compaction within the pores of carbonaceous spheres leading to the changes of the shell structure. The less compacted pores assembled nanoparticulates due to loosely distributed metal ions while the highly-compacted pores resulted in smoother shell structure which reduced both the specific surface area and overall pore size. Lastly, the results further established the specific surface area of the HMS were largely reliant on the shell (Ang et al., 2017).

Figure 6.1-7. The N₂ adsorption-desorption isotherms of (a) HMS-6, (c) HMS-24 and (e) HMS-48, and the respective pore size distribution (b) HMS-6, (d) HMS-24 and (f) HMS-48.

6.2. BACTERICIDAL EVALUATION AND MECHANISM

6.2.1. BACTERICIDAL EVALUATION WITHOUT VISIBLE LIGHT IRRADIATION

The bactericidal activity towards *E. coli* was investigated using HMS-6 without the influence of light. The activity was compared to a blank experiment using *E. coli* suspension without the application of photocatalyst. The results are tabulated in

Fig 6.2-1. The *E. coli* suspension without photocatalyst revealed slight decrease which might be due to the stirring of the aliquot suspension whereas, the presence of HMS-6 photocatalyst observed a gradual reduction by 40% in its cell viability over a period of 1h. The lack of photogenerated hydroxyl radicals ($\text{OH}^\bullet$) (Chong et al., 2010), suggests physical bacterial lysis contributed to the thorny surface morphology of the HMS-6 (H. Bai, Z. Liu, et al., 2013). The mixing action of the solution enabled movement of both HMS and *E. coli*, the contact between the two entities led to the rupturing of the cell wall membrane of the *E. coli* causing bacterial lysis.

Figure 6.2-1. Cell viability due to physical bacterial lysis using HMS-6 compared to a test with no photocatalyst.

6.2.2. BACTERICIDAL EVALUATION USING VISIBLE LIGHT IRRADIATION

The bactericidal activities of the HMS-6, HMS-24, and HMS-48 were evaluated under the influence of visible light irradiation and were compared with a photolysis study as baseline. The results are tabulated in Fig 6.2-2. The photolysis study observed minimal change in bacteria count, possibly due to the stirring conditions, which was similar to that of the blank experiment done in dark conditions. The

similarity in results suggest that majority of the UV-light was filtered out from the solar simulator. The presence of HMS with visible light demonstrated reduced cell viability of ~70% over a period of 1h. The reduction in cell viability correlated to increase in visible light absorbance by HMS-48, followed by HMS-24 and HMS-6. Apart from the physical lysis, light generated $\text{OH}^\bullet$ is known for bactericidal activity (Moncayo-Lasso et al., 2012). Since the major light source would be of the visible light spectrum (L. Liu & Chen, 2014), the generation of $\text{OH}^\bullet$ will depend on the Fe content (Yadav, Kolekar, Pawar, & Kim, 2016). Hence, the increased Fe-doped into the HMS reflected higher visible light absorbance which consequentially resulted in better bactericidal activity.

Figure 6.2-2. Cell Viability of HMS and Photolysis (without HMS) after 1h of visible light irradiation.

6.2.3. BACTERICIDAL MECHANISMS

The bactericidal mechanism of the HMS is shown in Fig 6.2-3. Reports showed the addition of Fe doping resulted in the formation of a reduction level $\text{Fe}^{3+}/\text{Fe}^{2+}$ below the conduction band and an oxidation level $\text{Fe}^{3+}/\text{Fe}^{4+}$ above the valence band of TiO_2 (Ali, Tripathi, Azam, et al., 2017; Asiltürk et al., 2009). The band alignment of the Fe^{3+} acts as electrons and hole traps to mitigate recombination through the

conversion of Fe^{3+} to Fe^{2+} or Fe^{4+} . The photoexcitation of HMS resulted in the migration of electron onto the conduction band of the Fe^{3+} to form Fe^{2+} , and the valence hole traps electrons converting Fe^{3+} to form Fe^{4+} . From the crystal field theory, Fe^{3+} having half-filled d orbital ($3d^5$) is relatively stable compared to the other two phases Fe^{2+} or Fe^{4+} (M. Zhou, Yu, & Cheng, 2006). The trapped charges in Fe^{2+} and Fe^{4+} will be released via the reduction of O_2 to O_2^- and the oxidation of OH^- to $\text{OH}^\bullet$, respectively. The contact of TiO_2 with *E. coli* was reported to be important for the inactivation of cells (Moncayo-Lasso et al., 2012; Zhukova, 2015). The 40% reduction of cell viability without visible light irradiation indicated that physical lysis contributed greatly in the bactericidal activity. Hence, the bactericidal mechanism can be subjected to: (1) The physical bacterial lysis through the contact between the thorn like hierarchical surface with the bacteria cell which ruptures the membrane wall resulting in the release of salts (H. Bai, Z. Liu, et al., 2013). (2) The attachment of the $1.5\ \mu\text{m}$ HMS onto the $0.5 \times 2\ \mu\text{m}$ *E. coli* (H. Bai, Z. Liu, et al., 2013) using the $0.3\ \mu\text{m}$ long thorns which pierced and attached onto the surface of the *E. coli* (Moncayo-Lasso et al., 2012). (3) The concurrent photo-activation of the Fe-doped TiO_2 which generated $\text{OH}^\bullet$ (Pulgarin, Kiwi, & Nadtochenko, 2012; W. J. Wang, Yu, & Wong, 2013). (4) The generated $\text{OH}^\bullet$ could easily be released to degrade the *E. coli* cell wall which surface has been damaged (Wanjuan Wang et al., 2011) or (5) enter the ruptured membrane and degrade the RNA/DNA of the *E. coli* which results in cell death (Keane et al., 2014).

Figure 6.2-3. The Fe-doped TiO_2 resulted in the formation of Fe^{3+} which trap charges at the conduction band (CB) through the conversion to Fe^{2+} and the hole at the valence band (VB) converting Fe^{3+} to Fe^{4+} . The band of the Fe^{3+}

mitigates recombination of electron-hole by trapping and releasing charges via the redox reaction with water. The HMS thorns of ~300 nm enable piercing and attachment onto the *E. Coli*. The cell membrane lysis allows for the access of OH[•] to enter and degrade the RNA/DNA causing cell death.

6.3. CONCLUSION

The versatility of the synthesis method was explored with Fe ions and demonstrated the direct synthesis of Hierarchical, Multi-shell, Micro-/Nano, Fe-doped TiO₂ Hollow Spheres (HMS). The fabrication route integrated multi-shell Fe-doped TiO₂ structure with uniform dispersion of Ti and Fe. Furthermore, the Ion Exchange approach illustrated the ion compaction within the carbonaceous pores and the correlation of the porosity and specific surface area within the shell structure, with increased ion compaction leading to reduced porosity and specific surface area after the calcination and crystallization of the Ti and Fe ions. The bactericidal activity suggested the combination of the physical lysis of HMS through the hierarchical thorn to damage the cell membrane and aided by the generation of OH[•] for the enhanced degradation of cell wall and exposed cell RNA/DNA.

7. CHAPTER

INTRODUCTION

This chapter applied Hierarchical, Multi-shell, Micro-/Nano, Fe-doped TiO₂ Hollow Spheres (HMS) in photoelectrocatalysis configuration for the degradation of organic pollutant and recovery of Cu metal from ionic Cu²⁺.

The configuration demonstrates the novel low temperature bind of HMS microspheres atop the lightweight and flexible indium tin oxide (ITO)/ polyethylene terephthalate (PET) thin film which acted as the support structure. Graphene Oxide (GO) was electrodeposited atop the ITO/PET thin film to produce the rGO Cathode. GO and HMS were sonicated to prepare a GO-HMS solution. The as prepared GO-HMS was evaporated atop the rGO Cathode. The GO/rGO interface promotes the binding of the two entities at 60°C which fabricates the HMS Anode.

The photoelectrocatalysis configuration was setup with a low voltage of 1.5 V and was investigated for the oxidation of organics pollutants and recovery of heavy metal from a solution containing heavy metal ions. The study demonstrates the novel simplification of clean water production which employs the electrons to cater for organics and heavy metals pollutants, while being simultaneously beneficial in each performance through the adapted use of redox process for sustainable and scalable design.

RESULTS AND DISCUSSION

7.1. MATERIAL CHARACTERIZATION

7.1.1. MORPHOLOGICAL CHARACTERIZATION OF HMS ANODE AND RGO CATHODE

The fabrication phases of the flexible thin film anode and cathode are revealed through the FESEM images shown in Fig 7.1-1. The surface morphology of the

indium tin oxide (ITO)/ polyethylene terephthalate (PET) thin film support layer is shown in (a) with a nanoparticulate surface consisting of ITO embedded into the PET layer. The reduction of graphene oxide (GO) through the electrodeposition process (Toh et al., 2014; Tong et al., 2013) produced the (b) rGO Cathode. The image revealed large sheet GO electrodeposited atop the ITO surface creating a smooth flat surface. Next, GO was bind with Hierarchical, Multi-shell, Micro-/Nano, Fe-doped TiO₂ Hollow Spheres (HMS) using sonication to produce GO-HMS shown in (c). The HMS revealed spherical structure with hierarchical thorns with a layer of transparent GO bound onto the surface of the HMS of 1.5 μm in diameter (P. Gao, Liu, Tai, Sun, & Ng, 2013; J. Liu et al., 2010). The stretched GO layer revealed the strong attraction forces between the GO and the HMS. The further evaporation of the GO-HMS atop the rGO Cathode is shown in (d) depicting the fabrication of the HMS Anode. The binding of the GO-HMS and rGO layer reveals the attachment of GO and the rGO thin film to ensure that the HMS are fixated onto the surface of the anode.

Figure 7.1-1. (a) Flexible ITO/PET thin film support, (b) electrodeposited rGO Cathode by reducing GO onto the ITO/PET under 3V for 5 mins, (c)

synthesized GO-HMS through sonication of GO and HMS solution for 90 mins, (d) Fabricated HMS Anode by drying GO-HMS atop the rGO Cathode.

7.1.2. FTIR CHARACTERIZATION OF HMS ANODE AND RGO CATHODE

The FTIR transmittance spectra of GO, HMS and GO-HMS are shown in Fig 7.1-2 (a). The bands of GO at 3400 cm^{-1} represent O-H stretching of carbonyl and/or carboxyl group, at 1720 cm^{-1} refer to C=O stretching of carboxyl groups and 1620 cm^{-1} are due to C=C skeletal vibration of unoxidized graphitic domain. A strong peak at 1100 cm^{-1} can be attributed to the C-O stretching vibration of alkoxy revealed that the graphite was successfully oxidised into hydrophilic GO (Toh et al., 2014). The broad band between 400 to 900 cm^{-1} for HMS and GO-HMS can be attributed to the Ti-O stretching vibrations (Trapalis et al., 2016). However, the GO-HMS observe C-H stretching vibration (Wegher, Viana, Ribeiro, & Deus, 2016) at 2984 cm^{-1} , and the expanded Fig 7.1-2 (b) reveal O-H vibration from the stretching of hydroxyl groups at 1390 cm^{-1} and C-O stretching in epoxy or alkoxy groups at 1045 cm^{-1} (Sim, Leong, Ibrahim, & Saravanan, 2014).

Fig 7.1-2 (c) depicts the absorption peaks of rGO Cathode and HMS Anode using PET film as the background. The difference in peak revealed similar 2984 cm^{-1} C-H stretching shown in GO-HMS of Fig 7.1-2 (a). The changes in peak pattern such as the major peak of 1250 cm^{-1} which is attributed to C=C (Bagri et al., 2010), the 1710 cm^{-1} attributed to COOH group (W. Gao, 2012), the 1150 cm^{-1} attributed to C-O-C group (Dumée et al., 2014), and the 877 cm^{-1} attributed to epoxide (L. Zhang et al., 2016) suggest the interfacial binding of GO-HMS with the rGO Cathode.

Figure 7.1-2. FTIR (a) Transmittance of GO-HMS, HMS and GO, (b) expanded image of (a) and the changes in GO-HMS at (c) Absorbance of rGO Cathode, HMS Anode and the difference in absorbance pattern between the cathode and anode, and (d) the expanded image of (c) with the changes at 877, 1150 and 1250 1710.

7.2. WATER TREATMENT PERFORMANCE EVALUATION

7.2.1. WATER TREATMENT PERFORMANCE EVALUATION USING CU-AZO COMPLEX

Three configurations were used to investigate changes to the organic degradation kinetics and heavy metal recovery, as shown in Fig 3.3-4. HMS Anode and rGO Cathode were linked using copper tapes and were studied in 3 different setups, (a) Power Supply configuration which entails a close circuit with 1.5 V battery, (b) Loop configuration forming a close circuit linking the anode and cathode with no power supplied. (c) Open circuit configuration which disconnects the anode and cathode simulating a photocatalytic oxidation (PCO) process. The experiment was

performed thrice in collation of the above-mentioned sequence using the same anode throughout all 9 sets of experiments using Cu-Azo complex as the target pollutant over a period of 1 h.

The pollutant degradation and the rate of degradation is shown in Fig 7.2-1 (a) and (b) while the heavy metal recovered is shown in Fig 7.2-1 (c). Among the three configurations, the introduction of the 1.5V power supply revealed the highest degradation rate constant of 0.012 which is 20% more compared to the open circuit configuration of 0.01. The enhanced photocatalytic oxidation can be attributed to the scavenging of electrons by the applied potential difference of the 1.5 V power supply. The recombination of the excited electrons was mitigated as the electrons migrated towards the HMS Anode, during which, the high charge mobility of GO facilitated the transfer of electrons (J. Liu et al., 2010). This promoted highly oxidative sites for the generation of hydroxyl radicals ($\text{OH}^\bullet$) for the degradation of organics (Juang et al., 2016). Hence, the recombination of electrons played the major role for the oxidation of organics, and could be enhanced by the manipulation of electrons through an external source. The system will require the rebalancing of the redox reaction through the inflow of electrons at the reductive cathode. These electrons were applied to recover Cu(s) through the reduction of Cu^{2+} ions. The ICP result tabulated in Fig 7.2-1 (c) depict the total Cu recovered after a period of 60 mins. The Power Supply configuration obtained a recovery of 0.0509 mg Cu per cm^2 of cathode surface area. The total copper removal efficiency was estimated to be ~68% based on the initial cathode surface area of 2 cm^2 . Whereas, the loop and open circuit configuration obtained close to insignificant amount of Cu at $0.2 \text{ }\mu\text{g}$ and $0.8 \text{ }\mu\text{g}$, per cm^2 cathode surface, respectively.

Figure 7.2-1 (a) The change in concentration for the three configurations. (b) The corresponding rate of degradation. (c) The recovery of mg copper per cm² cathode surface area.

To further verify the reduction of Cu^{2+} to Cu(s) , the FESEM/EDX analysis was performed for the surface of the rGO Cathode. The degradation of 30 mg Cu/L solution was investigated and the results are shown in Fig 22 of Appendix E. The imaging from Figs 7.2-3 (a) and (b) revealed the formation of micron sized copper particles. The EDX analysis revealed well-matched Cu elements recovered from (d) 10 mmol Cu/L (2497 mg Cu/L) as well as the (e) 30 mg Cu/L solution. Furthermore, the uniform dispersion of oxygen across images of (g), (h) and (i), coupled with the concentrated Cu element affirmed the reduction of Cu^{2+} into Cu(s) and the recovery on the graphene oxide layer. The formation of cubic Cu particles in the 30 mg Cu /L solution suggests the initial formation of Cu(s) , revealing rough surface morphology assembled by nanoparticulates. The 10 mmol Cu/L solution contained higher concentration of copper and a rod-like morphology was formed. The different morphological structure due to different amount of Cu reduced could be inferred as the growth change of Cu from the cubic to a rod like formation as more Cu assembled. Upon further inspection, uniform dispersion of Cu elements is observed in both EDX analyses. In contrast, the respective FESEM and EDX analyses of the Loop setup in Fig 7.2-2 (c) and (f) showed that Cu elements were not detected on the rGO Cathode, the dispersion of Cu in the Power Supply configuration then suggests the formation of Cu nanoparticles. Conversely, the absence of Cu nanoparticulate could be due to the lack of potential difference for reduction of Cu^{2+} to Cu(s) which required +0.34 eV (Hunsom, Pruksathorn, Damronglerd, Vergnes, & Duverneuil, 2005). Hence, the Loop and Open Circuit configuration that reported low Cu concentration in Fig 7.2-1 (c) was from adsorbed Cu ions on the rGO Cathode surface. Moreover, lower amount of Cu ions was adsorbed in the Loop than the Open Circuit configuration, and the slightly faster rate of organic degradation in the Loop configuration does point to the minor scavenging of electrons as the possible means of enhancing the oxidation process. The lower concentration of Cu adsorbed by the Loop configuration cathode might point to reductive electrons which partially reduced Cu^{2+} to Cu^+ which desorb back into the system. In the case of the Open Circuit setup, adsorption of the Cu azo complex onto the graphene oxide occurred. The results demonstrated that the adsorption of Cu onto the rGO Cathode was further expanded to recover larger

amounts of Cu through the reduction of Cu^{2+} to Cu(s) . This approach maximized the effective surface area of the rGO Cathode and in turn minimized the usage of GO. Furthermore, the FESEM/EDX images display the utility of the setup and its effectiveness in extracting Cu ions from the bonds of complexes and the recovery of Cu ions in solution as low as 30 mg Cu/L, using a low voltage setup.

Figure 7.2-2. FESEM imaging of reduced Cu particles in (a) 10 mmol/L Cu solution and (b) 30 mg/L Cu solution. (c) No observable Cu content from the Loop configuration after 1h. The corresponding EDX analysis of Cu (d) 10 mmol/L Cu solution and (e) 30 mg/L Cu solution. (f) The Loop rGO Cathode with no observed Cu content. The uniform dispersion of Oxygen (O) element (g) 10 mmol/L Cu solution, (h) 30 mg/L Cu solution, (i) Loop configuration.

The sum spectrum (j) 10 mmol/L Cu solution, (k) 30 mg/L Cu solution, (l) Loop configuration.

7.2.1. WATER TREATMENT PERFORMANCE EVALUATION AND MECHANISM USING AZO DYE

The experiment was performed using the Open Circuit and the Power Supply configuration with azo dye, AO7 as the target pollutant. The evaluation aims to investigate organic pollutant degradation without the presence of metal ions. The reaction was applied in alternation using the same anode and cathode and the samples were taken at a 10 mins interval.

The results revealed in Fig 7.2-3 (a) tabulates the degradation rate constant k of the 6 sets of reaction starting with the Open Circuit followed by the Power Supply configuration. A faster decolourization was observed without the addition of the CuSO_4 . The rate of degradation shown by the Cu-Azo complex compared to the azo dye portrayed greater persistence even after prolonged recovery of Cu ions suggesting that the molecular bonds have been altered. The difference between the reductive and oxidative region of the azo dye and the Cu-Azo complex was performed using cyclic voltammetry shown in Fig 23 of Appendix E. Furthermore, the rate constant of degradation of the azo dye was observed to stagnant at the 40 mins mark due to the faster breaking of the double bonds within the azo dyes (Zhong et al., 2011). The rate of degradation was therefore taken for the first 40 mins of the degradation curve, and is shown in the Fig 7.2-3 (b). Clearly, the rate constant of degradation fluctuated between the Open Circuit and the Power Supply configuration, resulting in a deceleration in the rate of degradation under the effects of photoelectrocatalysis in the Power Supply configuration by ~13% from 0.0367 to 0.032 min^{-1} . The configuration of the Open Circuit was akin to the PCO demonstrating enhanced rate of degradation.

Figure 7.2-3. (a) The change in decolourisation of the azo dye under the alternating configuration of Open Circuit (OC) and Power Supply (PS) and (b) its corresponding rate constant of degradation taken from the first 40 mins.

This demonstrated the influence of the reductive potential on the redox reaction within the system. The decolorization of azo dye was largely attributed to oxidation. Fig 25 of Appendix E revealed the oxidative role played by electrochemical process in the decolorization of the azo dye. The presence or absence of TiO_2 catalyst under dark condition, both affirmed the transfer of electrons from the oxidative anode towards the power supply due to the potential difference. The subsequent release of electrons into the reductive cathode played a less important role in the decolorization process. Compared to Cu-Azo complex evaluation of Chapter 7.2.1, the presence of Cu ions provided a reducing agent for the electrons at the cathode which balanced the redox reaction.

Fig 7.2-4 (a) illustrates the photocatalytic mechanism of the Open Circuit configuration. The doping of Fe into TiO_2 creates a $\text{Fe}^{3+}/\text{Fe}^{2+}$ conduction band below that of TiO_2 conduction band (Asiltürk et al., 2009). The photosensitization of dyes partakes in the electron transfer to the TiO_2 photocatalyst, causing a dye reduction (X. Zhang, D. D. Sun, et al., 2008). The photoexcited HMS generated electron-hole pairs. The electrons, in addition to the dye electron, were able to either migrate onto the $\text{Fe}^{3+}/\text{Fe}^{2+}$ band which reacts with O_2 to form O_2^- (Ali, Tripathi, Azam, et al., 2017), or onto graphene oxide where the electrons contributed to generation of reactive oxygen species (J. Liu et al., 2010). Simultaneously, the holes

created oxidation sites for the generation of $\text{OH}^\bullet$ to degrade the azo dyes (Chong et al., 2010).

The Power Supply Configuration in Fig 7.2-4 (b) illustrates the extraction of electrons out of the HMS Anode due to the potential difference which mitigated recombination and prompted oxidation by holes, aided by the $\text{Fe}^{3+}/\text{Fe}^{2+}$ and GO interface. Similarly, the balance of the redox reaction occurred at the rGO Cathode where electrons are reintroduced. It was reported that the introduction of dissolved oxygen at the cathode area, enabled the scavenging of electrons by O_2 to form reactive oxygen species (ROS) (Garcia-Segura et al., 2013; Juang et al., 2016). The lack of electron scavengers or reducing agents at the cathode surface created a recombination situation. As the decolorization of the AO7 was due to the oxidative anode within the system, and was attributed to the breaking of the azo bonds within the azo dyes (Pedro Silva et al., 2004; Zhong et al., 2011). The reduced rate of degradation does suggest that the electrons either disrupted the water chemistry by reducing $\text{OH}^\bullet$ back into hydroxide (OH^-) (Juang et al., 2016), reversing the overall degradation process.

Figure 7.2-4. (a) The mechanism of photocatalysis under the (a) Open Circuit Configuration compared to the (b) Power Supply Configuration for the degradation of Azo dye (AO7).

7.3. CLEAN WATER PRODUCTION MECHANISM

The overview of the clean water production mechanism is shown in Fig 7.3-1 which began with the (1) photocatalytic oxidation process in the anode. The photoexcitation of HMS generates electron-hole pair (2) which is drawn towards the power supply due to the potential difference created within the system. The scavenging of electrons is aided by the presence of $\text{Fe}^{3+}/\text{Fe}^{2+}$ and GO interface which mitigates the recombination of the electron-hole pair and facilitates the charge transfer due to high charge mobility. The generated holes, oxidizes water, which then produce $\text{OH}^\bullet$ for pollutant degradation. (3) The electrons were resupplied back into the system through the cathode, (4) and the conductive surface allowed for the electrochemical reduction of Cu^{2+} into Cu(s) . The photoelectrocatalysis caters to the degradation of organics and the recovery of heavy metal to produce clean water.

Figure 7.3-1. The (1) PCO which occurs at the anode initiating the excitation of electrons and (2) transfer towards the power supply due to the potential difference. (3) The generation of electrons from the power supply and the (4) electrochemical reduction which occurs at the cathode which reduce Cu^{2+} to Cu^+ and the recovery of Cu(s) .

Fig 7.3-2 illustrates the detailed scavenging of electrons and the oxidative holes as the crucial component for the degradation of organic pollutants. The transfer of electrons occurred at two components, the photoexcitation of TiO_2 resulted in the

electron-hole separation and the photosensitization of the Cu-azo complex which transferred electrons onto the conduction band of TiO₂ (S. S. Lee et al., 2013; X. Zhang, D. D. Sun, et al., 2008). The excited electrons were drawn via the potential difference towards the positive anode end of the power supply. The doping of Fe reported to develop reduction level of Fe³⁺/Fe²⁺ below the conduction band of TiO₂ and oxidation level of Fe³⁺/Fe⁴⁺ above the valence band of TiO₂ (Ali, Tripathi, Azam, et al., 2017; Asiltürk et al., 2009). The band alignment of the Fe³⁺ allowed the trapping of electron charges migrating from the TiO₂ conduction band which mitigated electron-hole recombination by converting Fe³⁺ to Fe²⁺. The migration of hole charges from the TiO₂ valence band traps in the Fe³⁺ to form Fe⁴⁺. Based on the crystal field theory, Fe³⁺ having half-filled d orbital (3d⁵) is relative stable compared to the other two oxidation states of Fe²⁺ or Fe⁴⁺ (M. Zhou et al., 2006). The release of electrons by Fe²⁺ occurred through the migration onto the graphene oxide on towards the anode, converting Fe²⁺ back to Fe³⁺. Concurrently, the Fe⁴⁺ oxidizes OH⁻ to generate OH[•] for the degradation of Cu-Azo Complex (X. Zhang, D. D. Sun, et al., 2008). The TiO₂-Fe³⁺/Fe²⁺-GO interface in addition to the potential difference and GO's high carrier mobility facilitated the overall transfer of electrons. The efficient extraction of electrons prevented recombination and promoted the stable generation of oxidative holes for OH[•] production. The Cu-azo complex degraded released Cu²⁺ ions which were drawn towards the negatively charged surface of the cathode. Simultaneously, the reintroduction of electrons at the cathode reduced the Cu²⁺ ions. The adsorbed Cu²⁺ on the rGO Cathode surface were reduced to Cu⁺ and finally to Cu(s) which then crystallized on the rGO (T.-C. Chen, Priambodo, Huang, & Huang, 2013). This resulted in the formation of uniform distribution of Cu(s) nanoparticles, which subsequently build up to largely Cu(s) cubic copper particles. Due to the conductive nature of Cu(s), the electrons were easily transferred onto the Cu(s) surface which became active nucleation sites for the build-up of Cu ions into larger Cu(s) microrods shown in Fig 7.2-2. The presence of Cu²⁺ functioned as the electron scavenger which prevented the possible reaction of OH[•] to OH⁻ (Juang et al., 2016). The specific utilization of electrons through photoelectrocatalysis enabled the enhanced rate of organic degradation through the scavenging of electrons for metal ion reduction.

Figure 7.3-2 Illustration of the photoelectrocatalysis mechanism which extracted electrons to promote stable oxidative sites for the generation of OH• for the degradation of Cu-Azo Complex. The specific utilization of the reintroduced electrons for the recovery of Cu ions attracted by the negative (-ve) charge promoted the reduction of Cu²⁺ to Cu(s) for the subsequent formation of Cu nucleation sites. The utilization of electrons prevented the reverse reaction of the OH• to OH⁻.

7.4. CONCLUSION

In summary, the photoelectrocatalysis demonstrated the concurrent recovery of heavy metals and pollutant degradation to produce clean water. The extraction of photoinduced electrons of the HMS Anode was due to the band alignment of TiO₂-Fe³⁺/Fe²⁺-GO interface with high carrier mobility, and facilitated the overall transfer of electrons and further mitigated the recombination of electron-hole pair. The specific utilization of electrons for the reduction of Cu ions, prevented the disruption of OH• production through the reverse reaction of OH• + e⁻ => OH⁻. Furthermore, the configuration offered an extrinsic enhancement to photocatalysis and further encompassed the simple recovery of heavy metal ions in the form of metal. The build-up of Cu reduced the need for large surface area adsorption as the growth of metals promoted nucleation sites on a thin film rGO surface. Although the target pollutant was a metal dye complex, wider range of wastewater pollutants could be achievable due to the non-specific target of pollutants for organic and inorganics of other metal types.

8. CHAPTER

8.1. CONCLUSION

The access to clean water and the over dependence on fossil fuel for water production puts sustainable water purification methods as the key challenge of the century. The burning of fossil fuels and the consequential climate change issues create uncertainties for the future water supply in urban city planning. Furthermore, the rapid growth in population and coupled with increasing standard of living in urban cities greatly affects the total demand for clean water. Three main target pollutants exist within water, disease causing pathogens, the organic pollutants, and water-soluble inorganics.

With the above concerns, sustainable water purification method photoelectrocatalysis was reported in this thesis. For the initial part of the research, the Hierarchical TiO₂ Hollow Spheres (HTHS) were fabricated to examine the morphological applicability in water treatment. Furthermore, carbonaceous spheres were chosen as the template for the synthesis of the hollow structure. The HTHS were assembled through the agglomerations of nanoparticles of 13.79 nm and hollow interior structure. The as-prepared HTHS demonstrated enhanced photocatalytic performance due to the reduced grain size, doping of carbon and the hollow interior which increased light harnessing. Furthermore, the enhanced flux performance and ease of recovery of the HTHS were shown. However, owing to the large morphological structure and size, flux was generally independent of superhydrophilic surface. The effectiveness of superhydrophilicity correlated to decreasing pore size due to higher water to metal oxide surface contact. However, the Ti-precursor was unable to penetrate the carbonaceous sphere to produce multi-shell hollow structure due to its highly-functionalized surface.

Subsequently, the studies focus on improving the synthesis method to fabricate multi-dimensional micro-/nano-reactor spheres having properties of multi-shell Hollow, Hierarchical, Heterojunctions Carbonaceous CuO/TiO₂ Spheres (HHHS). The approach synthesized scalable multi-shell TiO₂ hollow sphere without the use

of multiple templating step. In addition, the use of sustainable additives and the modification of the TiO_2 crystal were easily achieved. The $1.5\ \mu\text{m}$ HHHS revealed integrated structure assembled through 20-30 nm $\text{CuO/CuTi}_3\text{O}_8/\text{TiO}_2$ heterojunction and a mesoporous shell consisting of bimodal pore distribution of 3-5 nm and 20-30 nm with enhanced specific surface area of $30.6\ \text{m}^2/\text{g}$. The HHHS was assessed on its organic pollutant degradation and mechanism. The reactor type sphere first initiated pollutant degradation due to the hierarchical structures. The enhanced organic degradation was attributed to the p-n heterojunction of CuO/TiO_2 and the addition of a hypothetical CuTi_3O_8 . The triple heterojunction of carbonaceous- $\text{TiO}_2/\text{CuTi}_3\text{O}_8/\text{CuO}$ with the respective E_G of 3.1/2.8/1.65 eV, enabled the inward flow of electrons towards the bimodal mesoporous heterojunctioned shell while mitigating electron-hole recombination. Furthermore, the photoinduced superhydrophilicity of metal oxides aids in the fluid transfer in the mesoporous shell. The inward transfer of electrons creates oxidative surface which regenerate the porous shell for continual transfer of fluids and electrons.

After demonstrating the novel synthesis method, the adaptability and optimization of the method was investigated to deepen its understanding. The adaptability of the synthesis was explored by substituting copper for iron and fabricated Hierarchical, Multi-shell, Micro-/Nano, Fe-doped TiO_2 Hollow Spheres (HMS). The $1.5\ \mu\text{m}$ HMS revealed 300 nm long hierarchical thorn surfaces with a hollow multi-shell structure assembled with 20 nm nanoparticulates and a uniform dispersion of Fe ions. The optimization was applied by varying iron concentration in the carbonaceous spheres which proposed the ion exchange approach which demonstrated the inward diffusion of Ti ions due to the outward diffusion of the trapped Fe ions. Furthermore, the increased concentration of Ti-Fe ions demonstrated higher ion compaction within the pores which reduced the specific surface area and pores size. The synthesis of HMS from low iron concentrated spheres affirmed the penetration of the Ti ions for a multi-shell TiO_2 structure. The material was assessed for its bacteria degradation mechanism and effectiveness. The material revealed bactericidal capability of 40% after a period of 1h through the physical bacterial lysis by rupturing cell wall membrane. The enhanced photocatalytic lysis of bacteria of 70% was attributed to generation of hydroxyl

radicals ($\text{OH}^\bullet$) due to the Fe-doped band alignment of $\text{Fe}^{3+}/\text{Fe}^{2+}$ and $\text{Fe}^{3+}/\text{Fe}^{4+}$. The bactericidal mechanism proposed the possible attachment onto the cell wall membrane using the hierarchical thorns of HMS which degrades the exposed RNA/DNA.

Consequently, the photoelectrocatalysis configuration applied the Hierarchical, Multi-shell, Micro-/Nano, Fe-doped TiO_2 Hollow Spheres (HMS) to degrade organic pollutant and simultaneously recover Cu metal from Cu^{2+} ion solution. HMS was fixated onto indium tin oxide (ITO)/ polyethylene terephthalate (PET) flexible thin film using Graphene oxide (GO). The cathode was prepared using electrodeposition of GO atop the ITO/PET thin film which reduces the GO to reduced Graphene Oxide (rGO) cathode. The anode applied GO-HMS prepared using sonication and was evaporated atop the rGO Cathode. The GO/rGO interface promotes the binding of the GO-HMS and rGO at low temperature of 60 °C. The 1.5 V photoelectrocatalytic configuration demonstrated enhanced oxidation of organics pollutants by 20% and recovery of 68% heavy metals ions over a period of 1h. The enhanced oxidation of organics was attributed to the scavenging of electrons towards the anode due to the potential difference induced. In addition, the band alignment of $\text{TiO}_2/\text{Fe}^{3+}/\text{Fe}^{2+}$ and the GO's high electron mobility facilitated the transfer which effectively mitigated electron-hole recombination which maintained oxidative sites for $\text{OH}^\bullet$ production. The reintroduced electrons at the cathode were scavenged using the Cu ions as reducing agent for the recovery in the form of Cu(s). The recovery expanded the use of the cathode surface area to increase the overall amount of Cu(s) by the build-up of Cu metal nanoparticles. Furthermore, the electrons were prevented to recombine with hydroxide (OH^-) to form $\text{OH}^\bullet$. In summary, the photoelectrocatalysis study revealed the simplification of clean water production which manipulated the electrons to serve the purpose of degrading organics and recovering heavy metals pollutants, while being mutually beneficial in the process. Lastly, this offered an extrinsic enhancement to photocatalysis performance through the adapt use of redox for the sustainable and scalable design.

8.2. RECOMMENDATIONS AND FUTURE WORK

The thesis has covered the work pertaining to organics degradation, bacteria and heavy metal removal using modified TiO_2 reactor spheres and the photoelectrocatalysis configuration. However, future work is required to complement the studies reported in this thesis. Therefore, recommendations for the future works are summarised as follows:

- (i) Exploration of other types of mixed metal oxides such as but not limited to ZnMn_2O_4 or CoMn_2O_4 (G. Zhang & Lou, 2014) could be carried out using the ion exchange approach to study characteristic and performance changes with different combination of elements. Further investigation and characterisation could be made to ascertain the formation of CuTi_3O_8 . Detailed studies on the synthesis process could help better understand the changes associated with increased penetration duration by controlling the formation of the spherical outer shell under low temperature as well as the possible increase of shell numbers.
- (ii) The modified TiO_2 reactor spheres focuses either on UV-irradiation or visible light as the solar irradiation source. Therefore, there is an opportunity to investigate the applicability using the entire solar spectrum. The study will provide insights on the degradation mechanism and the migration of electrons under the effects of UV-visible spectrum.
- (iii) Extensive study should be carried out to investigate the stability of the photoelectrocatalysis such as, the reintroduced electrons and pollutant relationship to observe possible recombination of pollutant bond, the stability of both the graphene oxide binder and metal oxides. This will prevent the possible release of secondary contaminants into the treated water.
- (iv) The thesis applied the use of battery for the photoelectrocatalysis process. Investigation could be made to observe the electrochemical function of the photoelectrocatalysis reductive electrons. Lastly, a broader investigation could be carried out using solar cells as the power source, shifting the entire process towards a purely sustainable device.

9. CHAPTER

9.1.REFERENCE

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APPENDIX A

Kinetics of Photocatalytic Degradation of Organic Pollutants

The photocatalytic degradation of organic compounds is usually observed via the kinetics of Langmuir–Hinshelwood scheme (Dung et al., 2005; Gaya & Abdullah, 2008; Mills & Le Hunte, 1997).

$$r = -\frac{dC}{dt} = \frac{kKC}{1 + KC}$$

r = initial rate of photooxidation

C = the concentration of the reactant

t = irradiation time

k = rate constant of the reaction

K = reactant adsorption coefficient

At mM concentrations $C \ll 1$, the equation can be simplified to the apparent rate order equation (Kabra, Chaudhary, & Sawhney, 2004; Konstantinou & Albanis, 2004):

$$\ln \frac{C_t}{C_o} = kKt = K_{app}t$$

or

$$C_t = C_o e^{-K_{app}t}$$

K_{app} = first order rate constant obtained by the slope of the graph of $\frac{\ln C_o}{C}$ versus t

C_o = initial concentration of the organic pollutant.

The initial degradation rate could be written in a form conforming to the apparent first order rate law:

$$r_o = K_{app}C$$

Series of studies in the photodegradation of organic contaminants affirms the above first order rate equation (Caliman, Cojocaru, Antoniadis, & Poullos, 2007; J.-Q. Chen, Wang, Zhu, & Gao, 2007; Guettaï & Ait Amar, 2005; Lachheb et al., 2002; Valente, Padilha, & Florentino, 2006). In any case, Langmuir–Hinshelwood model serves as a basis for the photodegradation of organic compounds even if it could not directly give adequate fitting (Demeestere, Visscher, Dewulf, Leeuwen, & Langenhove, 2004).

APPENDIX B

Supplementary Information for Chapter 4

XRD Analysis and Indexing Information

Figure 3 HTS XRD indexing to Anatase TiO₂

Table 2 Scherrer Equation estimated grain size of the (101) Anatase Phase of the HTS and P25.

Denote	Unit	HTS	P25
2θ	$^{\circ}$	25.36	25.28
θ	$^{\circ}$	12.68	12.64
$\cos(\theta)$	-	0.98	0.98
FWHM	$^{\circ}$	0.585	0.400
FWHM (β)	radian	0.0102	0.0070
$\beta\cos(\theta)$	-	0.0100	0.0068
λ	nm	0.15418	0.15418
k	-	0.89	0.89
d_c	nm	13.79	20.17

Figure 4 Individual data of the PCO of (a) HTHS and (b) P25.

Figure 5 Individual data of the permeate flux of (a) UV HTHS, (b) Dark HTHS, (c) UV P25 and (d) Dark P25.

APPENDIX C

Supplementary Information for Chapter 5

FESEM images of HHHS

Figure 6 FESEM image of HHHS.

TEM images of HHHS Multi-shell structure

Figure 7 TEM image of inner sphere shown by the darker solid sphere within the round hollow shell

EDX Analysis

Figure 8 EDX analysis of HHHS

XRD Analysis and Indexing Information

Figure 9 HHHS XRD indexing to Anatase TiO₂, CuO & CuTi₃O₈

Figure 10 HHHS Individual XRD indexing to Anatase TiO₂

Figure 11 HHHS Individual XRD indexing to CuO

Figure 12 HHHS Individual XRD indexing to CuTi₃O₈

Figure 13 HHTS XRD indexing to Anatase TiO₂

Figure 14 Carbonaceous Spheres XRD pattern

Figure 15 Cu-C spheres XRD indexing to Copper Carbonate Hydroxide Hydrate

Kubelka-Munk Function

Figure 16 Kubelka-Munk function reflecting HHTS Carbonaceous TiO₂ with ~3.1 eV, the shift in the eV of the HHHS due to possible hypothetical CuTi₃O₈ with an ~2.8 eV and the presence of CuO with ~1.65 eV.

Table 3 Scherrer Equation estimated grain size of the (101) Anatase Phase and the (002) CuO phase of the HHHS and HHTS.

Denote	Unit	HHHS TiO₂ (101)	HHHS CuO (002)	HHTS TiO₂ (101)
2 θ	°	25.30	35.50	25.30
θ	°	12.65	17.75	12.65
Cos(θ)	-	0.98	0.95	0.98
FWHM	°	0.302	0.323	0.477
FWHM (β)	radian	0.0053	0.0056	0.0083
β Cos(θ)	-	0.0051	0.0054	0.0081
λ	nm	0.15418	0.15418	0.15418
k	-	0.89	0.89	0.89
d _c	nm	26.71	25.59	16.91

APPENDIX D

Supplementary Information for Chapter 6

Figure 17 HMS-6 XRD indexing to Anatase TiO₂

Figure 18 HMS-24 XRD indexing to Anatase and Rutile TiO₂

Figure 19 HMS-48 XRD indexing to Anatase TiO₂

Figure 20 TGA of HMS-48 and the weight reduction at 260 °C which reveal the oxidation of glycerolate and the carbonaceous spheres at 300 °C.

Figure 21 Individual plot of Dark experiment (a) blank with no catalyst, (b) with HMS-6

Figure 22 Individual plot of visible light bacteria degradation (a) Photolysis, (b) HMS-6, (c) HMS-24 and (d) HMS-48.

Table 4 Estimated grain size of the 101 Anatase Phase respective HMS using the Scherrer Equation

Denote	Unit	HMS-6 TiO ₂ A (101)	HMS-24 TiO ₂ A (101)	HMS-24 TiO ₂ A (110)	HMS-48 TiO ₂ A (101)
2θ	°	25.32	25.32	27.46	25.32
θ	°	12.66	12.66	13.73	12.66
Cos(θ)	-	0.976	0.976	0.971	0.976
FWHM	°	0.46	0.436	0.378	0.4
FWHM (β)	radian	0.0080	0.0076	0.0066	0.0070
βCos(θ)	-	0.0078	0.0074	0.0064	0.0068
λ	nm	0.15418	0.15418	0.15418	0.15418
k	-	0.89	0.89	0.89	0.89
d _c	nm	17.54	18.50	21.44	20.17

APPENDIX E

Supplementary Information for Chapter 7

Figure 23 Cathode after copper recovery (left to right) power supply, loop and open circuit.

Figure 24 (a) Degradation of 30 mg/L Cu Azo Complex after 1h. (b) Rate of Degradation of 30 mg/L Cu Azo Complex after 1h.

Figure 25 Cyclic Voltammetry of (a) Cu Azo Complex and (b) Azo Dye, using HMS Anode and rGO Cathode.

Figure 26 Rate of degradation of the Azo Dye for 40 mins in alternation of the Open Circuit and Power Supply Configuration.

Figure 27 Electrochemical oxidation of azo dye decolourisation at the anode (a) with and (b) without TiO_2 under dark for a period of 1h.