Synthesis of multifunctional hybrid materials via layered double hydroxides mediated route

Li, Yongmei

2017

Li, Y. (2017). Synthesis of multifunctional hybrid materials via layered double hydroxides mediated route. Doctoral thesis, Nanyang Technological University, Singapore.

<http://hdl.handle.net/10356/70602>

<https://doi.org/10.32657/10356/70602>

**Synthesis of Multifunctional Hybrid Materials via
Layered Double Hydroxides Mediated Route**

Li Yongmei

School of Materials Science and Engineering

A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Doctor of Philosophy

2015

Abstract

Hybrid materials in general could be classified into three categories: (i) mixed metal oxides (MMO), (ii) MMO with noble metal hybrid, and (iii) MMO with nanocarbon hybrid. In this research work, layered double hydroxides (LDH) mediated route is utilized to synthesize the three types of multifunctional hybrid materials. Studies will focus on understanding how the LDH mediated route lead to the intimately mixed morphology and strong interfacial interaction of the hybrid materials. The impact of these features on the functional property improvement is discussed thoroughly.

This research begins with a systematic investigation on the properties of ZnGaFe ternary MMO prepared via LDH mediated route, and non-LDH route (solid state reaction method) is used as a comparison. Detailed analysis reveals that the MMO derived from LDH mediated approach not only has uniform and well mixed morphology, but also possesses strong metal to metal interactions. All of these characteristic properties are reflected in the study of photocatalytic reactions.

To synthesis MMO-noble metal hybrid material, the noble metal ion ($[\text{AuCl}_4]^-$) intercalated ZnFe LDH is used as a solid state molecular precursor. Intimately mixed ZnFe MMO with uniformly decorated Au nanoparticles is obtained after low temperature calcination. In this work, the evolution of direct intercalated LDH structure is discussed in details. The intra-layer merging mechanism is proposed for the MMO growth during heat treatment. The morphology created is intimately mixed as compared with that of MMO obtained from inter-layer merging mechanism. The intimate interface could lead to favorable band alignment and excellent synergistic interactions for photocatalytic reactions.

The LDH mediated route for synthesis of MMO-CNT hybrid material is also attempted. NiFe LDH nano-plates were firstly deposited on CNT through electrostatic force. With controlled calcination process, NiFe MMO and CNT hybrid material is obtained. The nano sized NiFe MMO obtained from the LDH

Abstract

precursor is intimately mixed, which ensures the strong interaction between Ni and Fe in MMO. More importantly, the hybrid is featured with a unique in-grown structure which is formed due to the carbon reduction reaction during calcination. Instead of coupling through organic ligand or electrostatic force, the in-grown structure results to strong chemical bonding between MMO and CNT. The strong coupling is very favorable for the charge transfer process, and hence significantly improved the electrochemical property.

This thesis concludes the outcomes and findings from the three connected works. Some extended works that could benefit from the concept of LDH mediated synthesis route are proposed.

Acknowledgements

First of all, I wish to thank School of Materials Science and Engineering, Nanyang Technological University to give me the opportunity to pursue my PhD study. I feel very enjoyable and proud as a student of MSE. I am sure this great experience will be influential to my whole life time.

I would like to express my heartfelt gratitude to my supervisor Prof. Hu Xiao. His invaluable and patient instruction, helpful insight and constant encouragement throughout the years definitely have a great impact on my PhD study. Moreover, I must say Prof Hu not only supervises me in my research work, but also influences me in character building. His wisdom and attitude towards research and life is the standard that I could always learn and refer to.

I would like to thanks my co-supervisor Dr. Chi Dongzhi in IMRE who has shown keen interest in my research work and given me valuable advice. I also acknowledge Mr. Shen Yaodong, Dr. Liang Yen Nan, Dr. Liu Ming, Dr. Yin Ming, Dr. Yang Bingxing, Dr. Thelese Foong Ru Bao, Miss Cindy Ang, Dr. He haiyong, Dr. Fu Wei for their expert advice. I appreciate all my lab-mates for being extremely supportive and caring.

I must highlight the great contribution from my parents, Mr. Li Hongxiang and Mrs. Sun Shujin. Thanks for their great love since I was born. Thanks for everything given! Thanks providing me good education. Otherwise, I could not have the chance to pursue my PhD study in such world top university. This thesis is dedicated to them.

I especially thank my husband, Cheng Zhigao, who has accompanied me for so many years, to share my happiness and sadness, to face the difficulties together with me. Thanks for the continuous support and encouragement.

Last but not least, I would like to mention my two lovely baby, Cheng Xingyun and Cheng Yixin. They are definitely the best gifts to me during my PhD life. Thanks them to bring me the great happiness that I have never experienced. You are, the Little Apple, for me!

Page intentionally left blank

Table of Contents

Table of Contents

Abstract.....	i
Acknowledgements	iii
Table of Contents	v
Table Captions	ix
Figure Captions	xi
Abbreviations	xvii
 Chapter 1 Introduction.....	 1
1.1 Background and Hypothesis Statement.....	3
1.2 Objective and Scope	4
1.3 Dissertation Overview	4
1.4 Findings and Outcomes	6
 Chapter 2 Literature Review	 7
2.1 Layered double hydroxides	9
2.1.1 Material structure, synthesis and applications.....	9
2.1.2 Intercalation chemistry	12
2.1.3 Hybrid materials of layered double hydroxides and nanocarbons	15
2.2 Mixed metal oxide nanoparticles	21
2.2.1 Properties and applications of MMO nanoparticles	21
2.2.2 Synthesis methods of mixed metal oxide nanoparticles.....	23
2.2.3 Mixed metal oxide derived from calcinations of LDH	24
2.3 Photocatalyst of dye degradation	27

Table of Contents

2.4	Oxygen evolution reaction	30
2.5	Summary	32
	References	33
Chapter 3 ZnGaFe MMO Derived from LDH Mediated Precursor		41
3.1	Introduction	43
3.2	Experiments.....	44
3.2.1	Material and synthesis	44
3.2.2	Characterizations	45
3.2.3	Photocatalytic test.....	46
3.3	Results and Discussion.....	46
3.3.1	Structure and morphology of LDH and MMO.....	46
3.3.2	Metal to Metal interactions of MMO obtained via LDH synthesis route	52
3.3.3	Photocatalytic activities of MMO	58
3.4	Summary	63
	References	64
Chapter 4 ZnFe MMO and Au Hybrid.....		67
4.1	Introduction	69
4.2	Experiments.....	70
4.2.1	Materials and synthesis	70
4.2.2	Characterizations	71
4.2.3	Photocatalytic test.....	71
4.3	Results and Discussion.....	72
4.3.1	Structural properties of $[\text{CO}_3]^{2-}/\text{ZnFe}$ LDH and $[\text{AuCl}_4]^-/\text{ZnFe}$ LDH	72

Table of Contents

4.3.2	Structural properties of $[\text{CO}_3]^{2-}/\text{ZnFe}$ LDH and $[\text{AuCl}_4]^-/\text{ZnFe}$ LDH after calcinations	77
4.3.3	Photocatalytic ability of $[\text{CO}_3]^{2-}/\text{ZnFe}$ LDH, and $[\text{AuCl}_4]^-/\text{ZnFe}$ LDH based samples	83
4.4	Summary	88
	References	89
Chapter 5 NiFe MMO and CNT Hybrid		91
5.1	Introduction	93
5.2	Experiments.....	94
5.2.1	Materials and synthesis	94
5.2.2	Characterizations	95
5.2.3	Electrochemical performance test	96
5.3	Results and Discussion.....	96
5.3.1	Preparation and properties of NiFe MMO and CNT hybrid	96
5.3.2	Structure and morphology evolution study	107
5.3.3	Electrochemical performance measurement	110
5.4	Summary	114
	References	115
Chapter 6 Conclusion and Future Work		117
6.1	Discussion	119
6.1.1	LDH intermediate synthesis route vs. solid state reaction method	119
6.1.2	Direct intercalation of $[\text{AuCl}_4]^-$ ions into LDH and MMO growth from intra-layer merging	120
6.1.3	Spatial confinement for MMO growth and in-grown structure of MMO/CNT	120

Table of Contents	
6.2	Future works..... 121
6.2.1	Mixed metal oxide with spinel structure 121
6.2.2	Synthesis of gallium-zinc oxynitride solid solution 122
6.2.3	Hybrid structure with functional polymers 123
6.3	Potential impact..... 123
References	 125
Appendix A	 127
Appendix B	 131

Table Captions

Table Captions

Table 3.1 Area under ZnO (100) and (002) XRD peaks, and the area ratio of (002) to (100) for Zn₃Ga₁, Zn₃Ga_{0.9}Fe_{0.1}, Zn₃Ga_{0.7}Fe_{0.3}, Zn₃Ga_{0.5}Fe_{0.5}, and Zn₃Ga_{0.5}Fe_{0.5}_SSR.56

Table 5.1 Comparison of electrochemical performance of the previous reported relevant works.....113

Page intentionally left blank

Figure Captions

Figure 2.1	The LDH structure with intercalated carbonate ions. ^[12]	9
Figure 2.2	(A) Hexagonal shape of MgAl LDH ^[16] ; (B) Flower shape of MgAl LDH ^{17, 18} ; (C) Flower shape of MgAl LDH; (D) NiFe LDH plate laid on substrate; (E) LiAl LDH plate vertically aligned on substrate. ^[19]	10
Figure 2.3	Illustration of ion exchange reaction of layered double hydroxides. ^[45] ...	12
Figure 2.4	Delaminated (A) CoCo LDH; (B) NiCo LDH; (C) NiFe LDH. ^[58]	14
Figure 2.5	(A) possible hybrid structures of CNT and LDH: (a) CNTs adsorped on LDH surface; (b) intercalation of CNT into LDH; (c) LDH in situ grown on CNT; (d) CNT grown from LDH; (e) well aligned CNT grown from LDH; (f) CNT-array double helix grown from LDH; and (B) possible hybrid structures of graphene and LDH: (a) intercalation of graphene into LDH; (b) LDH laid on graphene; (c) LDHs vertically aligned on graphene; (d) graphene in situ grown on LDH. ^[72]	16
Figure 2.6	SEM image of NiAl LDH and graphene composite. ^[76]	17
Figure 2.7	(A) Graphene oxide intercalated NiFe LDH through ion exchange method; (B) XRD spectrum of NiFe-CO ₃ LDH, NiFe-Cl LDH, and NiFe-GO LDH, where the (003) peak of GO intercalated NiFe LDH show obvious left shift; (C) SEM image of GO intercalated NiFe LDH (arrays point to the small nanoplate). ^[77]	18
Figure 2.8	NiFe LDH and GO super-lattice hybrid structure formed by self-assembly. ^[78]	18
Figure 2.9	In situ growth of NiFe LDH on exfoliated graphene oxide. ^[79]	19
Figure 2.10	Synthesis of CoAl LDH – CNT composite through assembly of delaminated LDH. ^[80]	19
Figure 2.11	(A) SEM; (B, C) TEM images of NiFe-CNT hybrid material; (D) XRD spectrum of NiFe LDH-CNT, and Ni(OH) ₂ -CNT; (E) Schematic draw of NiFe LDH-CNT structure. ^[81]	20

Figure Captions

Figure 2.12	Schematic illustration of synthesis and microstructure of NiMn LDH-CNT composite. ^[82]	20
Figure 2.13	Band gap structures of some commonly discussed semiconductors. ^[83]	21
Figure 2.14	(A) Band gap structure of TiO ₂ and Fe ₂ O ₃ under dark environment; and (B) band gap structure with Fermi level alignment under illumination with visible light. ^[93]	23
Figure 2.15	TGA study of MgAl/CO ₃ LDH thermal decomposition. ^[106]	25
Figure 2.16	Schematic illustration of phase transformation during calcinations of LDH precursor. ^[42]	26
Figure 2.17	(A) UV/vis diffuse reflectance spectra of the as-prepared (GaN) _{1-x} (ZnO) _x ; (B) Energy band gap of (GaN) _{1-x} (ZnO) _x as a function of x. The x value of (GaN) _{1-x} (ZnO) _x samples A-E are defined as x = 0.46 for A, x = 0.66 for B, x = 0.72 for C, x=0.78 for D and x = 0.81 for E. ^[122]	27
Figure 2.18	photocatalyst process occurred at catalyst surface after light absorption. ^[123]	28
Figure 2.19	Calculated band edge positions of (MnO) _{1-x} ZnO _x reveal potential visible light photocatalyst. ^[125]	29
Figure 2.20	Schematic representation of charge transfer mechanism in zinc-iron mixed oxides for photocatalyst of dye degradation reaction. ^[102]	30
Figure 2.21	(A) optical images of Ni form before (left) and after (right) NiFe LDH deposition; SEM image of NiFe LDH deposited Ni form at (B) low magnification; (C) high magnification. ^[75]	32
Figure 3.1	XRD spectra (A) and thermal decomposition behavior (B) of LDH-0, LDH-0.1, LDH-0.3, LDH-0.5.....	47
Figure 3.2	XRD spectra of ZnGaFe MMO prepared through LDH mediated synthesis route.	48
Figure 3.3	(A) Thermal decomposition behavior of Zn ₃ Ga _{0.5} Fe _{0.5} _SSR; and (B) XRD spectra of Zn ₃ Ga _{0.5} Fe _{0.5} _SSR.....	49
Figure 3.4	TEM images of Zn ₃ Ga _{0.5} Fe _{0.5} (A) and Zn ₃ Ga _{0.5} Fe _{0.5} _SSR (B); and (C) representative labels of the TEM fringe d spacing for the corresponding crystal planes.....	51

Figure Captions

- Figure 3.5** (A) XRD spectra of $\text{Zn}_3\text{Ga}_{0.5}\text{Fe}_{0.5}\text{SSR}$ (i) and $\text{Zn}_3\text{Ga}_{0.5}\text{Fe}_{0.5}$ (ii) at the region of 27° to 39° ; and (B) XRD spectra of Zn_3Ga_1 , $\text{Zn}_3\text{Ga}_{0.9}\text{Fe}_{0.1}$, $\text{Zn}_3\text{Ga}_{0.7}\text{Fe}_{0.3}$, and $\text{Zn}_3\text{Ga}_{0.5}\text{Fe}_{0.5}$ at the region of 28° to 34° , where the half width at half maximum (HWHM) of ZnO (100) crystal plane are compared. The HWHM of $\text{Zn}_3\text{Ga}_1\text{Fe}$, $\text{Zn}_3\text{Ga}_{0.9}\text{Fe}_{0.1}$, $\text{Zn}_3\text{Ga}_{0.7}\text{Fe}_{0.3}$, and $\text{Zn}_3\text{Ga}_{0.5}\text{Fe}_{0.5}$ are 0.83° , 0.80° , 0.71° , 0.69°53
- Figure 3.6** XPS spectra of (A) Zn 2p; and (B) Ga 2p for Zn_3Ga_1 ; (C) Zn 2p; and (D) Ga 2p for $\text{Zn}_3\text{Ga}_{0.5}\text{Fe}_{0.5}$57
- Figure 3.7** XPS spectrum of Fe 2p for $\text{Zn}_3\text{Ga}_{0.5}\text{Fe}_{0.5}$58
- Figure 3.8** (A) Photocatalytic activities; and (B) The absorption of Zn_3Ga_1 , $\text{Zn}_3\text{Ga}_{0.9}\text{Fe}_{0.1}$, $\text{Zn}_3\text{Ga}_{0.7}\text{Fe}_{0.3}$, $\text{Zn}_3\text{Ga}_{0.5}\text{Fe}_{0.5}$, and $\text{Zn}_3\text{Ga}_{0.5}\text{Fe}_{0.5}\text{SSR}$59
- Figure 3.9** Illustration of energy band structure of (A) $\text{Zn}_3\text{Ga}_{0.5}\text{Fe}_{0.5}$; and (B) $\text{Zn}_3\text{Ga}_{0.5}\text{Fe}_{0.5}\text{SSR}$61
- Figure 4.1** Powder XRD spectra of as prepared $[\text{CO}_3]^{2-}/\text{ZnFe}$ LDH and $[\text{AuCl}_4]^-/\text{ZnFe}$ LDH.73
- Figure 4.2** Morphology of (a) $[\text{CO}_3]^{2-}/\text{ZnFe}$ LDH; and (b) $[\text{AuCl}_4]^-/\text{ZnFe}$ LDH; The d-spacings of 0.27 nm, 0.29 nm, and 0.23 nm belonged to $[\text{CO}_3]^{2-}/\text{ZnFe}$ LDH, $[\text{AuCl}_4]^-/\text{ZnFe}$ LDH structures, and Au^0 respectively.74
- Figure 4.3** Global views of (a-i) as-prepared $[\text{CO}_3]^{2-}/\text{ZnFe}$, (a-ii) $[\text{CO}_3]^{2-}/\text{ZnFe}(200^\circ\text{C})$, (a-iii) $[\text{CO}_3]^{2-}/\text{ZnFe}(300^\circ\text{C})$, (b-i) as-prepared $[\text{AuCl}_4]^-/\text{ZnFe}$, (b-ii) $[\text{AuCl}_4]^-/\text{ZnFe}(200^\circ\text{C})$ and (b-iii) $[\text{AuCl}_4]^-/\text{ZnFe}(300^\circ\text{C})$. The results of (b) showed good dispersion of Au species as well as growth of Au^0 and mixed oxides without uncontrolled agglomeration under low-temperature calcination.75
- Figure 4.4** Illustrations of formation of (a) $[\text{CO}_3]^{2-}/\text{ZnFe}$ LDH and $[\text{AuCl}_4]^-/\text{ZnFe}$ LDH structures; and (b) MMO structures after calcinations.77
- Figure 4.5** The thermo-gravimetric properties of as-prepared $[\text{CO}_3]^{2-}/\text{ZnFe}$ LDH and $[\text{AuCl}_4]^-/\text{ZnFe}$ LDH.78
- Figure 4.6** Powder XRD spectra of $[\text{CO}_3]^{2-}/\text{ZnFe}$ LDH and $[\text{AuCl}_4]^-/\text{ZnFe}$ LDH after calcination at 200°C and 300°C . The reference XRD spectra of standard Au, ZnO, FeO, and Fe_2O_3 are included for comparison.79

Figure Captions

- Figure 4.7** Morphologies of (a-i) $[\text{CO}_3]^{2-}/\text{ZnFe}$ (200 °C), (a-ii) $[\text{CO}_3]^{2-}/\text{ZnFe}$ (300 °C); and (b-i) $[\text{AuCl}_4]^-/\text{ZnFe}$ (200 °C), (b-ii) $[\text{AuCl}_4]^-/\text{ZnFe}$ (300 °C); (c-i) and (c-ii) low and high magnification views of $[\text{AuCl}_4]^-/\text{ZnFe}$ (300 °C). The d-spacings of ~0.27 nm, 0.21 nm, 0.23 nm, 0.24 nm, and 0.28 nm belong to $[\text{AuCl}_4]^-/\text{ZnFe}$ LDH structures, Fe_2O_3 (202), Au^0 (111), ZnO (101), and ZnO (100) respectively.81
- Figure 4.8** EDX spectrum of $[\text{AuCl}_4]^-/\text{ZnFe}$ (300 °C). The inset table shows weight % and atomic % of FeK, ZnK, and AuL element. The inset bright field TEM image shows the scanned region of EDX spectrum.....83
- Figure 4.9** Absorbance change of methylene blue dye solutions which shows the photocatalytic ability of the $[\text{CO}_3]^{2-}/\text{ZnFe}$ LDH and $[\text{AuCl}_4]^-/\text{ZnFe}$ LDH based samples, k is the reaction rate constant of pseudo-first order kinetics.84
- Figure 4.10** Absorption spectra of different $[\text{CO}_3]^{2-}/\text{ZnFe}$ LDH and $[\text{AuCl}_4]^-/\text{ZnFe}$ LDH based samples. An improved absorbance in high wavelength region can be achieved with the incorporation of Au species after calcination....85
- Figure 4.11** Schematic representation of (a) charge transfer across the band gap structure; and (b) synergetic interactions between metal oxides of $[\text{AuCl}_4]^-/\text{ZnFe}$ (300 °C).....87
- Figure 5.1** TEM image of (A) CNT-LDH catalyst; (B) CNT-MMO catalyst, where some CNT outside fringe discontinuity is clearly shown as highlighted...97
- Figure 5.2** Low magnification TEM images of (A) CNT-LDH; (B) CNT-MMO; (C) SEM image of CNT-LDH; and (D) SEM image of CNT-MMO.....98
- Figure 5.3** TGA curves of CNT, CNT-LDH, LDH, simulated CNT/LDH (the simulated weight loss curve for CNT/LDH is the sum of weight loss for 30 wt% CNT and 70 wt% LDH, which is the same ratio as in CNT-MMO catalyst).99
- Figure 5.4** XPS spectrum of (A) C 1s of CNT-MMO, the deconvolution reveals 283.6 eV corresponding to Ni3C bonding energy; (B) Ni 2p_{3/2} of CNT-MMO, the deconvolution reveals NiO and Ni⁰ binding energy; (C) Fe 2p_{3/2} for

Figure Captions

	CNT-MMO, the binding energy at 709.9 eV is corresponding to FeO, and 711.9 eV binding energy is corresponding to FeOOH.	100
Figure 5.5	TEM images of (A) and (B) CNT-MMO catalyst; (C) CNT-MMO-600 °C	101
Figure 5.6	XRD spectra of (i) CNT-LDH; (ii) NiFe LDH; (iii) CNT-MMO; and (iv) Calcined NiFe LDH.	102
Figure 5.7	XPS spectrum of CNT-LDH, the inset table shows the details data for calculating of Ni/Fe atomic ratio.	103
Figure 5.8	XPS spectrum of (A) Ni 2p _{3/2} ; and (B) Fe 2p _{3/2} for CNT-LDH.	104
Figure 5.9	TEM image of CNT-MMO catalyst, showing the existence of FeOOH nanoparticle, and the size is about 3-5 nm.	105
Figure 5.10	(A) STEM dark field image of CNT-MMO; (B) The overlapped image of elemental mapping distribution, which shows the Ni, Fe, and O of CNT-MMO for the position corresponding to the image (A); and (C-E) Elemental mapping of Ni, Fe, and O for catalyst CNT-MMO.	106
Figure 5.11	XPS binding energy of Ni 2p for CNT-MMO catalyst, the distance between Ni 2p _{1/2} and Ni 2p _{3/2} is 17.8 eV.	107
Figure 5.12	(A) XRD spectra of CNT-MMO-0.5 hr (i) and CNT-MMO-3 hr (ii); (B) TEM image of CNT-MMO-0.5 hr; and (C) TEM image of CNT-MMO-3 hr.	108
Figure 5.13	Low magnification TEM images of (A) CNT-MMO-0.5 hr; and (B) CNT-MMO-3 hr.	109
Figure 5.14	Growth mechanism of CNT-MMO during calcination: (A) structure of CNT-LDH catalyst; (B) structure of CNT-MMO-0.5 hr, where NiFe LDH are converted to MMO, but only on the surface of CNT; (C) in-grown structure of CNT-MMO catalyst, where NiO growth into CNT wall through chemical reaction with external CNT wall; (D) structure of CNT-MMO-3 hr, where CNT structure is destroyed due to over-reaction of CNT and NiO.	110
Figure 5.15	(A) iR corrected polarization curves of CNT-MMO and CNT-LDH catalysts in 1 M, 0.1 M KOH solution. The catalyst loading is 0.28	

Figure Captions

- mg/cm²; (B) Schematic drawing of OER process for CNT-MMO catalyst;
 (C) The iR corrected polarization curves for CNT-LDH, CNT-MMO,
 CNT-MMO-0.5 hr, and CNT-MMO-3 hr hybrid catalyst under 1M KOH
 solution; (D) The iR corrected polarization curves of CNT-MMO, CNT-
 LDH, calcined CNT, calcined LDH, and physical mixture of calcined
 CNT with calcined LDH in 1M KOH solution.....111
- Figure 5.16** (A) The tafel plot of CNT-LDH and CNT-MMO measured in 1M KOH
 solution at sweep rate of 5 mV/cm²; (B) The stability test of CNT-LDH
 and CNT-MMO under 1 M KOH solution.114
- Figure A.1** Photograph of the catalyst powder of Zn₃Ga₁, Zn₃Ga_{0.9}Fe_{0.1}, Zn₃Ga_{0.7}Fe_{0.3},
 and Zn₃Ga_{0.5}Fe_{0.5} and Zn₃Ga_{0.5}Fe_{0.5}_SSR from the left to the right127
- Figure A.2** Schematic draw of the experimental setup for photocatalytic reaction 127
- Figure A.3** SEM images of (A-i) Zn₃Ga₁, (B-i) Zn₃Ga_{0.9}Fe_{0.1}, (C-i) Zn₃Ga_{0.7}Fe_{0.3}, (D-i)
 Zn₃Ga_{0.5}Fe_{0.5}, and the particle size statistical measurement of (A-ii)
 Zn₃Ga₁, (B-ii) Zn₃Ga_{0.9}Fe_{0.1}, (C-ii) Zn₃Ga_{0.7}Fe_{0.3}, (D-ii)
 Zn₃Ga_{0.5}Fe_{0.5}.....128
- Figure A.4** Molecular structure of methylene blue..... 128
- Figure A.5** Photocatalytic degradation of MB by (A) Zn₃Ga₁; (B) Zn₃Ga_{0.9}Fe_{0.1}; (C)
 Zn₃Ga_{0.7}Fe_{0.3}; (D) Zn₃Ga_{0.5}Fe_{0.5}; (E) photolysis; (F) Zn₃Ga_{0.5}Fe_{0.5}_SSR.....129
- Figure B.1** Photographs of (A) [CO₃]²⁻/ZnFe(300 °C) and (B) [AuCl₄]⁻/ZnFe(300 °C) .
131
- Figure B.2** Schematic draw of the experimental set for photocatalytic reaction... ..131
- Figure B.3** Photocatalytic degradation of MB by (A) [CO₃]²⁻/ZnFe LDH; (B) [CO₃]²⁻
 /ZnFe(200 °C); (C) [CO₃]²⁻/ZnFe(300 °C); (D) [AuCl₄]⁻/ZnFe LDH; (E)
 [AuCl₄]⁻/ZnFe(200 °C); and (F) [AuCl₄]⁻/ZnFe(300 °C)..... 132

Abbreviations

Abbreviations

MMO	Mixed Metal Oxides
LDH	Layered Double Hydroxides
CNT	Carbon Nanotube
TGA	Thermal Gravity Analysis
OER	Oxygen Evolution Reaction
XRD	X-Ray Diffraction
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
STEM	Scanning Transmission Electron Microscopy
SAED	Selected Area Electron Diffraction
XPS	X-ray Photonelectron Spectroscopy
SPR	Surface Plasmonic Resonance
EDX	Energy Dispersive X-ray spectroscopy
MB	Methylene Blue
CV	Cyclic Voltammetry
RHE	Reversible Hydrogen Electrode
HWHM	Half Width at Half Maximum

Page intentionally left blank

Chapter 1

Introduction

This chapter begins with the description of background information of mixed metal oxides hybrid materials and main issue towards elaboration of the functional properties, which is the degree of mixing and interfacial reaction. This research hypothesis that layered double hydroxides mediated synthesis route could be taken to prepare hybrid materials with intimately mixing morphology and strong interfacial bonding between each component. The objective and scope are outlined, and the dissertation overview is included. The main findings and outcomes of this research are also summarized.

Page intentionally left blank

1.1 Background and Hypothesis Statement

Mixed metal oxides (MMO) which refers to the mixture of two metal oxides is prepared to make use of the desirable attributes from each single metal oxide. Usually, they can give multifunctional properties that single metal oxide cannot offer. For examples, they can achieve: (i) enhanced visible light absorption; (ii) increased carrier life; (iii) increased electron conductivity; (iv) fast redox behavior; or (v) modified redox potential. In addition, MMO could be coupled with noble metals or nanocarbons like carbon nanotube (CNT) to further enhance their functional properties. The three types of materials are most commonly discussed in the literature and show excellent functional properties in broad applications. However, the functioning of the hybrid critically relies on the morphology and synergistic interaction between each component.

To realize excellent synergistic interaction, few challenges need to be addressed, such as the degree of mixing and interfacial interaction. High degree of mixing could create large interfacial contact which provides one of the fundamental requirements for the synergistic interactions. Strong interfacial interaction could significantly magnify the role of each component as compared with simple physical contact or coupling through weak interactions (e.g. Van der Waals force, hydrogen bonding, or electrostatic interactions).

To achieve intimately mixed morphology and strong interfacial interactions, our strategy is to pre-mix the metal cations intimately in a solid state precursor instead of direct synthesis. Layered double hydroxides (LDH) can be considered as the ideal solid state molecular precursor. In LDH single layer nano-sheet, different metal cations are intimately mixed at atomic level and bonded with hydroxyl group in octahedral coordination. The LDH mediated route opens the possibility to control the growth of MMO nanoparticles, such as the size, morphology, and structure. More importantly, metal to metal interactions could be generated during the merging of metal cations for MMO growth. In addition, this LDH mediated route provides high flexibility on the choice of metal element selection, doping, and intercalation, as well as the possibility of

atomic layer deposition. Meanwhile, the LDH mediated approach is facile, low toxic, low temperature synthesis, and easy to scale up.

This LDH mediated approach is especially significant to synthesis MMO based hybrid material. The positive surface charge of LDH makes it highly feasible to couple with a wide range of negatively charged agents. It is also possible to generate new structural properties (hierarchical structure) and create high degree of structural homogeneity. All of the above advantages make it a highly attractive candidate to derive multifunctional hybrid materials.

In this research work, the strategy of LDH mediated synthetic route is used to synthesize MMO, MMO-noble metal, and MMO-nanocarbon hybrid materials. In all the above three scenarios, it is hypothesized that:

LDH synthesis route could create multifunctional hybrid material with intimately mixing morphology and strong interfacial interaction between each component.

1.2 Objective and Scope

With the selection of three types of material system (MMO, MMO-noble metal, and MMO-nanocarbon), the objective of this research is to investigate the role of LDH solid state molecular precursor in creating the intimately mixed morphology and strong interfacial interaction between each component of the hybrid. The studies focus on understanding the mechanism of unique morphology evolution and the strong interaction between each component, as well as how they impact on the functional properties.

1.3 Dissertation Overview

This thesis is organized as the follows.

Chapter 2 reviews the LDH material in details, including the material structure, the available synthetic method, the unique properties and various applications. Subsequently, the same aspects of MMO nanoparticles are discussed. After that, previous works on

MMO obtained via calcinations of LDH precursor are reviewed. This chapter further discussed the mechanism and selected studied of utilizing photocatalyst for dye degradation and oxygen evolution reaction (OER).

Chapter 3 discusses the well mixed morphology and good metal to metal interactions of ternary MMO (ZnGaFe mixed oxides) that was obtained through LDH mediated synthesis route. This is compared with the properties of ZnGaFe MMO which was synthesized using solid state reaction method. For the MMO prepared through LDH mediated synthesis route, good synergistic interaction between the metal oxides is revealed in the study of its photocatalytic property.

Chapter 4 presents the scenario of incorporating noble metals (Au nanoparticles) with ZnFe MMO. $[\text{AuCl}_4]^-/\text{ZnFe}$ LDH is synthesized through direct intercalation of $[\text{AuCl}_4]^-$ ions, and used as precursor to obtain ZnFe mixed oxides with Au hybrid. Results show that ZnFe MMO is intimately mixed with uniformly decorated Au nanoparticles, and the morphology of ZnFe MMO obtained from $[\text{CO}_3]^{2-}$ intercalated LDH precursor was used as a comparison. The mechanism of unique morphology evolution is discussed in details. This chapter again demonstrates how the unique morphology affects the synergistic interaction of this system, especially how the function of noble metals manifests in the role of photocatalyst.

Chapter 5 includes the study of NiFe MMO and CNT hybrid, which was obtained from controlled calcination of the LDH precursor. The role of LDH synthesis route in creating the intimately mixed morphology and favorable metal to metal interaction of this hybrid is reported. In particular, a unique in-grown structure with CNT is created, and strong chemical bonding between CNT and MMO is built up. Contributed by the unique morphology and strong interfacial coupling, excellent performance of oxygen evolution reaction (OER) is elucidated again based on the synergistic interactions within the hybrid.

Chapter 6 concludes the thesis, lists the major contributions, and gives brief recommendations for future works.

1.4 Findings and Outcomes

This research leads to several novel outcomes:

1. Demonstrating the well mixing morphology and good metal to metal interactions of MMO synthesized from low temperature calcination of the LDH precursor.
2. Establishing the methodology of direct intercalating noble metal ions into LDH.
3. Understanding the mechanism of MMO morphology evolution from intra-layer merging upon calcination.
4. Studying intimately mixing morphology of MMO and strong interfacial coupling between MMO and CNT in an in-grown structure.
5. Investigating and understanding the impact of the intimately mixing morphology and strong coupling of (i) MMO, (ii) MMO with noble metal, and (iii) MMO with CNT towards the photochemical and electrochemical property of the hybrid.

Chapter 2

Literature Review

This chapter summarizes the LDH materials and MMO hybrids, as well as their unique properties and applications in details. In addition, the general concepts of photocatalysis of dye degradation and oxygen evolution reaction are reviewed as well as some recent studies.

Page intentionally left blank

2.1 Layered double hydroxides

2.1.1 Material structure, synthesis and applications

Layered double hydroxides (LDH) is also called anionic clay or hydrotalcite. It is a layered material consisting of numbers of two dimensional hexagonal nano-sheet (Figure 2.1). The general chemical formula is $M^{2+}_{1-x}M^{3+}_x(OH)_2(A^{n-})_{x/n} \cdot mH_2O$, where M^{2+} and M^{3+} are divalent and trivalent metal cations respectively, and A^{n-} is the non-framework intercalated charge compensating anion.^[1,2] The layered structure is a brucite ($Mg(OH)_2$) like structure, where x fraction of M^{2+} (such as Mg^{2+} , Zn^{2+} , Ni^{2+} , etc.) is replaced by M^{3+} (e.g., Al^{3+} , Cr^{3+} , Fe^{3+} etc). The metal cations in the single LDH nano-sheet are intimately mixed at atomic level. A net positive charge is balanced by intercalated counter ions (e.g., CO_3^{2-} , Cl^- , SO_4^{2-})^[3,4]. The most widely studied LDH includes $MgAl$ LDH^[5-8], $ZnAl$ LDH^[9-11], and $ZnCr$ LDH^[4,11].

Figure 2.1 The LDH structure with intercalated carbonate ions.^[12]

Depending on the physical and chemical requirements, the nature of M^{2+} and M^{3+} could be a large variation of metallic elements as long as there is not too much difference in radius.^[2] In addition, x in the formula $M^{2+}_{1-x}M^{3+}_x(OH)_2(A^{n-})_{x/n} \cdot mH_2O$ could be varied in a wide range (0.17 - 0.33) without disrupting the structure.^[1,13] Furthermore, the negative compensating ions could be easily exchanged; the exchange ability of anions increases with increasing charge and decreasing ionic radius. The order for simple inorganic anions decreases in the order $CO_3^{2-} > HPO_4^{2-} > SO_4^{2-}$ for divalent anions and $OH^- > F^- > Cl^- > Br^- > NO_3^- > \Gamma^-$ for monovalent anions.^[11,14,15] The capability of intercalating various counter ions into LDH layer makes LDH highly flexible to tune the physical and chemical properties.

In addition to the compositional flexibility, the morphology of LDH can be in hexagonal plate (Figure 2.2A)^[16] or flower shape (Figure 2.2B and Figure 2.2C)^[17,18]. They could be laid on substrate (Figure 2.2D) or vertically aligned on substrate (Figure 2.2E)^[19].

Figure 2.2 (A) Hexagonal shape of MgAl LDH^[16]; (B) Flower shape of MgAl LDH^{17, 18}; (C) Flower shape of MgAl LDH; (D) NiFe LDH plate laid on substrate; (E) LiAl LDH plate vertically aligned on substrate.^[19]

Besides the advantage of compositional and structural flexibility, synthesis of LDH is facile and easily scaled up with very good reproducibility. It has been successfully synthesized by different methods including hydrothermal^[8,14,20], sol-gel routes^[6,21], reconstruction method^[7,22], and co-precipitation method^[6,11,23,24]. Only the most commonly used method i.e., co-precipitation will be discussed here. The co-precipitation method involves a mixture solution of M^{2+} and M^{3+} titrated into the solution containing counter anionic ions to be intercalated at a constant pH. The successful synthesis, as well as the crystallinity, size and morphology of the LDH structure are highly dependent on the growing conditions, like the co-precipitation pH, co-precipitation rate, aging temperature and time, or post hydrothermal treatment.^[15] The solution pH for LDH formation should be in the range that both of the M^{2+} and M^{3+} hydroxide precipitate. For example, pH 10 has been shown to be the suitable value for Mg/Al LDH formation.^[25] Co-precipitation rate affects the homogeneity of LDH crystal size. Low co-precipitation rate usually results a wide range of crystal size because the crystal forms at the beginning of precipitation has longer time to grow.^[13] Aging time affects the size of LDH crystal.^[26] Elevated temperature is usually preferred for better crystallinity.^[27] ZnFe LDH is considered quite difficult to synthesis, because ZnO will tend to form at high pH value (large than >12); while $Fe(OH)_3$ tend to polymerize at low pH value.^[28]

LDH is very attractive for various applications, e.g., additives for polymers^[29,30], catalyst^[1,31,32], drug delivery^[33-35], water treatment^[21], and photocatalyst^[4,23,24,36,37]. Exfoliated LDH was also used for supercapacitor^[38], dye-sensitized solar cell^[39], and lithium ion batteries^[40]. LDH acts also as a good precursor for doping transition metals inside metal oxide through adjustment of the LDH composition.^[41] In addition, well crystallized spinel structures can be obtained through high temperature calcination of LDH.^[42]

LDH has a very large surface area, and allows water to penetrate into the interlayer, therefore LDH is also used as a good photocatalyst reaction site. Hong et. al. synthesized well dispersed Mg/Al LDH acting a support for photosensitizer and co-catalyst Pt nanoparticles and electron transfer media for efficient H_2 evolution and enhanced recyclability.^[43]

The photocatalytic activity of LDH is also explained by the mechanism of metal to metal charge transfer.^{[36], [24]} The covalent bonding between M^{2+} and M^{3+} introduce new energy levels in the band gap, hence promote visible light absorption.^[36] Mohapatra et. al. explained that one electron from M^{3+} is transferred into M^{2+} during photo excitation, and then react with O_2 to create superoxide radical O_2^- for dye degradation. In the end of this cycle, M^{4+} is reduced to M^{3+} by accepting electrons from the dye.^[24]

LDH is also recognized as a doped semiconductor, the band gap of divalent metal oxide is modified with trivalent metal oxide by introducing the transition state into the energy levels, so that charge transition is promoted under visible light excitation.^{[4], [44]} Silva et al. showed that (Zn/Cr) LDH has an efficiency which is 1.6 times higher than traditional photocatalyst WO_3 at the same condition in O_2 evolution.^[23]

2.1.2 Intercalation chemistry

High ionic exchange capability is one of the important features of LDH. Ion exchange process involves pre-synthesis of the LDH structure and then dispersing the LDH material into the solution containing the anionic ions that to be intercalated. The anionic ions in the solution will replace the counter ions in LDH structure as shown in Figure 2.3.^[45] This is the most commonly used methodology to intercalated ions that are difficult to intercalate by direct co-precipitation method.

Figure 2.3 Illustration of ion exchange reaction of layered double hydroxides.^[45]

The advantage of ion exchange method is that the LDH structure could be well maintained, and the high variety of anionic ions that could be exchanged, such as simple

inorganic ions^[46,47], polymers ions^[48], DNA^[49], noble metal ions^[50,51], metal coordination compound^[24,52]. Many review papers have been published to study the ion exchange chemistry of LDH.^[53-55]

There are three general requirements for ion exchange reaction. Firstly, the anionic ions to be intercalated in the solution must be at very high concentration. Secondly, the ion exchange solution is usually kept in carbon dioxide free atmosphere to avoid any carbonate ions in the solution. Thirdly, the pre-synthesis LDH was usually intercalated with non-carbonate ions, e.g. NO_3^- , Cl^- , or SO_4^{2-} either directly intercalated or ion exchanged with carbonate intercalated LDH. This is because the carbonate ions had very high affinity for intercalation; it is considered the most difficult ions to be replaced. Although de-intercalation of carbonate ions could be achieved using acid-salt mixture solution ($\text{HNO}_3 + \text{NaNO}_3$ or $\text{HCl} + \text{NaCl}$)^[56], this is only valid for Cl^- or NO_3^- ions to replace CO_3^{2-} . One more step is required if the target counter ion is other than Cl^- or NO_3^- . Therefore, the ion exchange method is quite complex. Calcination and rehydration method is an alternative method to intercalate other ions into LDH layer.

Calcination treatment to carbonate ion intercalated LDH causes decarbonization and dehydroxylation reactions, and converts LDH into MMO. However, the LDH structure could be reconstructed after rehydration for several hours. During rehydration process, negative counter ions in the rehydration solution could be intercalated into the LDH layer. This is so called “memory effect”, which is one of the important features of LDH.^[11] Due to this “memory effect” property, calcined LDH could be used to absorb harmful negative ions. Rocha et al. showed that when the calcination was done at 550 °C, it required 24 hours for the rehydration process, and 3 days rehydration was required when calcination was done at 750 °C. Only partial rehydration could be obtained if calcination was done at 1000 °C.^[22]

Similar to cationic clays such as montmorillonite, anionic clay LDH could also be delaminated into single layer nano-sheet, although it is a bit more difficult than montmorillonite.^[57] Delamination of LDH is usually carried out through the bottom up method, in which LDH is first ion exchanged with large and weakly charged anionic counter ions e.g. dodecyl sulfate and followed by long time wildly ultra-sonication. The

common solvent for the ultra-sonication process is usually formamide, butanol, N,N-Dimethylformamide–Ethanol Mixture, and water.^[57] The delaminated LDH solution is usually transparent, as shown in Figure 2.4.

Figure 2.4 Delaminated (A) CoCo LDH; (B) NiCo LDH; (C) NiFe LDH.^[58]

The restacking properties of delaminated LDH is firstly demonstrated by leroux et al.^[59] They firstly synthesized Cl^- intercalated ZnAl LDH, and followed by delamination in butanol solution. After evaporating the solvent, the product was dissolved in K_2CO_3 solution, and ZnAl LDH intercalated with carbonate ion was obtained.^[59] liu et al. delaminated NO_3^- intercalated CoAl LDH, and restacked with an anionic polymer, poly(sodium styrene 4-sulfonate) onto quartz plate through layer-by-layer self-assembly.^[60] Molecules without any charge could also be intercalated into LDH layer through delamination and restacking method. Polystyrene intercalated ZnAl LDH was also synthesized through delaminating ZnAl(Cl) LDH and restack in sodium dodecyl sulfate solution with loading of polystyrene molecules.^[61]

Noble metals could greatly enhance the photocatalytic activities as good co-catalyst by enhanced visible light absorption and storing excess electrons generated from the excited metal oxide and promotes charge separation.^{[62], [63]} One of the great advantages of LDH is the facileness to intercalate noble metals into the structure. Various methods have been reported to successfully incorporate noble metals e.g., Ag, Au, Pt into LDH structure. Hong et al. successfully loaded Pt quantum dots onto Mg/Al LDH by reduction of

H_2PtCl_6 .^[43] Pd nanoparticles were loaded to LDH through delamination and restacking method.^[64] Ag nanoparticles could also be deposited on LDH crystal by reducing Ag^+ in aqueous solution.^[65] Zhao et al. fabricated LDH with Au nano-particle in the interlayer via layer-by-layer assembly technique on FTO substrate using electrostatic interaction as the driving force.^[16] Other methods include anion exchange^[66], hydrothermal method^[51,65], and reconstruction method^[67,68].

2.1.3 Hybrid materials of layered double hydroxides and nanocarbons

Organic electron conducting materials (or nanocarbons) includes carbon quantum dots, CNT, and graphene. They have excellent physical and chemical properties, e.g. high strength, good thermal conductivity, and good electron conductivity. They have been very popular materials for combination with polymers to improve their mechanical properties, thermal properties, or alter the electronic conductivity.^[69] Due to the excellent electronic conductivity, they are also used to improve the functional property of metal oxide or mixed metal oxides to by coupling with them to form hybrid material e.g., graphene/ TiO_2 ^[70], CNT/ ZnO ^[71], and etc.

In the recent years, they are explored to form various hybrid structures with LDH material to improve the electron conductivity of LDH, and hence to enhance the functional properties of LDH. Zhao et al. discussed some possible hybrid structures of CNT/LDH (Figure 2.5A), graphene/LDH (Figure 2.5B).^[72]

Figure 2.5 (A) possible hybrid structures of CNT and LDH: (a) CNTs adsorped on LDH surface; (b) intercalation of CNT into LDH; (c) LDH in situ grown on CNT; (d) CNT grown from LDH; (e) well aligned CNT grown from LDH; (f) CNT-array double helix grown from LDH; and (B) possible hybrid structures of graphene and LDH: (a) intercalation of graphene into LDH; (b) LDH laid on graphene; (c) LDHs vertically aligned on graphene; (d) graphene in situ grown on LDH.^[72]

LDH materials like ZnCo LDH^[73], NiTi LDH^[74], and NiFe LDH^[75] have very good electrochemical activity, while CNT and graphene could provide good electron conductivity. Coupling LDH with CNT or graphene is now a very popular strategy for the energy conversion and storage applications.^[72] High surface area exposed to catalyst reaction, high contact area of nanocarbons with LDH, and good interfacial coupling are the general main aspects of engineering strategies to enhance the electrochemical performance.

Xu et. al. synthesized vertically aligned NiAl LDH nano-sheet array on both side of graphene layers, as shown in Figure 2.6.^[76] In this structure, the coupling with graphene provided excellent charge transportation, and the mesoporous structure of LDH provided large specific surface area for reaction site. Therefore, excellent super capacitor performance was generated attribute to this sandwich structure.

Figure 2.6 SEM image of NiAl LDH and graphene composite.^[76]

Long et al. synthesized graphene oxide intercalated NiFe LDH through ion exchange method as shown in Figure 2.7A. The graphene oxide intercalation was demonstrated by XRD (003) peak shift, which is corresponding to 1.1 nm interlayer spacing, as shown in Figure 2.7B. This interlayer spacing is consistent with the thickness of graphene oxide. The SEM image of Figure 2.7C shows the morphology of this graphene intercalated LDH. Due to the strong coupling between graphene oxide and NiFe LDH, excellent electrochemical performance for OER is reported.^[77]

Figure 2.7 (A) Graphene oxide intercalated NiFe LDH through ion exchange method; (B) XRD spectrum of NiFe-CO₃ LDH, NiFe-Cl LDH, and NiFe-GO LDH, where the (003) peak of GO intercalated NiFe LDH show obvious left shift; (C) SEM image of GO intercalated NiFe LDH (arrays point to the small nanoplate).^[77]

Similar work was done by Ma et. al., the delaminated NiFe LDH is self-assembled with GO nano-sheet and forming a hybrid material, as shown in Figure 2.8. This hybrid material exhibited excellent electrochemical performance for water oxidation due to the synergistic effect derived from face-to-face interfacial hybridization of NiFe LDH and conductive graphene layer.^[78]

Figure 2.8 NiFe LDH and GO super-lattice hybrid structure formed by self-assembly.^[78]

In situ growth of NiFe LDH on exfoliated graphene oxide was reported in the year of 2010.^[79] The synthesis route is illustrated in Figure 2.9. In this report, the NiFe LDH nano-plates were in situ deposited on grapheme oxide through electro static coupling. Meanwhile, the grown LDH nano-plates prevented the restacking of reduced graphene oxide.

Figure 2.9 In situ growth of NiFe LDH on exfoliated graphene oxide.^[79]

Assembly of delaminated LDH and oxidized CNT was reported to synthesis CoAl LDH and CNT hybrid material.^[80] The synthesis route is illustrated in Figure 2.10. The intercalated CNT effectively improved the conductivity of the catalyst. As reported, this composite generated high specific capacitance, long cycle stability and high energy storage as supercapacitor electrode.

Figure 2.10 Synthesis of CoAl LDH – CNT composite through assembly of delaminated LDH.^[80]

Gong et al. demonstrated that the combination of active catalyst NiFe LDH and electron conducting material CNT could significantly improve the oxygen evolution activity. The performance was reported to exceed that of commercial Ir catalysts. In their study, NiFe LDH plates were adsorbed on oxidized CNT through electro-static force.^[81] The structure is shown in Figure 2.11.

Figure 2.11 (A) SEM; (B, C) TEM images of NiFe-CNT hybrid material; (D) XRD spectrum of NiFe LDH-CNT, and Ni(OH)₂-CNT; (E) Schematic draw of NiFe LDH-CNT structure.^[81]

Zhao et al. directly synthesized NiMn LDH on oxidized CNT through co-precipitation method. In this structure, LDH plates were vertically standing on CNT, as shown in Figure 2.12. The combination of high active pseudocapacitive hydroxide and conductive CNT exhibited promising energy storage ability as supercapacitor.^[82]

Figure 2.12 Schematic illustration of synthesis and microstructure of NiMn LDH-CNT composite.^[82]

2.2 Mixed metal oxide nanoparticles

2.2.1 Properties and applications of MMO nanoparticles

Several types of common MMO discussed in the literature possess crystal formula belonging to several general structures: Perovskites (ABO_3), Scheelites (ABO_4), Spinel (AB_2O_4), and Palmeirites ($\text{A}_3\text{B}_2\text{O}_8$). These types of MMO has only one crystal phase that is reflected in the XRD spectrum. On the other side, MMO can also refer to mixture of two metal oxides e.g. mixture of ZnO with Fe_2O_3 , TiO_2 with V_2O_5 , and TiO_2 with SnO_2 . The XRD spectrum reflects two metal oxides with different crystal phase. Our work will focus on the second type of MMO nanoparticles.

The band gap structures of several mostly studied semiconductors are shown in Figure 2.13. Semiconductors with large band gap structure, e.g. TiO_2 , could only absorb UV light, which limit its functional properties like photocatalyst of dye degradation or water splitting. Low band gap semiconductors e.g. Fe_2O_3 have very good visible light absorption, but functional property is limited due to the short carrier life time and low conduction band level.

Figure 2.13 Band gap structures of some commonly discussed semiconductors.^[83]

Coupling of two or more semiconductors can give multifunctional properties that single metal oxide cannot offer. For examples, they can achieve: (i) enhanced visible light absorption of wide band gap semiconductors when coupling with low band gap semiconductors^[84-86], (ii) increased carrier life time by favorable band gap alignment for charge transfer^[87-89], or (iii) increased electron conductivity.

ZnO is one of the widely studied semiconductors. It has wide and direct band gap (3.4eV)^[90], large exciton binding energy (60 meV)^[90], and high electron mobility (230 cm²/Vs at 300K)^[91]. These promising properties enable ZnO to be used for various optoelectronic applications including transparent thin film transistor, gas sensor, light emitting diodes, and inverted solar cell.^[92] One facile strategy to tailor or enhance the functional properties of ZnO is coupling it with other appropriate semiconductors. For instance, combining ZnO with low band gap semiconductors like Fe₂O₃ could improve the visible light absorption and photocatalytic performance. The electron conductivity of ZnO thin film could also be enhanced by doping with Al₂O₃ or SnO₂.

Although Fe₂O₃ has the conduction band lower and the valence band higher than that of TiO₂ as shown in Figure 2.13. When they are mixed together, the band gap structure is altering as the heterojunction is build up at the interface between these two metal oxides. With the Fermi level alignment, the conduction band and valence band of Fe₂O₃ will be shifted higher than that of TiO₂ as shown in Figure 2.14A. This band gap structure is favorable for the charge transfer process (Figure 2.14B).^[93]

Figure 2.14 (A) Band gap structure of TiO_2 and Fe_2O_3 under dark environment; and (B) band gap structure with Fermi level alignment under illumination with visible light.^[93]

Besides photocatalyst applications, transition metal oxide materials are also widely studied for electrochemical applications like supercapacitor, battery, oxygen evolution reaction, and oxygen reduction reaction owing to their good redox properties. One of the popular strategies to improve the electrochemical performance is to mix two or more metal oxides, for example Ni-Co^[94,95], Ni-Fe^[96-98], Mn-Co^[99] and Ni-Zn-Co oxides^[100]. This is because mixing metal oxides could introduce abundant structural defects and ensure fast redox reactions.^[101]

2.2.2 Synthesis methods of mixed metal oxide nanoparticles

Mixed metal oxides nanoparticles could be synthesized via various methods, such as sol-gel method^[84,89], solution combustion method^[102], homogeneous precipitation^[103], hydrothermal^[104], core shell coating^[105], electrodeposition, chemical vapor deposition, and solid state reaction method. Among them, sol-gel, hydrothermal, and solid state reaction method are most widely used in the literature.

Sol gel method is a solution phase process. The precursor is typically metal alkoxide. To synthesis MMO, two metal alkoxide precursors are mixed in organic solvent for hydrolysis and condensation. Hydrothermal method is another solution phase process that

commonly used to synthesis MMO. Generally, inorganic metal precursors are mixed in aqueous solution together with OH^- releasing agent (pH adjustment) and citrate agent if necessary. The solution is then put in autoclave and subjected for heat treatment. MMO prepared via solution phase synthesis method is usually poor crystallized and the surface is binding with organic ligand, which limit its functional properties. Hence high temperature treatment is required to remove the organic ligand and improve the crystallinity. However, it is possible to introduce agglomeration during the high temperature treatment.

In solid state reaction process, inorganic metal oxide precursors are mixed in solid phase and subject to grinding process. After that, the mixture of precursor powder is put in high temperature treatment to convert into mixed metal oxides. The advantages of this method are large scale synthesis and high crystallinity. However, the degree of mixing is usually poor.

2.2.3 Mixed metal oxide derived from calcinations of LDH

Thermalgravity analysis (TGA) is an important methodology to study the kinetics of LDH thermal decomposition during heat treatment. As shown in Figure 2.15, thermal decomposition of LDH usually consists of three stages of weight loss with increased temperature, and the total loss is ~47 wt%.^[106] Using MgAl/CO_3 LDH as an example, the first stage occurs at around 94 °C with a loss of 13 wt%, which is corresponding to the physically adsorbed interlayer water. The 2nd stage weight loss is at around 300 °C for 20 wt%, and the last stage is at round 450 °C for 13.8 wt%. The two events are usually overlapped and corresponding to the removal of intercalated anionic counter ions and dehydroxylation of the LDH layers.^[106]

Figure 2.15 TGA study of MgAl/CO₃ LDH thermal decomposition.^[106]

Zhao et. al. had studied the detailed phase transformation of ZnAl LDH to metal oxides during calcination.^[42] With increased calcination temperature, the process involved the collapse of initial LDH plate (200 °C), nucleation and growth of oxides (300 °C– 500 °C), and lastly formation of spinel (above 500 °C) (Figure 2.16). The layered structure is maintained until 200 °C, followed by amorphous nucleation of ZnO doped with Al³⁺ from 200 °C – 400 °C. Further calcination until 500 °C resulted in oriented crystal growth of ZnO doped with Al³⁺. When the temperature is above 500 °C, Al³⁺ was released from ZnO and started formation of ZnAl₂O₄ spinel structure and ZnO. Physical mixture of ZnO and ZnAl₂O₄ was obtained after 800 °C. Despite the general applicability, the actual temperature response of LDH varies depending on the nature of the metal elements and the counter ions.

Figure 2.16 Schematic illustration of phase transformation during calcinations of LDH precursor.^[42]

Due to the “memory effect” of LDH, MMO from calcination of LDH precursor is also used to adsorb harmful negative ions, including vanadate anion^[107], perchlorate^[108,109], phosphate^[110], Fluoride anions^[111,112], and anionic dyes^[113]. The calcination temperature^[108,110], elements of LDH^[109], solution pH^[111,112], and the co-existing anions^[112] all effect the adsorption process.

MMO obtained by calcination of LDH precursor at low temperatures (<500 °C) generally have high specific surface area. They have been used for gas adsorption and subsequent reduction by the nature of metal oxides, such as SO_x adsorption and reduction^[114], NO_x decomposition^[115].

Besides the high specific surface area, calcined LDH also have semiconductor properties. It was reported that calcined ZnAlFe LDH at 723 K result mixed oxides with high surface area and low band gap value of 2.54-2.04 eV, and good results of photo degradation of phenol and cresol were obtained under UV light illumination.^[116] The well mixing morphology of MMO and interactions between metal oxides was not mentioned. In addition, good efficiency of dye sensitized solar cell was reported by calcination of ZnTi LDH.^[117] Furthermore, UV-absorbing application^[42] and catalysis^[118] were explored for

MMO from calcined LDH. ZnFe LDH was used as precursor for synthesis of ZnO–ZnFe₂O₄ MMO and porous assembly of ZnFe₂O₄ nanoparticles applied for lithium electrode.^[119]

ZnGa LDH was used as precursor to synthesis (GaN)_{1-x}(ZnO)_x solid solution. (GaN)_{1-x}(ZnO)_x solid solution is an interesting semiconductor and has shown great potential for photocatalyst under visible light irradiation.^[120] The energy band gap of the material could be engineered through adjusting the content of ZnO.^[121] Traditional method to synthesis (GaN)_{1-x}(ZnO)_x is through nitridation of Ga₂O₃ and ZnO mixture. However, this process requires high temperature and pressure, and limits ZnO content could be diffused in.^[122] Wang et al. reported facile synthesis of Zn rich (GaN)_{1-x}(ZnO)_x solid solution through nitridation of ZnGa LDH. With varying the Zn/Ga ratio in ZnGa LDH precursor, ZnO content in the solid solution could be well adjusted. Therefore, very good visible light absorption could be obtained and the energy band gap could be engineered as shown in Figure 2.17.^[122]

Figure 2.17 (A) UV/vis diffuse reflectance spectra of the as-prepared (GaN)_{1-x}(ZnO)_x; (B) Energy band gap of (GaN)_{1-x}(ZnO)_x as a function of x. The x value of (GaN)_{1-x}(ZnO)_x samples A-E are defined as x = 0.46 for A, x = 0.66 for B, x = 0.72 for C, x = 0.78 for D and x = 0.81 for E.^[122]

2.3 Photocatalyst of dye degradation

Photocatalytic reaction of dye degradation requires electron excitation from the valence band of metal oxides to conduction band upon light absorption and charge transport to the catalyst surface, as shown in Figure 2.18. Some of the excited electron and hole pairs could possibly recombine before they reach the catalyst surface. The recombined electron and hole pairs are not involved in the photocatalytic reaction.

Figure 2.18 photocatalyst process occurred at catalyst surface after light absorption.^[123]

The efficiently transferred hole will reach to the catalyst surface and react with H_2O in the solution and generate free radicals of $\text{OH}^\bullet$. The generated electron that could diffuse to the semiconductor surface will react with O_2 to form free radicals of $\text{O}_2^{\bullet-}$. The superoxide radicals ($\text{O}_2^{\bullet-}$) and hydroxyl radical ($\text{OH}^\bullet$) will react with dye molecules to form dye products. This explains the discoloration of the dye solution after prolonged irradiation.

In this process, efficient charge transfer and long carrier life time are essential factors for good photocatalytic properties. MMO could exhibit excellent photocatalytic properties for dye degradation due to efficient charge transfer at the interface that resulted from appropriate band structure such as TiO_2 with SnO_2 MMO^[124], and ZnO with SnO_2 MMO^[88]. Coupling visible light sensitive metal oxide could improve the visible light absorption efficiency such as TiO_2 with V_2O_5 MMO^[84] and ZnO with Fe_2O_3 MMO^[102].

Kanan et al. studied the band gap variation of MnO by alloying it with ZnO . Based on their calculation.^[125] The band gap of the solid solution could be as low as 2.6 eV by 50 % loading of ZnO , as shown in Figure 2.19. More importantly, their studies shows the band edge position advantages remains, the conduction band is above CO_2 reduction energy level, and the valence band is below the O_2 oxidation energy level.^[125]

Figure 2.19 Calculated band edge positions of $(\text{MnO})_{1-x}\text{ZnO}_x$ reveal potential visible light photocatalyst.^[125]

Zinc oxide is a wide band gap semiconductor with limited visible light absorption, while iron oxide has been reported to have very short charge carrier life time.^[126] Pradhan et al. synthesized zinc-iron mixed oxide through a solution combustion method.^[102] The UV-vis studies show that the visible light absorption of ZnO was significantly improved. The charge transfer at the interface increased the charge carrier life time. The efficient charge transfer between zinc oxide and iron oxide with Fermi level alignment is shown in Figure

2.20. The photocatalysis activity study for dye degradation show that the best result was achieved with the catalyst consisting of 50 % zinc oxide and 50 % iron oxide.^[102]

Figure 2.20 Schematic representation of charge transfer mechanism in zinc-iron mixed oxides for photocatalyst of dye degradation reaction.^[102]

2.4 Oxygen evolution reaction

OER is an electrochemical oxidation process to convert water into oxygen, in which form energy is stored. It plays a very important role in energy conversion and storage applications, e.g. water splitting and rechargeable metal air batteries.^[81,127,128] Seeking for efficient OER catalysts has received considerable attention in the field of energy related research. OER process can be carried out in acid solution or basic solution. In acid solution, the half-cell equation is expressed as:

where two water molecules are converted into four protons, one oxygen molecule, and four electrons.

In basic solution, the half-cell equation is described as:

where four hydroxyl groups are converted into four water molecules, one oxygen molecule, and four electrons.

It is clear that four electrons are involved in this reaction regardless of acidic or basic solution, therefore this electrochemical process requires large over potential to overcome the barrier.^[129] Various catalysts are studied to lower down the over potential. RuO_2 and IrO_2 are so far reported the most active catalyst for OER, but they are expensive and scarce.^[130] Other materials include La, Sr, Ba based perovskites^[131,132], and transition metals like Ni, Co, Fe, Mn, Sn, Ti, V hydroxide or oxides.^[133] Among them, Ni based catalysts are intensively studied in the recent years and very good catalyst activity as well as stability in alkaline solution was reported, including NiO , Ni(OH)_2 ,^[134] Ni-Fe oxyhydroxide ($\text{Ni}_{1-x}\text{Fe}_x\text{OOH}$),^[135-137] and NiFe layered double hydroxide,^[75,138]

It is generally accepted that incorporation of Fe element could improve the electrochemical performance of Ni based catalyst. Trotochaud et al. reported that there are mainly two contributions of Fe.^[137] Firstly, the conductivity of the catalysts was improved. Secondly, Fe could affect the electronic structure of NiOOH , which makes it more favorable for OER activity.^[137]

NiFe LDH is now a very popular material for OER activity, and also used as anode catalyst for zinc air batteries or hydrogen evolution reactions.^[139,140] To improve the electrochemical activity, electron conducting materials like CNT^[81,141], graphene^[77,142,143] had been used to form a hybrid structure with the active catalyst as discussed in the earlier section. Besides, carbon quantum dots was also used to form hybrid structure with NiFe LDH.^[144] In addition, NiFe LDH was also in situ deposited on Ni foam during synthesis and form a three dimensional film, as shown in Figure 2.21. The direct contact with the electrode significantly improved the OER activity.^[75,145]

Figure 2.21 (A) optical images of Ni form before (left) and after (right) NiFe LDH deposition; SEM image of NiFe LDH deposited Ni form at (B) low magnification; (C) high magnification.^[75]

2.5 Summary

LDH, with a general formula of $M^{2+}_{1-x}M^{3+}_x(OH)_2(A^{n-})_{x/n} \cdot mH_2O$, is a layered brucite ($Mg(OH)_2$) like structure. The replacement of M^{2+} by M^{3+} results a net positive charge on the surface of each single layer which is balanced by the counter anions (A^{n-}) in the interlayers. LDH has high flexibility on the choice of composition and morphology. Therefore, it could meet various physical and chemical property requirements. In addition, the intercalation and exfoliation possibility and the facile synthesis method make it more attractive. MMO is one of the most widely studied in the literature for its multifunctional properties. It is usually synthesized by sol-gel method, hydrothermal, solid state reaction, and homogeneous precipitation. It is also obtained via calcination of the LDH precursor in the literature. Calcination of LDH will result collapse of initial LDH plate, nucleation and growth of oxides, and formation of spinel at high temperature. MMO obtained from calcination of LDH is usually used for harmful anion adsorption applications due to the “memory effects” of LDH. MMO has been widely studied for photocatalytic applications owing to several advantages. For example, the light absorption could be improved through coupling with visible light sensitive semiconductors to generate photoexcited electron-hole pair. Efficient charge transfer could be achieved at the interface of the MMO when appropriate band structure is built up. Oxygen evolution reaction requires a high potential to overcome the large energy barrier. Besides the intrinsic property, the conductivity of the catalyst is the key to achieve a low over potential. The most commonly used strategy in the literature is doping electron conducting element like Fe, or coupling with electron conducting materials, e.g. CNT and graphene.

References

- 1 Zhang, F., Xiang, X., Li, F. & Duan, X. Catal Surv Asia 2008, 12, 253-265.
- 2 Goh, K.-H., Lim, T.-T. & Dong, Z. Water Research 2008, 42, 1343-1368.
- 3 Bravo-Suárez, J. J., Páez-Mozo, E. A. & Oyama, S. T. Química Nova 2004, 27, 601-614.
- 4 Parida, K. & Mohapatra, L. Dalton Transactions 2012, 41, 1173-1178.
- 5 Del Arco, M. et al. Journal of Pharmaceutical Sciences 2004, 93, 1649-1658.
- 6 Prinetto, F., Ghiotti, G., Graffin, P. & Tichit, D. Microporous and Mesoporous Materials 2000, 39, 229-247.
- 7 Millange, F., Walton, R. I. & O'Hare, D. Journal of Materials Chemistry 2000, 10, 1713-1720.
- 8 Xu, Z. P. & Lu, G. Q. Chemistry of Materials 2005, 17, 1055-1062.
- 9 Zhang, F. et al. Angewandte Chemie International Edition 2008, 47, 2466-2469.
- 10 Patzkó, Á. et al. Colloids and Surfaces A: Physicochemical and Engineering Aspects 2005, 265, 64-72.
- 11 P. Newman, S. & Jones, W. New Journal of Chemistry 1998, 22, 105-115.
- 12 Rives, V. & Angeles Ulibarri, M. a. Coordination Chemistry Reviews 1999, 181, 61-120.
- 13 Zhao, Y., Li, F., Zhang, R., Evans, D. G. & Duan, X. Chemistry of Materials 2002, 14, 4286-4291.
- 14 Xu, Z. P. et al. Journal of the American Chemical Society 2005, 128, 36-37.
- 15 He, J. et al. Vol. 119 Structure & Bonding (eds X. Duan & David Evans) 89-119 (Springer Berlin / Heidelberg, 2006).
- 16 Zhao, J. et al. Journal of Materials Chemistry 2011, 21, 13926-13933.
- 17 Wang, M. et al. Sci. Rep. 2014, 4.
- 18 Zhang, J., Xie, X., Li, C., Wang, H. & Wang, L. RSC Advances 2015, 5, 29757-29765.
- 19 Hsieh, Z.-L., Lin, M.-C. & Uan, J.-Y. Journal of Materials Chemistry 2011, 21, 1880-1889.

- 20 Xu, Z. P., Stevenson, G., Lu, C.-Q. & Lu, G. Q. The Journal of Physical Chemistry B 2006, 110, 16923-16929.
- 21 Zhao, Y., He, S., Wei, M., Evans, D. G. & Duan, X. Chemical Communications 2010, 46, 3031-3033.
- 22 Rocha, J., del Arco, M., Rives, V. & A. Ulibarri, M. Journal of Materials Chemistry 1999, 9, 2499-2503.
- 23 Silva, C. u. G., Bouizi, Y. s., Fornés, V. & García, H. Journal of the American Chemical Society 2009, 131, 13833-13839.
- 24 Mohapatra, L., Parida, K. & Satpathy, M. The Journal of Physical Chemistry C 2012, 116, 13063-13070.
- 25 Seron, A. & Delorme, F. Journal of Physics and Chemistry of Solids 2008, 69, 1088-1090.
- 26 Panda, H. S., Srivastava, R. & Bahadur, D. Bulletin of Materials Science 2011, 34, 1599-1604.
- 27 Klemkaite, K., Prosycevas, I., Taraskevicius, R., Khinsky, A. & Kareiva, A. Central European Journal of Chemistry 2011, 9, 275-282.
- 28 Radha, A. & Kamath, P. Bulletin of Materials Science 2003, 26, 661-666.
- 29 Nyambo, C., Songtipya, P., Manias, E., Jimenez-Gasco, M. M. & Wilkie, C. A. Journal of Materials Chemistry 2008, 18, 4827-4838.
- 30 Chen, W. & Qu, B. Journal of Materials Chemistry 2004, 14, 1705-1710.
- 31 Wang, Z., Liu, F. & Lu, C. Chemical Communications 2011, 47, 5479-5481.
- 32 Choudary, B. M. et al. Green Chemistry 2001, 3, 257-260.
- 33 Xu, Z. P. & Lu, G. Q. Pure Appl. Chem. 2006, 78, 1771-1779.
- 34 Choi, S.-J. & Choy, J.-H. Nanomedicine 2011, 6, 803-814.
- 35 Ladewig, K., Xu, Z. P. & Lu, G. Q. Expert Opinion on Drug Delivery 2009, 6, 907-922.
- 36 Lee, Y. et al. Energy & Environmental Science 2011, 4, 914-920.
- 37 Teramura, K., Iguchi, S., Mizuno, Y., Shishido, T. & Tanaka, T. Angewandte Chemie International Edition 2012, 51, 8008-8011.
- 38 Wang, L. et al. Chemical Communications 2011, 47, 3556-3558.
- 39 Wang, J. et al. Energy & Fuels 2010, 24, 6463-6467.

- 40 Latorre-Sanchez, M. et al. Carbon 2012, 50, 518-525.
- 41 Wang, L. et al. Chemical Communications 2010, 46, 3911-3913.
- 42 Zhao, X., Zhang, F., Xu, S., Evans, D. G. & Duan, X. Chemistry of Materials 2010, 22, 3933-3942.
- 43 Hong, J., Wang, Y., Pan, J., Zhong, Z. & Xu, R. Nanoscale 2011, 3, 4655-4661.
- 44 Gunjakar, J. L., Kim, T. W., Kim, H. N., Kim, I. Y. & Hwang, S.-J. Journal of the American Chemical Society 2011, 133, 14998-15007.
- 45 Oh, J.-M., Park, D.-H. & Choy, J.-H. Chemical Society Reviews 2011, 40, 583-595.
- 46 Costantino, U., Vivani, R., Bastianini, M., Costantino, F. & Nocchetti, M. Dalton Transactions 2014, 43, 11587-11596.
- 47 Pan, G. X. et al. Advanced Materials Research 2011, 287, 2102-2105.
- 48 Aguzzi, A., Ambroggi, V., Costantino, U. & Marmottini, F. Journal of Physics and Chemistry of Solids 2007, 68, 808-812.
- 49 Choy, J.-H., Kwak, S.-Y., Jeong, Y.-J. & Park, J.-S. Angewandte Chemie International Edition 2000, 39, 4041-4045.
- 50 Beaudot, P., De Roy, M. E. & Besse, J. P. Journal of Solid State Chemistry 2001, 161, 332-340.
- 51 Beaudot, P., De Roy, M. E. & Besse, J. P. Journal of Solid State Chemistry 2004, 177, 2691-2698.
- 52 Dula, R. et al. Applied Catalysis A: General 2002, 230, 281-291.
- 53 Meyn, M., Beneke, K. & Lagaly, G. Inorganic Chemistry 1990, 29, 5201-5207.
- 54 Radha, A. V., Vishnu Kamath, P. & Shivakumara, C. Solid State Sciences 2005, 7, 1180-1187.
- 55 Khan, A. I. & O'Hare, D. Journal of Materials Chemistry 2002, 12, 3191-3198.
- 56 Iyi, N., Matsumoto, T., Kaneko, Y. & Kitamura, K. Chemistry of Materials 2004, 16, 2926-2932.
- 57 Wang, Q. & O'Hare, D. Chemical Reviews 2012, 112, 4124-4155.
- 58 Song, F. & Hu, X. Nat Commun 2014, 5.
- 59 Leroux, F. et al. Journal of Materials Chemistry 2001, 11, 105-112.
- 60 Liu, Z. et al. Journal of the American Chemical Society 2006, 128, 4872-4880.

- 61 Qiu, L., Chen, W. & Qu, B. *Polymer Degradation and Stability* 2005, 87, 433-440.
- 62 Gomes Silva, C. u., Juárez, R., Marino, T., Molinari, R. & García, H. *Journal of the American Chemical Society* 2010, 133, 595-602.
- 63 Mohamed, H. H., Dillert, R. & Bahnemann, D. W. *Chemistry – A European Journal* 2012, 18, 4314-4321.
- 64 Choudary, B. M., Madhi, S., Chowdari, N. S., Kantam, M. L. & Sreedhar, B. *Journal of the American Chemical Society* 2002, 124, 14127-14136.
- 65 Chen, C., Gunawan, P., Lou, X. W. & Xu, R. *Advanced Functional Materials* 2012, 22, 780-787.
- 66 Li, S.-P., Xu, J.-J. & Chen, H.-Y. *Materials Letters* 2005, 59, 2090-2093.
- 67 Carja, G., Kameshima, Y., Nakajima, A., Dranca, C. & Okada, K. *International Journal of Antimicrobial Agents* 2009, 34, 534-539.
- 68 Nityashree. N, N. N. & Menezes, P. *Applied Nanoscience*, 1-7.
- 69 Kim, H., Abdala, A. A. & Macosko, C. W. *Macromolecules* 2010, 43, 6515-6530.
- 70 Štengl, V., Popelková, D. & Vláčil, P. *The Journal of Physical Chemistry C* 2011, 115, 25209-25218.
- 71 Zhu, Y. et al. *Advanced Materials* 2006, 18, 587-592.
- 72 Zhao, M.-Q., Zhang, Q., Huang, J.-Q. & Wei, F. *Advanced Functional Materials* 2012, 22, 675-694.
- 73 Li, Y., Zhang, L., Xiang, X., Yan, D. & Li, F. *Journal of Materials Chemistry A* 2014, 2, 13250-13258.
- 74 Zhao, Y. et al. *Chemical Science* 2014, 5, 951-958.
- 75 Lu, Z. et al. *Chemical Communications* 2014, 50, 6479-6482.
- 76 Xu, J. et al. *Journal of Materials Chemistry A* 2014, 2, 1022-1031.
- 77 Long, X. et al. *Angewandte Chemie International Edition* 2014, 53, 7584-7588.
- 78 Ma, W. et al. *ACS Nano* 2015, 9, 1977-1984.
- 79 Li, H., Zhu, G., Liu, Z.-H., Yang, Z. & Wang, Z. *Carbon* 2010, 48, 4391-4396.
- 80 Yu, L. et al. *Physical Chemistry Chemical Physics* 2014, 16, 17936-17942.
- 81 Gong, M. et al. *Journal of the American Chemical Society* 2013, 135, 8452-8455.
- 82 Zhao, J. et al. *Advanced Functional Materials* 2014, 24, 2938-2946.
- 83 Kudo, A. & Miseki, Y. *Chemical Society Reviews* 2009, 38, 253-278.

- 84 Wu, J. C. S. & Chen, C.-H. Journal of Photochemistry and Photobiology A: Chemistry 2004, 163, 509-515.
- 85 Shen, Y., Foong, T. R. B. & Hu, X. Applied Catalysis A: General 2011, 409–410, 87-90.
- 86 Jin, Q., Fujishima, M. & Tada, H. The Journal of Physical Chemistry C 2011, 115, 6478-6483.
- 87 Kawahara, T., Konishi, Y., Tada, H., Tohge, N. & Ito, S. Langmuir 2001, 17, 7442-7445.
- 88 Uddin, M. T. et al. Inorganic Chemistry 2012, 51, 7764-7773.
- 89 Kitiyanan, A., Ngamsinlapasathian, S., Pavasupree, S. & Yoshikawa, S. Journal of Solid State Chemistry 2005, 178, 1044-1048.
- 90 Look, D. C. Materials Science and Engineering: B 2001, 80, 383-387.
- 91 Yang, X., Xu, C. & Giles, N. C. Journal of Applied Physics 2008, 104, 073727.
- 92 Janotti, A. & Walle, C. G. V. d. Reports on Progress in Physics 2009, 72, 126501.
- 93 Peng, L., Xie, T., Lu, Y., Fan, H. & Wang, D. Physical Chemistry Chemical Physics 2010, 12, 8033-8041.
- 94 Trotochaud, L., Ranney, J. K., Williams, K. N. & Boettcher, S. W. Journal of the American Chemical Society 2012, 134, 17253-17261.
- 95 Yang, Y., Fei, H., Ruan, G., Xiang, C. & Tour, J. M. ACS Nano 2014, 8, 9518-9523.
- 96 Smith, R. D. L. et al. Science 2013, 340, 60-63.
- 97 Fominykh, K. et al. ACS Nano 2015.
- 98 Landon, J. et al. ACS Catalysis 2012, 2, 1793-1801.
- 99 Liu, J. et al. Advanced Materials 2011, 23, 2076-2081.
- 100 Wang, H., Gao, Q. & Hu, J. Journal of Power Sources 2010, 195, 3017-3024.
- 101 Wang, R. & Yan, X. Sci. Rep. 2014, 4.
- 102 Pradhan, G. K., Martha, S. & Parida, K. M. ACS Applied Materials & Interfaces 2011, 4, 707-713.
- 103 Kim, J. H., Choi, W. C., Kim, H. Y., Kang, Y. & Park, Y.-K. Powder Technology 2005, 153, 166-175.

- 104 Jayalakshmi, M. & Balasubramanian, K. International Journal of Electrochemical Science 2009, 4, 571-581.
- 105 Zhang, J. et al. Nanotechnology 2011, 22, 185501.
- 106 Valente, J. S., Rodriguez-Gattorno, G., Valle-Orta, M. & Torres-Garcia, E. Materials Chemistry and Physics 2012, 133, 621-629.
- 107 Song, H.-l. et al. Transactions of Nonferrous Metals Society of China 2013, 23, 3337-3345.
- 108 Yiqiong, Y., Naiyun, G., Yang, D. & Guoping, Y. Water Environment Research 2013, 85, 331-339.
- 109 Yang, Y., Gao, N., Chu, W., Zhang, Y. & Ma, Y. Journal of Hazardous Materials 2012, 209–210, 318-325.
- 110 Cheng, X., Huang, X., Wang, X. & Sun, D. Journal of Hazardous Materials 2010, 177, 516-523.
- 111 Ma, W., Zhao, N., Yang, G., Tian, L. & Wang, R. Desalination 2011, 268, 20-26.
- 112 Lv, L., He, J., Wei, M., Evans, D. G. & Duan, X. Journal of Hazardous Materials 2006, 133, 119-128.
- 113 El Gaini, L., Lakraimi, M., Sebbar, E., Meghea, A. & Bakasse, M. Journal of Hazardous Materials 2009, 161, 627-632.
- 114 Sanchez-Cantu, M., Perez-Diaz, L. M., Maubert, A. M. & Valente, J. S. Catalysis Today 2010, 150, 332-339.
- 115 Yu, J. J., Wang, X. P., Tao, Y. X., Hao, Z. P. & Xu, Z. P. Industrial & Engineering Chemistry Research 2007, 46, 5794-5797.
- 116 Mantilla, A., Tzompantzi, F., Fernández, J. L., Góngora, J. A. I. D. & Gómez, R. Catalysis Today 2010, 150, 353-357.
- 117 Teruel, L., Bouizi, Y., Atienzar, P., Fornes, V. & Garcia, H. Energy & Environmental Science 2010, 3, 154-159.
- 118 Wang, J., Lei, Z. Y., Qin, H., Zhang, L. H. & Li, F. Industrial & Engineering Chemistry Research 2011, 50, 7120-7128.
- 119 Woo, M. A., Kim, T. W., Kim, I. Y. & Hwang, S.-J. Solid State Ionics 2011, 182, 91-97.
- 120 Maeda, K. et al. Journal of the American Chemical Society 2005, 127, 8286-8287.

- 121 Lee, K., Tienes, B. M., Wilker, M. B., Schnitzenbaumer, K. J. & Dukovic, G. Nano Letters 2012, 12, 3268-3272.
- 122 Wang, J. et al. Journal of Materials Chemistry 2011, 21, 4562-4567.
- 123 Nakata, K. & Fujishima, A. Journal of Photochemistry and Photobiology C: Photochemistry Reviews 2012, 13, 169-189.
- 124 Vinodgopal, K., Bedja, I. & Kamat, P. V. Chemistry of Materials 1996, 8, 2180-2187.
- 125 Kanan, D. K. & Carter, E. A. The Journal of Physical Chemistry C 2012, 116, 9876-9887.
- 126 Toroker, M. C. & Carter, E. A. Journal of Materials Chemistry A 2013, 1, 2474-2484.
- 127 Cheng, F. & Chen, J. Chemical Society Reviews 2012, 41, 2172-2192.
- 128 Walter, M. G. et al. Chemical Reviews 2010, 110, 6446-6473.
- 129 Gong, M. & Dai, H. Nano Res. 2015, 8, 23-39.
- 130 Lee, Y., Suntivich, J., May, K. J., Perry, E. E. & Shao-Horn, Y. The Journal of Physical Chemistry Letters 2012, 3, 399-404.
- 131 Suntivich, J. et al. Nat Chem 2011, 3, 546-550.
- 132 Stoerzinger, K. A. et al. The Journal of Physical Chemistry Letters 2015, 6, 1435-1440.
- 133 Subbaraman, R. et al. Nat Mater 2012, 11, 550-557.
- 134 Gao, M. et al. Journal of the American Chemical Society 2014, 136, 7077-7084.
- 135 Friebe, D. et al. Journal of the American Chemical Society 2015, 137, 1305-1313.
- 136 Chemelewski, W. D., Rosenstock, J. R. & Mullins, C. B. Journal of Materials Chemistry A 2014, 2, 14957-14962.
- 137 Trotochaud, L., Young, S. L., Ranney, J. K. & Boettcher, S. W. Journal of the American Chemical Society 2014, 136, 6744-6753.
- 138 Long, X., Xiao, S., Wang, Z., Zheng, X. & Yang, S. Chemical Communications 2015, 51, 1120-1123.
- 139 Li, Y. et al. Nat Commun 2013, 4, 1805.
- 140 Gong, M. et al. Nat Commun 2014, 5.

- 141 Andersen, N. I., Serov, A. & Atanassov, P. Applied Catalysis B-Environmental 2015, 163, 623-627.
- 142 Ma, W. et al. Acs Nano 2015, 9, 1977-1984.
- 143 Yu, X., Zhang, M., Yuan, W. & Shi, G. Journal of Materials Chemistry A 2015, 3, 6921-6928.
- 144 Tang, D. et al. ACS Applied Materials & Interfaces 2014, 6, 7918-7925.
- 145 Lu, X. & Zhao, C. Nat Commun 2015, 6.

Chapter 3

ZnGaFe MMO Derived from LDH Mediated Precursor

This chapter presents a systematic study on the advantages of LDH mediated route on creating the well mixing morphology and metal to metal interactions of MMO as compared with solid state reaction method. Briefly, ZnGaFe LDH with varied Ga to Fe ratio was successfully synthesized. Low temperature calcination converts LDH into MMO. The morphology of MMO is studied through high magnification TEM images, which shows directly shows well mixed morphology of three metal oxides. The good metal to metal interactions that benefit from the LDH mediated route is thoroughly analyzed through XRD and XPS studies. Furthermore, this work also discusses how the well mixing morphology and metal to metal interactions of MMO benefit the excellent synergistic interactions in photocatalytic reaction.

Page intentionally left blank

3.1 Introduction

Layered double hydroxides (LDH), in another name of anionic clay or hydrotalcite, is a class of two dimensional layered material with a general structure of $M^{2+}_{1-x}M^{3+}_x(OH)_2(A^{n-})_{x/n} \cdot mH_2O$.^[1,2] The basic property, intercalation and exfoliation property, wide range of possible composition and stoichiometry, memory effects, and facile synthesis make it highly attractive in various applications, e.g. additives for polymers^[3,4], photocatalyst^[5-9], and electrochemical applications^[10,11]. Besides these functional properties, LDH is also used as a carrier for drug delivery application^[12-14] and catalysis support^[15].

One of the important applications of LDH is to synthesis metal oxides as a solid state precursor. The conversion to metal oxides is done via calcination treatment. Depending on the calcination condition, metal oxides can be prepared in mainly three crystal phase depending on the calcination condition. The metal oxides obtained from low temperature calcined LDH can be in amorphous phase, it is well known for the memory effect property. They can be used for adsorption of toxic anions in water treatment^[16,17], and harmful gas adsorption^[18,19]. With high temperature calcination (~ 800 °C), well crystallized spinel structures can be obtained.^[20] In addition, LDH could also act as a solid state precursor to synthesis of well crystallized mixed metal oxides (MMO) with moderate calcination treatment.

There are a lot of advantages to synthesis well crystallized MMO from low temperature calcination (below 400 °C) of its LDH precursor. Firstly, the divalent and trivalent metal ions could be a wide range of elements as long as there is not too much difference in atomic radius.^[2] Secondly, the ratio of M^{2+}/M^{3+} could be varied in a wide range without disrupting the structure.^[1] Hence, this LDH mediated route to synthesis MMO offers a large flexibility in designing MMO with various compositions or introduction of doping. For example, doping transition metals inside metal oxides could be obtained through composition adjustment of its LDH precursor^[21]. More importantly, the divalent and trivalent metal ions are intimately mixed in the single LDH nano-sheet at atomic level.

Therefore, well mixed morphology of metal oxides could be obtained after low temperature calcination. Homogeneous distribution of MMO from LDH precursor is mentioned in the literature,^[22] but not been studied in details, especially for MMO in photocatalyst applications.

In this work, ZnGaFe LDH is used as an example for systematic study on the well mixed morphology and good metal to metal interactions of ZnGaFe ternary MMO. The excellent synergetic interaction on the functional property of photocatalyst reaction is discussed.

3.2 Experiments

3.2.1 Material and synthesis

Reagent grade zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), gallium (III) nitrate hydrate ($\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$), iron (III) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), and sodium carbonate (Na_2CO_3) are purchased from Sigma Aldrich and used without further purification.

For ZnGaFe LDH synthesis, the following procedure is taken:

- 100ml of DI water was subjected to vigorous stirring of >1000rpm at room temperature.
- A pH electrode was immersed into the solution for pH monitoring.
- 10 ml mixture aqueous solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.6 M), $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.2 M) was titrated into DI water using syringe pump with titration rate of 50ml/hr.
- At the same time, the mixture solution of NaOH (1 M) and Na_2CO_3 (0.4 M) was titrated manually to keep the pH at 9 while providing the carbonate counter-ions into the solution.
- After titration, the solution was stirred for 24 hr (>1000 rpm).
- The as-prepared solid product was separated from the solution and wash with DI water, followed by collection of solid portion by centrifuge, this process is repeated several times until pH reach 7.
- Drying at 80°C for 24 hours and grinding it into fine powder form and LDH powder is obtained. The dried powder is around 300 ~ 500 mg.

In the precursor solution, the molar ratio $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} : [\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O} + \text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}]$ is kept at 3:1, and $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O} : \text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ is varied from 1:0 (named as **LDH-0**), 0.9:0.1 (named as **LDH-0.1**), 0.7:0.3 (named as **LDH-0.3**), and 0.5:0.5 (named as **LDH-0.5**).

To synthesis ZnGaFe MMO, the LDH of LDH-0, LDH-0.1, LDH-0.3, and LDH-0.5 were subjected to calcinations at 300 °C for 2 hr, and denoted as **Zn₃Ga₁**, **Zn₃Ga_{0.9}Fe_{0.1}**, **Zn₃Ga_{0.7}Fe_{0.3}**, and **Zn₃Ga_{0.5}Fe_{0.5}**. The photograph of the catalyst powder is shown in Figure A.1 at Appendix A.

For reference, ZnGaFe MMO, which has the same composition with Zn₃Ga_{0.5}Fe_{0.5}, was prepared by solid state reaction method, denoted as **Zn₃Ga_{0.5}Fe_{0.5}SSR**. In details, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ with the molar ratio of 3:0.5:0.5 was mixed in solid phase, granulated for 30 min, and calcined at 400 °C for 2 hr.

3.2.2 Characterizations

X-ray diffraction (XRD) data was obtained using Bruker D8 diffractometer at Bragg angle of 2θ from 5 ° to 80 ° by using Cu - K α radiation ($\lambda = 1.5418 \text{ \AA}$) with a step size of 0.02 ° and 1.15 °/min. All the samples were tested in the same condition, and the sample amount was 100 mg.

Morphologies were observed by scanning electron microscopy (SEM) FESEM 6340F, and transmission electron microscopy (TEM) JEOL 2010. X-Ray Photoelectron Spectroscopy (XPS) were done by VG ESCALAB 220I-XL instrument equipped with a monochromatic Al K α X-ray source (1486.7 eV photons). The binding energy was calibrated with C (1s) neutral carbon peak at 285.0 eV. Thermal decomposition behaviors were analyzed through thermogravimetric analyzer (TGA) TA instrument Q500, with a ramp rate 10 °C/min under air atmosphere. The UV-vis absorption study is carried with Lambda 750 UV/vis/NIR spectrophotometer (Perkin-Elmer, USA) under wavelength range of 300 nm to 800 nm through reflection. An integration sphere is installed in this equipment. The dynamic light scattering is done by Malvern Zetasizer Nano ZS.

3.2.3 Photocatalytic test

To test the photocatalytic ability of the MMO catalysts in organic dye degradation, 30 mg catalyst was mixed with 30 ml 10^{-5} M methylene blue (MB) solution in a 50 ml glassware bottle (catalyst concentration 1 mg/ml). Before the photocatalyst test, the solution was kept in the dark under stirring for overnight to allow the adsorption of the organic dye reaching equilibrium. During the test, the solution was under constantly stirring with oxygen supply at the rate of 300 cc/min. The catalyst solution was illuminated with visible light by 300 W Xeon light (Newport model 66902) mounted with 420 nm light filter. The catalyst solution was at 30 cm distance to the light source. The solution with 5 min, 10 min, 30 min of visible light illumination were collected and subjected to centrifugation, and the clear solutions were analyzed under Shimadzu UV 2501PC UV-vis recording Spectrophotometer under wavelength range of 500 nm to 700 nm. The schematic draw of this experimental setup is shown in Figure A.2 at Appendix A.

3.3 Results and Discussion

3.3.1 Structure and morphology of LDH and MMO

XRD spectra of $[\text{CO}_3]^{2-}$ intercalated ZnGaFe LDH samples are shown in Figure 3.1A. Typical LDH diffraction peaks are assigned with the corresponding crystal plane. 2θ position of (003) peak is at 11.54° . According to Bragg's law $n\lambda = 2d\sin\theta$, the interlayer spacing is calculated as 7.6 Å, which is consistent with the reported $[\text{CO}_3]^{2-}$ intercalated LDH interlayer spacing.^[23] With the increased loading of Fe^{3+} content, the peak intensity is reduced gradually (all the samples were at the same quantity for XRD test), which indicates decreased LDH crystallinity. The decreased crystallinity could also demonstrate the successful insertion of Fe^{3+} into the LDH structure. This is also reported in the literature that the textural property of LDH could be affected by the successfully insertion of Fe^{3+} as reported.^[24] Successful incorporation of Fe^{3+} into the LDH structure is crucial for the photocatalytic property, as Fe_2O_3 could act as recombination centers if the excess of Fe^{3+} agglomerate into large particles.

Figure 3.1 XRD spectra (A) and thermal decomposition behavior (B) of LDH-0, LDH-0.1, LDH-0.3, LDH-0.5.

The thermal decomposition behavior of the LDH precursor as well as the corresponding DTA curve is studied as shown in Figure 3.1B. The weight loss at ~ 120 $^{\circ}\text{C}$ is corresponding to the adsorbed and interlayer water. The dehydroxylation and decomposition of the counter ion $[\text{CO}_3]^{2-}$ is at ~ 280 $^{\circ}\text{C}$. Therefore, calcination at 300 $^{\circ}\text{C}$ is taken to ensure the full conversion of LDH to metal oxides. Low temperature

calcination treatment is one of the important advantages of LDH. Agglomerations and wild growth of particles could be inhibited during the phase transformation.

The XRD spectra of Zn_3Ga_1 , $\text{Zn}_3\text{Ga}_{0.9}\text{Fe}_{0.1}$, $\text{Zn}_3\text{Ga}_{0.7}\text{Fe}_{0.3}$, and $\text{Zn}_3\text{Ga}_{0.5}\text{Fe}_{0.5}$ MMO obtained from the corresponding LDH precursor are shown in Figure 3.2. Interestingly, only typical ZnO X-ray diffraction pattern (PDF # 361451) is shown, and the diffraction peaks are generally very wide. The reason for such unusual wide peaks should be analyzed together with the TEM images, which are discussed later. Gallium oxide and iron oxide characteristic diffraction pattern are not identified, and the reason will be discussed in the later section.

Figure 3.2 XRD spectra of ZnGaFe MMO prepared through LDH mediated synthesis route.

To synthesis $\text{Zn}_3\text{Ga}_{0.5}\text{Fe}_{0.5}$ _SSR, the corresponding nitrate precursor is calcined at 400 °C, which is higher than the temperature used for MMO synthesis via LDH route (300 °C). However, 400 °C calcination temperature is essential to successfully synthesize MMO via solid state reaction method, because the conversion to metal oxide requires temperature higher than 380 °C as shown in Figure 3.3A.

Figure 3.3 (A) Thermal decomposition behavior of $\text{Zn}_3\text{Ga}_{0.5}\text{Fe}_{0.5}\text{SSR}$; and (B) XRD spectra of $\text{Zn}_3\text{Ga}_{0.5}\text{Fe}_{0.5}\text{SSR}$.

The XRD spectrum of $\text{Zn}_3\text{Ga}_{0.5}\text{Fe}_{0.5}\text{SSR}$ is shown in Figure 3.3B. The ZnO diffraction peaks with sharp and high intensity are clearly shown. Ga_2O_3 and Fe_3O_4 characteristic diffraction patterns are also identified.

The TEM images of $\text{Zn}_3\text{Ga}_{0.5}\text{Fe}_{0.5}$ and $\text{Zn}_3\text{Ga}_{0.5}\text{Fe}_{0.5}$ _SSR are shown in Figure 3.4A and Figure 3.4B. ZnO, $\beta\text{-Ga}_2\text{O}_3$, FeO, Fe_2O_3 , and Fe_3O_4 nano-crystals are labeled by analyzing the d spacing. The corresponding representatives of the labeled circle can be found in Figure 3.4C.

In the TEM images, ZnO nano-crystals are labeled with red circle. For $\text{Zn}_3\text{Ga}_{0.5}\text{Fe}_{0.5}$ as shown in Figure 3.4A, the (002) crystal plane with d spacing of 0.26 nm is identified, and the size varies from 8 to 20 nm. Ga_2O_3 nano-crystals are labeled with blue color. For $\text{Zn}_3\text{Ga}_{0.5}\text{Fe}_{0.5}$, both of (020) and (111) crystal plane with corresponding d spacing of 0.15 nm and 0.29 nm are found for Ga_2O_3 . The particle size is about 5-15 nm. Fe_2O_3 nano-crystals with size of ~5 nm are labeled with d spacing of 0.251 nm in Figure 3.4A, which is corresponding to (110) crystal plane.^[25] Some crystals of FeO about 8-15 nm are found with d spacing of 0.215 nm corresponding to (220) plane.^[26] In addition, Fe_3O_4 nano crystals about 5-8 nm are observed, which have (111) and (220) crystal plane with d spacing of 0.48 nm and 0.30 nm.^[27] Furthermore, $\alpha\text{-FeOOH}$ about 8 nm is observed with d spacing of 0.5 nm, which is corresponding to (020) crystal plane.^[28]

By contrast, the morphology of $\text{Zn}_3\text{Ga}_{0.5}\text{Fe}_{0.5}$ _SSR exhibits agglomerations of large ZnO nanocrystals (20-30 nm) in majority as shown in Figure 3.4B. GaOOH nanocrystal with d-spacing of 0.49 nm and size about 20 nm is observed around ZnO nanocrystals. $\alpha\text{-FeOOH}$ with d-spacing of 0.5 nm and size about 15 nm is also identified. However, $\beta\text{-Ga}_2\text{O}_3$ and Fe_2O_3 are not shown. Since the XRD spectrum in Figure 3.3B shows very sharp peak of $\beta\text{-Ga}_2\text{O}_3$ and Fe_2O_3 , it is believed that $\beta\text{-Ga}_2\text{O}_3$ and Fe_2O_3 should exist at another location as clusters.

Figure 3.4 TEM images of Zn₃Ga_{0.5}Fe_{0.5} (A) and Zn₃Ga_{0.5}Fe_{0.5}_SSR (B); and (C) representative labels of the TEM fringe d spacing for the corresponding crystal planes.

The morphology and particle size of Zn_3Ga_1 , $\text{Zn}_3\text{Ga}_{0.9}\text{Fe}_{0.1}$, $\text{Zn}_3\text{Ga}_{0.7}\text{Fe}_{0.3}$, and $\text{Zn}_3\text{Ga}_{0.5}\text{Fe}_{0.5}$ are studied by the SEM images (see Appendix A Figure A.3). Figure A.3A shows Zn_3Ga_1 are in the shape of nanoplates which is about 300 nm in diameter, and the nanoplate become finer particles with the loading of Fe (from B to D). The statistical measurements on particles size are all centered at about 300 nm, although variations on the range of particles size exist. (see Appendix A Figure A.3).

3.3.2 Metal to Metal interactions of MMO obtained via LDH synthesis route

Doping in ZnO crystals:

The XRD spectra of $\text{Zn}_3\text{Ga}_{0.5}\text{Fe}_{0.5}$ _SSR and $\text{Zn}_3\text{Ga}_{0.5}\text{Fe}_{0.5}$ from 27 ° to 39 ° are shown in Figure 3.5A. Comparing with $\text{Zn}_3\text{Ga}_{0.5}\text{Fe}_{0.5}$ _SSR, $\text{Zn}_3\text{Ga}_{0.5}\text{Fe}_{0.5}$ obtained via LDH mediated route shows ZnO (100), (002), and (101) peaks shift to the lower angle by 0.25 °. The peak shift indicates ZnO is doped by interstitials.

Figure 3.5 (A) XRD spectra of $\text{Zn}_3\text{Ga}_{0.5}\text{Fe}_{0.5}$ SSR (i) and $\text{Zn}_3\text{Ga}_{0.5}\text{Fe}_{0.5}$ (ii) at the region of 27° to 39° ; and (B) XRD spectra of Zn_3Ga_1 , $\text{Zn}_3\text{Ga}_{0.9}\text{Fe}_{0.1}$, $\text{Zn}_3\text{Ga}_{0.7}\text{Fe}_{0.3}$, and $\text{Zn}_3\text{Ga}_{0.5}\text{Fe}_{0.5}$ at the region of 28° to 34° , where the half width at half maximum (HWHM) of ZnO (100) crystal plane are compared. The HWHM of Zn_3Ga_1 , $\text{Zn}_3\text{Ga}_{0.9}\text{Fe}_{0.1}$, $\text{Zn}_3\text{Ga}_{0.7}\text{Fe}_{0.3}$, and $\text{Zn}_3\text{Ga}_{0.5}\text{Fe}_{0.5}$ are 0.83° , 0.80° , 0.71° , 0.69° .

Analysis of ZnO wide diffraction peak in XRD spectra:

The ZnO diffraction peaks of $\text{Zn}_3\text{Ga}_{0.5}\text{Fe}_{0.5}$ are generally much wider than that of $\text{Zn}_3\text{Ga}_{0.5}\text{Fe}_{0.5}\text{-SSR}$ as shown in Figure 3.5A. In details, the half width at half maximum (HWHM) of ZnO (100) peak for $\text{Zn}_3\text{Ga}_{0.5}\text{Fe}_{0.5}$ is 0.69° , whereas, the HWHM for $\text{Zn}_3\text{Ga}_{0.5}\text{Fe}_{0.5}\text{-SSR}$ is 0.12° . The large difference is shown. The wide diffraction peak of $\text{Zn}_3\text{Ga}_{0.5}\text{Fe}_{0.5}$ indicates the smaller crystal size, which is confirmed with the TEM analysis (Figure 3.4A and Figure 3.4B). Smaller crystal size creates more interface, which is very beneficial to the synergetic interactions between metal oxides.

Nevertheless, the reason for such unusual large HWHM of $\text{Zn}_3\text{Ga}_{0.5}\text{Fe}_{0.5}$ should be more than small crystal size. It is reported that peak broadening could be caused by lattice imperfections, such as strain and defect.^[29,30] We believe the lattice imperfections should be the most important reason behind the wide XRD peaks. The existence of defects in ZnO crystal is also shown in UV-vis study of $\text{Zn}_3\text{Ga}_1\text{ MMO}$ at Figure 3.8B, which shows visible light absorption. The details will be discussed in the later section. The defects in ZnO crystals should be caused by interacting with gallium oxide or iron oxide. This is because the metal cations (Zn, Ga, Fe) are intimately mixed in the LDH single layer at atomic level, the strong interaction between different metal oxides could be resulted during the merging of metal cations for MMO growth. Besides lattice defects, we propose the strong interactions could also affect the morphology of metal oxides crystals, such as the size, crystal orientation, and exposure of crystal facet. Further study worth explore.

To study the effect of gallium oxide or iron oxide on ZnO peak broadening, the HWHM of ZnO (100) peak for all the MMO from LDH mediated route are compared with increased amount of Fe^{3+} (Figure 3.5B). In details, the HWHM of Zn_3Ga_1 , $\text{Zn}_3\text{Ga}_{0.9}\text{Fe}_{0.1}$, $\text{Zn}_3\text{Ga}_{0.7}\text{Fe}_{0.3}$, and $\text{Zn}_3\text{Ga}_{0.5}\text{Fe}_{0.5}$ are 0.83° , 0.80° , 0.71° , and 0.69° respectively. This result indicates that the peak broadening effect is weaken with increased amount of Fe^{3+} . Although, the contribution of ZnO lattice imperfection from iron oxide is not excluded, it is clearly that gallium oxide is more important in ZnO peak broadening. The strong interaction between zinc oxide and gallium oxide is benefited from the well mixing morphology of MMO obtained via LDH mediated route.

Analysis of Ga_2O_3 and Fe_2O_3 in XRD spectra:

In $Zn_3Ga_{0.5}Fe_{0.5}$, each of the Ga^{3+} and Fe^{3+} atomic ratio is 12.5 at%. As discussed earlier, both gallium oxide and iron oxide are not identified in the XRD spectrum of $Zn_3Ga_{0.5}Fe_{0.5}$. However, the TEM image in Figure 3.4A clearly shows well crystallized gallium oxide and iron oxide crystals. The possibility of amorphous phase state for gallium oxide and iron oxide could be excluded. As compared with the XRD spectra of $Zn_3Ga_{0.5}Fe_{0.5}$ _SSR in Figure 3.5A, it is possible that the peaks of Ga_2O_3 (002) (202) and (111) overlap with ZnO (100) and (101). The peak of Fe_2O_3 (104) overlaps with ZnO (002). The overlapping could come from the weak intensity due to the well distribution, and the peak broadening effect due to the strong interaction with ZnO. This overlapping indirectly demonstrate the well mixing morphology and strong metal to metal interactions.

Effects of Fe^{3+} on ZnO crystal orientation:

To analysis the effects of Fe^{3+} on ZnO crystal growth for the MMO derived from LDH precursor, the deconvolution area of ZnO (100) and (002) diffraction peaks were analyzed, and the ratio was calculated as shown in Table 3.1. With the increased amount of Fe^{3+} , the area ratio of (002) to (100) is gradually increased from 0.95 (Zn_3Ga_1) to 1.01 ($Zn_3Ga_{0.9}Fe_{0.1}$), 1.47 ($Zn_3Ga_{0.7}Fe_{0.3}$), and 1.58 ($Zn_3Ga_{0.5}Fe_{0.5}$). This result indicates that Fe^{3+} favors ZnO (002) crystal growth and results increased crystallinity for this crystal plane. In addition, compared with $Zn_3Ga_{0.5}Fe_{0.5}$, the area ratio of (002) to (001) for $Zn_3Ga_{0.5}Fe_{0.5}$ _SSR is only 0.53 at the same composition. The strong interaction between Fe^{3+} and Zn^{2+} in the MMO obtained via LDH synthesis route is clearly shown.

Table 3.1 Area under ZnO (100) and (002) XRD peaks, and the area ratio of (002) to (100) for Zn_3Ga_1 , $\text{Zn}_3\text{Ga}_{0.9}\text{Fe}_{0.1}$, $\text{Zn}_3\text{Ga}_{0.7}\text{Fe}_{0.3}$, $\text{Zn}_3\text{Ga}_{0.5}\text{Fe}_{0.5}$, and $\text{Zn}_3\text{Ga}_{0.5}\text{Fe}_{0.5}\text{-SSR}$.

Sample	Area (100)	Area (002)	Area ratio (002) to (100)
$\text{Zn}_3\text{Ga}_1\text{Fe}_0$	1017	971	0.95
$\text{Zn}_3\text{Ga}_{0.9}\text{Fe}_{0.1}$	926	937	1.01
$\text{Zn}_3\text{Ga}_{0.7}\text{Fe}_{0.3}$	596	874	1.47
$\text{Zn}_3\text{Ga}_{0.5}\text{Fe}_{0.5}$	491	778	1.58
$\text{Zn}_3\text{Ga}_{0.5}\text{Fe}_{0.5}\text{-SSR}$	6474	3438	0.53

Interaction between Ga^{3+} and Fe^{3+} :

The XPS spectrum of Zn_3Ga_1 reveals that Zn 2p3/2 binding energy is at 1021.4 eV as shown in Figure 3.6A, corresponding to ZnO oxidation state. Ga 2p3/2 binding energy is at 1117.8 eV as shown in Figure 3.7B, corresponding to Ga_2O_3 oxidation state. The XPS spectrum in Figure 3.6C shows that Zn 2p3/2 binding energy for $\text{Zn}_3\text{Ga}_{0.5}\text{Fe}_{0.5}$ is the same with Zn_3Ga_1 , which is at 1021.4 eV. However, the Ga 2p3/2 binding energy for $\text{Zn}_3\text{Ga}_{0.5}\text{Fe}_{0.5}$ is found to be 1117.4 eV, which is 0.4 eV lower than that of Zn_3Ga_1 , as shown in Figure 3.6D. Ga 2p3/2 binding energy for the oxidation state of Ga_2O_3 is usually in the range of 1116.9 to 1117.8 eV, so Ga^{3+} for $\text{Zn}_3\text{Ga}_{0.5}\text{Fe}_{0.5}$ is still in the oxidation state of Ga_2O_3 , which is consistent with the TEM analysis. However, the reduced binding energy indicates that Ga^{3+} in $\text{Zn}_3\text{Ga}_{0.5}\text{Fe}_{0.5}$ has strong interaction with Fe^{3+} since there is no difference in Zn 2p3/2 binding energy.

Figure 3.6 XPS spectra of (A) Zn 2p; and (B) Ga 2p for Zn_3Ga_1 ; (C) Zn 2p; and (D) Ga 2p for $\text{Zn}_3\text{Ga}_{0.5}\text{Fe}_{0.5}$.

Meanwhile, the Fe 2p binding energy in the XPS spectrum of $\text{Zn}_3\text{Ga}_{0.5}\text{Fe}_{0.5}$ reveals Fe^{2+} oxidation state, as shown in Figure 3.7. FeO and Fe_3O_4 nano-crystals are also observed in TEM image (Figure 3.4A). This result indicates that some of Fe^{3+} is reduced.

Figure 3.7 XPS spectrum of Fe 2p for $\text{Zn}_3\text{Ga}_{0.5}\text{Fe}_{0.5}$.

3.3.3 Photocatalytic activities of MMO

The photocatalytic activities of MMO synthesized via LDH mediated route and solid state reaction method are studied through dye degradation test under visible light illumination. The molecular structure of MB is shown in Appendix A Figure A.4. Before photocatalysis process is carried out, the solution is put in the dark to allow the dye adsorption reaching equilibrium, and the fraction MB adsorbed by each catalyst is calculated and shown in Appendix A Table A.1. The results of photocatalytic activities are shown in Figure 3.8A, and the UV-vis spectra of dye degradation are shown in Appendix A Figure A.5. In this study, pseudo first order equation is used to qualitatively analyze the photocatalytic reaction kinetic for dye degradation: $Kt = \ln(C_0/C)$, where C_0 and C are the dye concentration at time zero and time t , and K is the first order reaction rate constant. The reaction rate constant K for each sample as shown in Figure 3.8A is calculated.

Figure 3.8 (A) Photocatalytic activities; and (B) The absorption of Zn_3Ga_1 , $\text{Zn}_3\text{Ga}_{0.9}\text{Fe}_{0.1}$, $\text{Zn}_3\text{Ga}_{0.7}\text{Fe}_{0.3}$, $\text{Zn}_3\text{Ga}_{0.5}\text{Fe}_{0.5}$, and $\text{Zn}_3\text{Ga}_{0.5}\text{Fe}_{0.5_SSR}$.

MB has visible light absorption from 700 nm to 500 nm. In the absence of catalyst, photolysis of MB may occur, which cause degradation of MB molecule. This process is studied as shown in Figure 3.8A. With 30 min of light illumination, 9% of dye concentration reduction is observed for photolysis reaction, which is considered quite high as compared with the literature. This is because the photolysis measurement is done

in the presence of O_2 , which may oxidize MB through photosensitization reaction. Nevertheless, with the initial reaction rate constant of 0.0049 min^{-1} , it is still the lowest as compared to those with catalyst.

As shown in Figure 3.8A, Zn_3Ga_1 exhibits considerably high photocatalytic activity under visible light illumination, and the UV-vis absorption study shows a small absorption hump from 680 nm to 420 nm for Zn_3Ga_1 , which indicates the visible light absorption (Figure 3.8B). This is very interesting as the band gap of ZnO and Ga_2O_3 are about 3.2 eV and 4.9 eV respectively, which is not sensitive to visible light. The reason for such wide range visible light absorption could be the free electrons and large amount of defects in ZnO, which is caused by Ga^{3+} doping and strong interaction with Ga_2O_3 as discussed earlier. Therefore, it exhibits high photocatalytic activity under visible light illumination.

However, $Zn_3Ga_{0.9}Fe_{0.1}$ gives much lower value of reaction rate constant than that of Zn_3Ga_1 as shown in Figure 3.8A. One of the reasons could be the dye adsorption capability, which is 10% lower than that of Zn_3Ga_1 (see Appendix A Table A.1). Another reason for decreased reaction rate constant should come from the lower light absorption. $Zn_3Ga_{0.9}Fe_{0.1}$ does not show the visible light absorption caused by Fe_2O_3 (from 600 nm to 480 nm) in Figure 3.8B. With 10 at% of Fe^{3+} replacement of Ga^{3+} (2.4 wt% of Fe_2O_3 in the ternary MMO), the absence of visible light absorption could reflect the homogeneous distribution of Fe_2O_3 in MMO. In addition, the small absorption hump (680 nm to 420 nm) as shown in the UV-Vis study of Zn_3Ga_1 (Figure 3.8B) is also disappeared when 10 at% of Ga^{3+} is replaced by Fe^{3+} ($Zn_3Ga_{0.9}Fe_{0.1}$). This indicates the doping and defect concentration in ZnO crystals is decreased, because the interaction of Fe_2O_3 with ZnO is weaker than that of Ga_2O_3 . Therefore, the 10 at% of Fe^{3+} replacement, which is 2.5 at% of MMO, is very significant to the morphology, structure and properties of MMO.

With further increased amount of Fe^{3+} loading (from $Zn_3Ga_{0.9}Fe_{0.1}$ to $Zn_3Ga_{0.5}Fe_{0.5}$), the photocatalytic activity is significantly improved. This is as expected, since the increased loading of Fe^{3+} could improve the visible light absorption, which is also shown in the UV-Vis study (Figure 3.8B). Besides the improved visible light absorption, the increased amount of Fe^{3+} creates more heterojunctions that are strongly favorable for charge

transfer in photocatalytic reactions. In addition, the dye adsorption capability is increased from $\text{Zn}_3\text{Ga}_{0.9}\text{Fe}_{0.1}$ to $\text{Zn}_3\text{Ga}_{0.5}\text{Fe}_{0.5}$ as reflected by the fraction of equilibrium dye adsorption study (see Appendix A Table A.1). The increased dye adsorption capability is strongly beneficial to photocatalytic reaction.

With The reaction rate constant of $\text{Zn}_3\text{Ga}_{0.5}\text{Fe}_{0.5}$ _SSR that prepared via solid state reaction method is 0.00544 min^{-1} , which is very close to the value of photolysis (0.0049 min^{-1}). $\text{Zn}_3\text{Ga}_{0.5}\text{Fe}_{0.5}$ has the same composition and similar dye adsorption capability with $\text{Zn}_3\text{Ga}_{0.5}\text{Fe}_{0.5}$ _SSR (the fraction of dye adsorption in the dark is 34% for $\text{Zn}_3\text{Ga}_{0.5}\text{Fe}_{0.5}$ and 33% for $\text{Zn}_3\text{Ga}_{0.5}\text{Fe}_{0.5}$ _SSR as shown in Appendix A Table A.1). The only difference is the synthesis route. $\text{Zn}_3\text{Ga}_{0.5}\text{Fe}_{0.5}$, synthesized via LDH route, has a reaction rate constant 0.06783 min^{-1} . This is about 12.5 times than that of $\text{Zn}_3\text{Ga}_{0.5}\text{Fe}_{0.5}$ _SSR. The key reason comes from the well mixed morphology and metal to metal interactions of $\text{Zn}_3\text{Ga}_{0.5}\text{Fe}_{0.5}$. The metal oxides in $\text{Zn}_3\text{Ga}_{0.5}\text{Fe}_{0.5}$ are intimately in contact, which favors the energy band structure formation at the heterojunction as illustrated in Figure 3.9A. With Fermi level alignment, the conducting band and valance band of Fe_2O_3 are tuned higher than that of ZnO at the interface as shown in Figure 3.9A. This band gap structure strongly favors the charge transfer process.

Figure 3.9 Illustration of energy band structure of (A) $\text{Zn}_3\text{Ga}_{0.5}\text{Fe}_{0.5}$; and (B) $\text{Zn}_3\text{Ga}_{0.5}\text{Fe}_{0.5}$ _SSR.

The dye degradation process for ZnGaFe MMO catalysts are discussed as the following. Upon light absorption, the electron is excited to the conduction band of Fe_2O_3 and could be efficiently transferred to ZnO, and hence creating electron hole pair ($e_{\text{CB}}^- + h_{\text{VB}}^+$). The transferred electron could react with O_2 to form superoxide radicals $\text{O}_2^{\cdot-}$. The hole at Fe_2O_3 valence band could diffuse to the surface and react with H_2O in the solution and generate hydroxyl radical $\text{OH}^{\cdot}$. The superoxide radicals ($\text{O}_2^{\cdot-}$) and hydroxyl radical ($\text{OH}^{\cdot}$) will react with dye molecules to form dye products.

The detailed process is described below:

$\text{Zn}_3\text{Ga}_{0.5}\text{Fe}_{0.5}\text{SSR}$, with particle size about 20 – 30 nm (SEM image shown in Appendix A Figure A.7), has similar dye adsorption capability with $\text{Zn}_3\text{Ga}_{0.5}\text{Fe}_{0.5}\text{SSR}$ as shown in Appendix A Table A.1. However, without good interactions and intimate contact between metal oxides, the energy band structure in this system is as illustrated in Figure 3.9B without Fermi level alignment. The electron and hole excited at Fe_2O_3 site could not be efficiently transferred because of this energy band structure. Due to the short carrier life time, Fe_2O_3 nanoparticles act as a recombination center for excited charges. Although considerable photocatalytic activity of $\text{Zn}_3\text{Ga}_{0.5}\text{Fe}_{0.5}\text{SSR}$ after 30 min is observed, we believe this is due to light scattering of big particles which enlarged the photolysis

reaction. Without synergistic interaction between ZnO, Ga₂O₃ and Fe₂O₃, the photocatalytic activity is only the sum of their separate effect.

3.4 Summary

In this work, a series of ZnGaFe LDH with varied Ga to Fe ratio was synthesized, and corresponding ternary ZnGaFe MMO was obtained after calcination. Compared with solid state reaction method, the MMO synthesized via LDH approach exhibits well mixed morphology and metal to metal interactions. The well mixed morphology is directly shown in the TEM image. The metal to metal interactions and well mixing are all reflected in the XRD spectra, e.g. peak shift and broadening of ZnO diffraction pattern, preferred ZnO (002) crystal growth, and non-detection of well crystallized Ga₂O₃ and iron oxide in the XRD spectrum. In addition, the redox interaction between Ga³⁺ and Fe³⁺ is also analyzed by the XPS study. Due to the well mixed morphology and metal to metal interactions, excellent synergistic interaction is demonstrated through the functional property of photocatalytic study.

References

- 1 Zhang, F., Xiang, X., Li, F. & Duan, X. Catal Surv Asia 2008, 12, 253-265.
- 2 Goh, K.-H., Lim, T.-T. & Dong, Z. Water Research 2008, 42, 1343-1368.
- 3 Nyambo, C., Songtipya, P., Manias, E., Jimenez-Gasco, M. M. & Wilkie, C. A. Journal of Materials Chemistry 2008, 18, 4827-4838.
- 4 Chen, W. & Qu, B. Journal of Materials Chemistry 2004, 14, 1705-1710.
- 5 Parida, K. & Mohapatra, L. Dalton Transactions 2012, 41, 1173-1178.
- 6 Lee, Y. et al. Energy & Environmental Science 2011, 4, 914-920.
- 7 Mohapatra, L., Parida, K. & Satpathy, M. The Journal of Physical Chemistry C 2012, 116, 13063-13070.
- 8 Silva, C. u. G., Bouizi, Y. s., Fornés, V. & García, H. Journal of the American Chemical Society 2009, 131, 13833-13839.
- 9 Teramura, K., Iguchi, S., Mizuno, Y., Shishido, T. & Tanaka, T. Angewandte Chemie International Edition 2012, 51, 8008-8011.
- 10 Wang, L. et al. Chemical Communications 2011, 47, 3556-3558.
- 11 Latorre-Sanchez, M. et al. Carbon 2012, 50, 518-525.
- 12 Xu, Z. P. & Lu, G. Q. Pure Appl. Chem. 2006, 78, 1771-1779.
- 13 Choi, S.-J. & Choy, J.-H. Nanomedicine 2011, 6, 803-814.
- 14 Ladewig, K., Xu, Z. P. & Lu, G. Q. Expert Opinion on Drug Delivery 2009, 6, 907-922.
- 15 Hong, J., Wang, Y., Pan, J., Zhong, Z. & Xu, R. Nanoscale 2011, 3, 4655-4661.
- 16 Ma, W., Zhao, N., Yang, G., Tian, L. & Wang, R. Desalination 2011, 268, 20-26.
- 17 Lv, L., He, J., Wei, M., Evans, D. G. & Duan, X. Journal of Hazardous Materials 2006, 133, 119-128.
- 18 Sanchez-Cantu, M., Perez-Diaz, L. M., Maubert, A. M. & Valente, J. S. Catalysis Today 2010, 150, 332-339.
- 19 Yu, J. J., Wang, X. P., Tao, Y. X., Hao, Z. P. & Xu, Z. P. Industrial & Engineering Chemistry Research 2007, 46, 5794-5797.

- 20 Zhao, X., Zhang, F., Xu, S., Evans, D. G. & Duan, X. *Chemistry of Materials* 2010, 22, 3933-3942.
- 21 Wang, L. et al. *Chemical Communications* 2010, 46, 3911-3913.
- 22 Teruel, L., Bouizi, Y., Atienzar, P., Fornes, V. & Garcia, H. *Energy & Environmental Science* 2010, 3, 154-159.
- 23 Parida, K. M. & Mohapatra, L. *Chemical Engineering Journal* 2012, 179, 131-139.
- 24 Parida, K., Satpathy, M. & Mohapatra, L. *Journal of Materials Chemistry* 2012, 22, 7350-7357.
- 25 Wirth, C. T. et al. *Chemistry of Materials* 2012, 24, 4633-4640.
- 26 Lak, A. et al. *Nanoscale* 2013.
- 27 Dong, Y. et al. *Physical Chemistry Chemical Physics* 2013, 15, 7174-7181.
- 28 Cornell, R. M., Mann, S. & Skarnulis, A. J. *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases* 1983, 79, 2679-2684.
- 29 Scardi, P., Leoni, M. & Beyerlein, K. R. *Zeitschrift für Kristallographie Crystalline Materials* 2011, 226, 924-933.
- 30 Enzo, S., Fagherazzi, G., Benedetti, A. & Polizzi, S. *Journal of Applied Crystallography* 1988, 21, 536-542.

Page intentionally left blank

Chapter 4

ZnFe MMO and Au Hybrid

With the previous discussions on the MMO obtained via LDH mediated route, this chapter will continue to discuss noble metal decorated MMO hybrid prepared via LDH mediated route. In short, this work combines in situ intercalation of layered double hydroxide (LDH) and low temperature calcinations to prepare highly photo-catalytic intimately mixed metal oxides with well-dispersed gold nano-particles. The LDH crystallization is discussed, and the intra-layer merging growth mechanism of MMO conversion during the heat treatment process is reported. This LDH mediated synthesis route created intimately mixed metal oxides with well-dispersed Au nano-particle. This unique microstructure significantly enhanced the synergistic interactions for the hybrid, which greatly improved the photocatalytic ability by 43 times. Such improvement is unprecedented even on other noble metal decorated photocatalyst materials and is elucidated based on the mechanism of morphology evolution.

Page intentionally left blank

4.1 Introduction

Noble metals like Ag, Au, Pt, and Pd are usually incorporated within metal oxide (such as TiO_2) as a co-catalyst to improve the photocatalytic activity. The improvement is contributed by surface plasmonic resonance (SPR) effects, enhanced visible light absorption, and suppressed electron-hole recombination.^[1-3] Bian Z. et. al. enhanced the photocatalytic activity of TiO_2 by 29 times after decoration with Au nanoparticles.^[4] Comparing with single phase metal oxide, MMO combined with noble metal were much less explored in studies of photocatalyst.

As mentioned in the earlier chapter, MMO can provide multifunctional properties like improved visible light absorption, higher carrier conductivity, and efficient charge transfer due to the existence of heterojunction at the interface.^[5,6] Calcination of LDH is a facile technique to achieve intimately mixed morphology of MMO. To achieve intimately mixed morphology of MMO with noble metal, calcination of noble metal intercalated LDH could be an efficient way.

Well-dispersed noble metals on LDH^[7,8] were usually achieved via reconstruction of LDH,^[9] anion exchange^[10], reduction of metallic salts^[11], layer-by-layer assembly^[12], as well as incipient wetness impregnation method^[13]. However, good photocatalytic ability of noble-metal/metal-oxide catalyst usually requires high temperature calcination ($>500\text{ }^\circ\text{C}$).^[13-15] However, all of the above methods are indirect methods which involve the pre-synthesis of LDH precursor followed by reduction of noble metal ions or exchange with the existing counter anions; some of them even require prior exfoliation of the LDH material. Direct intercalation of noble metals into LDH interlayer with unique crystallization pathway was not reported before.

In this work, a modified low supersaturation co-precipitation method was used to directly intercalate $[\text{AuCl}_4]^-$ into Zn/Fe LDH interlayer. $[\text{CO}_3]^{2-}/\text{ZnFe}$ LDH was also prepared using the same method to serve as baseline references. With $[\text{AuCl}_4]^-$ intercalation, the ZnFe LDH crystallization pathway was affected and 'pseudo-amorphous' crystal structures was produced. The photocatalytic ability of the low temperature calcined

$[\text{AuCl}_4]^-/\text{ZnFe}$ products showed extraordinary improvement by 43 times compared with calcined $[\text{CO}_3]^{2-}/\text{ZnFe}$ LDH. Discussions will be focused on crystallization and morphological evolution during the in situ intercalation and calcination processes.

4.2 Experiments

4.2.1 Materials and synthesis

Reagent grade zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), iron (III) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), sodium tetrachloroaurate(III) dihydrate ($\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$), sodium carbonate (Na_2CO_3), and methylene blue (MB) were purchased from Sigma Aldrich and used without further purification.

For $[\text{AuCl}_4]^-/\text{ZnFe}$ LDH synthesis, the following procedure is taken:

- 100 ml of $\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$ aqueous solution (0.04 M) was subjected to vigorous stirring of $>1000\text{rpm}$ at room temperature.
- A pH electrode was immersed into the solution for pH monitoring.
- 10 ml mixture aqueous solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.6 M) and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.2 M) was titrated into DI water using titration apparatus.
- At the same time, the solution of NaOH (1 M) was titrated using another titration apparatus to keep the pH at 10.
- After titration, the solution was sealed and stirred for 18 hr ($>1000\text{ rpm}$).
- The as-prepared solid product was separated from the solution and wash with DI water, separated through centrifuge, and this process is repeated several times until pH reach 7.
- Drying at 90°C for 24 hours and grinding it into fine powder form and LDH powder is obtained.

For $[\text{CO}_3]^{2-}/\text{ZnFe}$ LDH synthesis, the procedures were the same, except for the replacement of $\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$ with Na_2CO_3 . Low temperature calcinations of the as-prepared products at 200°C and 300°C for 5 hours were carried out, and denoted as $[\text{AuCl}_4]^-/\text{ZnFe}(200^\circ\text{C})$ and $[\text{AuCl}_4]^-/\text{ZnFe}(300^\circ\text{C})$ respectively. The photographs of the catalyst powder for $[\text{CO}_3]^{2-}/\text{ZnFe}(300^\circ\text{C})$ and $[\text{AuCl}_4]^-/\text{ZnFe}(300^\circ\text{C})$ are shown in the Figure B.1 at Appendix B.

4.2.2 Characterizations

Morphology of synthesized products were observed using transmission electron microscopy (TEM) by JEOL 2100F. Powder X-ray diffraction (XRD) was performed by Shimadzu XRD-600 diffractometer with Cu-K α radiation source ($\lambda = 1.54 \text{ \AA}$) using measurement step-size of 0.02° and scan-rate of $2^\circ/\text{min}$. Energy dispersive X-ray spectroscopy (EDX) was done using transmission electron microscope (JEOL 2100F) equipped with EDX detector. Shimadzu UV 2501PC UV-Vis spectrophotometer was used to measure absorption of synthesized products and photocatalytic test samples. Thermo-gravimetric analysis (TGA) was carried out using TA Q500 that provided information on weight loss during constant-rate heating test (heating rate= $8^\circ\text{C}/\text{min}$) under atmosphere of synthetic air.

4.2.3 Photocatalytic test

The organic dye solution used for photocatalytic test was 10^{-5} M methylene blue (MB) solution which is within the measurement range of the absorption spectroscopy. The catalyst concentration is 0.7 mg/mL at which concentration the solution is stable and homogeneously dispersed. For photocatalytic reactions, 30 mL solution of each sample was prepared at 50 mL glassware bottle. Before photocatalytic tests, all the samples were kept in dark for 2 hours to allow complete dyes adsorption onto the synthesized products. Irradiation was done with solar simulator (Newport model 66902) at 1 meter distance with light filter that gives light spectrum of one solar, the light intensity is $100 \text{ mW}/\text{cm}^2$ at the position of the catalyst solution. During the photocatalyst test, the catalyst solution is with simultaneous O_2 bubbling at the rate of $300 \text{ cc}/\text{min}$ and stirring to ensure homogenous mixing. The extent of photocatalytic degradation of MB was studied by measuring absorption of solutions at different irradiation intervals. The schematic draw of this experimental setup is shown in Figure B.2 at Appendix B.

4.3 Results and Discussion

4.3.1 Structural properties of $[\text{CO}_3]^{2-}/\text{ZnFe}$ LDH and $[\text{AuCl}_4]^{-}/\text{ZnFe}$ LDH

The XRD spectra of as prepared $[\text{CO}_3]^{2-}/\text{ZnFe}$ LDH and $[\text{AuCl}_4]^{-}/\text{ZnFe}$ LDH are shown in Figure 4.1. For as-prepared $[\text{CO}_3]^{2-}/\text{ZnFe}$ LDH, the diffraction peak at 12° corresponds to a d_{003} spacing of 7.38 Å (spectrum (i) in Figure 4-1). This is attributed to the intercalated $[\text{CO}_3]^{2-}$ (planar diagonal structure with diameter ~ 2.4 Å) within LDH layers.

Figure 4.1 Powder XRD spectra of as prepared $[\text{CO}_3]^{2-}/\text{ZnFe LDH}$ and $[\text{AuCl}_4]^{-}/\text{ZnFe LDH}$. The reference XRD spectra of standard Au, ZnO, FeO, and Fe_2O_3 are included for comparison.

Interestingly, for as-prepared $[\text{AuCl}_4]^{-}/\text{ZnFe LDH}$, XRD spectrum showing ‘pseudo-amorphous’ microstructure, i.e., phase containing plane-crystals that are too thin or small

for effective diffraction of incident X-ray, reflected as a broad diffraction hump at the 2θ region of 30° to 40° (spectrum (ii) in Figure 4.1). This is based on the fact that there is no distinct characteristic LDH peak for as-prepared $[\text{AuCl}_4]^-/\text{ZnFe}$ LDH despite the clearly observed LDH crystals in TEM images (Figure 4.2b). The broad diffraction ‘hump’ indicates a broad distribution of lattice parameters. More information on the microstructure and morphology are obtained from the TEM images.

Figure 4.2 Morphology of (a) $[\text{CO}_3]^{2-}/\text{ZnFe}$ LDH; and (b) $[\text{AuCl}_4]^-/\text{ZnFe}$ LDH; The d-spacings of 0.29 nm, 0.27 nm, and 0.23 nm belonged to $[\text{CO}_3]^{2-}/\text{ZnFe}$ LDH, $[\text{AuCl}_4]^-/\text{ZnFe}$ LDH structures, and Au^0 respectively.

Shown in Figure 4.2 are the morphologies of as prepared $[\text{CO}_3]^{2-}/\text{ZnFe}$ LDH and $[\text{AuCl}_4]^-/\text{ZnFe}$ LDH, the corresponding global views are shown in Figure 4.3. For as-prepared $[\text{CO}_3]^{2-}/\text{ZnFe}$ LDH, planar and edged crystals with good size uniformity can be observed (Figure 4.2a). The d-spacing is measured to be 0.29 nm. Estimated from the global views (Figure 4.3), the diameter of the layered crystals is ~ 5 nm-15 nm (centered at ~ 10 nm).

With the presence of $[\text{AuCl}_4]^-$, expanded and non-regular LDH crystals were observed together with higher contrast regions. The higher contrast regions in TEM images were contributed by the Au species (similar to ‘staining’ effect by heavy atoms) (Figure 4.2b). Such contrast was helpful in identifying regions that were spatially rich of Au species. As observed from the global views of the $[\text{AuCl}_4]^-/\text{ZnFe}$ LDH (Figure 4.3b-i), Au species were well-dispersed within the synthesized products.

Figure 4.3 Global views of (a-i) as-prepared $[\text{CO}_3]^{2-}/\text{ZnFe}$, (a-ii) $[\text{CO}_3]^{2-}/\text{ZnFe}(200\text{ }^\circ\text{C})$, (a-iii) $[\text{CO}_3]^{2-}/\text{ZnFe}(300\text{ }^\circ\text{C})$, (b-i) as-prepared $[\text{AuCl}_4]^-/\text{ZnFe}$, (b-ii) $[\text{AuCl}_4]^-/\text{ZnFe}(200\text{ }^\circ\text{C})$ and (b-iii) $[\text{AuCl}_4]^-/\text{ZnFe}(300\text{ }^\circ\text{C})$. The results of (b) showed good dispersion of Au species as well as growth of Au^0 and mixed oxides without uncontrolled agglomeration under low-temperature calcination.

For as-prepared $[\text{AuCl}_4]^-/\text{ZnFe}$ LDH, although its XRD spectrum shows a ‘pseudo-amorphous’ phase, nano-crystals were clearly observed under TEM image (Figure 4.2b).

The crystals are not randomly distributed, but existed intimately with Au species. By analyzing the d-spacing, besides a few Au^0 crystals (with d-spacing of 0.23 nm corresponding to (111) crystal plane) found (caused by 90 °C drying condition), most of the crystals are with d-spacing around 0.27 nm. The crystals could be confirmed as LDH crystals with $[\text{AuCl}_4]^-$ or hydrolyzed $[\text{AuCl}_4]^-$ species as intercalating agent. The evidences of decreased d-spacing from ~ 0.29 nm (with $[\text{CO}_3]^{2-}$ intercalation) to ~ 0.27 nm and the lack of detection of (003) peak in XRD spectrum shows disruption of both layered crystal growth and layer stacking in $[\text{AuCl}_4]^-/\text{ZnFe}$ LDH structure formation.

Comparing with $[\text{CO}_3]^{2-}$ intercalation, disrupted LDH structure is a result of direct intercalation of $[\text{AuCl}_4]^-$. Figure 4.4a illustrated the different formation mechanism of the two structures. The top right graph of Figure 4.4a shows a well crystallized and ordered layer stacking for $[\text{CO}_3]^{2-}/\text{ZnFe}$ LDH. With $[\text{AuCl}_4]^-$ intercalation, both of the layered crystallization and the layer stacking were disrupted (bottom right graph of Figure 4.4a). The disruption is believed to be contributed by the in situ synthesis process that gave rise to strong interactions (electrostatic and hydrogen bonding) between the counter anions $[\text{AuCl}_4]^-$ and metal cation layers Zn^{2+} and Fe^{3+} . In addition, the disruption could come from the hydrolysis of $[\text{AuCl}_4]^-$, which generated $[\text{AuCl}_4]^-$, $[\text{Au}(\text{OH})\text{Cl}_3]^-$, $[\text{Au}(\text{OH})_2\text{Cl}_2]^-$, $[\text{Au}(\text{OH})_3\text{Cl}]^-$ and Cl^- . The detailed intercalation mechanism of this system worth to be further explored. Figure 4.4b illustrates the MMO structure of $[\text{CO}_3]^{2-}$ and $[\text{AuCl}_4]^-$ intercalated ZnFe LDH after calcinations, which will be discussed in the following section.

Figure 4.4 Illustrations of formation of (a) $[\text{CO}_3]^{2-}/\text{ZnFe}$ LDH and $[\text{AuCl}_4]^{-}/\text{ZnFe}$ LDH structures; and (b) MMO structures after calcinations.

4.3.2 Structural properties of $[\text{CO}_3]^{2-}/\text{ZnFe}$ LDH and $[\text{AuCl}_4]^{-}/\text{ZnFe}$ LDH after calcinations

4.3.2.1 Thermo-gravimetric properties of $[\text{CO}_3]^{2-}/\text{ZnFe}$ LDH and $[\text{AuCl}_4]^{-}/\text{ZnFe}$ LDH

TGA results, providing information on weight change of as-prepared $[\text{CO}_3]^{2-}/\text{ZnFe}$ LDH and $[\text{AuCl}_4]^{-}/\text{ZnFe}$ LDH with increased temperature, were essential for studying evolutions of morphologies, compositions, and crystal phases. Figure 4.5 shows the TGA curves of as-prepared $[\text{CO}_3]^{2-}/\text{ZnFe}$ LDH and $[\text{AuCl}_4]^{-}/\text{ZnFe}$ LDH, both of them have similar weight loss profiles. However, for each of them, the weight losses happened at distinctly different temperature ranges.

Figure 4.5 The thermo-gravimetric properties of as-prepared $[\text{CO}_3]^{2-}/\text{ZnFe}$ LDH and $[\text{AuCl}_4]^{-}/\text{ZnFe}$ LDH.

For as-prepared $[\text{CO}_3]^{2-}/\text{ZnFe}$ LDH, 1st stage weight loss of adsorbed and interlayer water happened at ~ 100 °C, and the subsequent 2nd stage weight loss included the dehydroxylation and the anion decomposition at ~ 240 °C. They are usually two overlapped events.^[16] As-prepared $[\text{AuCl}_4]^{-}/\text{ZnFe}$ LDH exhibited a delayed and much slower weight loss upon calcinations. 1st stage loss of adsorbed and interlayer water was delayed until 140 °C. At 200 °C calcinations, $[\text{AuCl}_4]^{-}/\text{ZnFe}$ LDH had barely undergone the dehydroxylation process. At 300 °C calcinations, $[\text{AuCl}_4]^{-}/\text{ZnFe}$ LDH experienced larger extent of dehydroxylation and $[\text{AuCl}_4]^{-}$ decomposition. Collapse of LDH structure was delayed until 410 °C. It should be highlighted that the delayed thermal decomposition behavior is contributed by successful $[\text{AuCl}_4]^{-}$ intercalation. Firstly, $[\text{AuCl}_4]^{-}$ possess much lower volatility than $[\text{CO}_3]^{2-}$. Secondly, the strong interaction between the $[\text{AuCl}_4]^{-}$ and the LDH layers also contribute to the delayed decomposition process. Furthermore, the decomposition of $[\text{AuCl}_4]^{-}$ lead to release of Cl_2 and growth of Au nano-particles, which inhibit merging of LDH layers into agglomerated MMO.

Shown in Figure 4.6, the disappearance of 12 ° peak for $[\text{CO}_3]^{2-}/\text{ZnFe}(200\text{ °C})$ and $[\text{CO}_3]^{2-}/\text{ZnFe}(300\text{ °C})$ indicated collapse of LDH structure (spectra (i) and (ii) in Figure 4.6). Emergence of diffraction peaks assignable to ZnO, FeO, and Fe_2O_3 indicated the formation of MMO. ZnO (100) crystallite size is 15.4 nm, as calculated from Sherrer's equation.

Figure 4.6 Powder XRD spectra of $[\text{CO}_3]^{2-}/\text{ZnFe}$ LDH and $[\text{AuCl}_4]/\text{ZnFe}$ LDH after calcination at 200 °C and 300 °C. The reference XRD spectra of standard Au, ZnO, FeO, and Fe_2O_3 are included for comparison.

For $[\text{AuCl}_4]^-/\text{ZnFe}$ LDH based sample, the XRD spectrum indicate growth of gold nanoparticles at 200 °C and 300 °C calcinations (spectra (iii) and (iv) in Figure 4.6). MMO only formed during calcination at 300 °C. Based on Scherrer's equation, Au crystallite size is 9.2 nm, and ZnO crystallite size is 10.8 nm. This result is consistent with TGA results that show gradual dehydroxylation at 300 °C calcinations. Iron oxide diffraction is not shown in $[\text{AuCl}_4]^-/\text{ZnFe}(300\text{ °C})$ XRD spectrum due to even smaller size than that of ZnO, which poorly diffract incident x-ray.

The TEM images of calcined $[\text{CO}_3]^{2-}/\text{ZnFe}$ LDH and $[\text{AuCl}_4]^-/\text{ZnFe}$ LDH further corroborated our proposed crystallization schemes.

4.3.2.2 Morphology of $[\text{CO}_3]^{2-}/\text{ZnFe}$ LDH and $[\text{AuCl}_4]^-/\text{ZnFe}$ LDH after calcinations

Different morphologies of calcined $[\text{CO}_3]^{2-}/\text{ZnFe}$ LDH and $[\text{AuCl}_4]^-/\text{ZnFe}$ LDH are shown in the TEM images (Figure 4.7). For $[\text{CO}_3]^{2-}/\text{ZnFe}$ LDH, hexagonal morphology is retained after 200 °C calcination (Figure 4.7a-i), although the XRD spectrum (Figure 4.6i) shows $[\text{CO}_3]^{2-}/\text{ZnFe}(200\text{ °C})$ mainly consisted of MMO crystal phase. The hexagonal structures further collapsed and agglomerated after 300 °C calcination (Figure 4.7a-ii). The measured d-spacings are about 0.24 nm and 0.21 nm, which correspond to ZnO (101) and Fe_2O_3 (202) respectively.

Figure 4.7 Morphologies of (a-i) $[\text{CO}_3]^{2-}/\text{ZnFe}(200\text{ }^\circ\text{C})$, (a-ii) $[\text{CO}_3]^{2-}/\text{ZnFe}(300\text{ }^\circ\text{C})$; and (b-i) $[\text{AuCl}_4]^{-}/\text{ZnFe}(200\text{ }^\circ\text{C})$, (b-ii) $[\text{AuCl}_4]^{-}/\text{ZnFe}(300\text{ }^\circ\text{C})$; (c-i) and (c-ii) low and high magnification views of $[\text{AuCl}_4]^{-}/\text{ZnFe}(300\text{ }^\circ\text{C})$. The d-spacings of $\sim 0.27\text{ nm}$, 0.21 nm , 0.23 nm , 0.24 nm , and 0.28 nm belong to $[\text{AuCl}_4]^{-}/\text{ZnFe}$ LDH structures, Fe_2O_3 (202), Au^0 (111), ZnO (101), and ZnO (100) respectively.

For $[\text{AuCl}_4]^-/\text{ZnFe}$ LDH, further calcination at 200 °C and 300 °C rendered the Au nanoparticles to grow and became more structurally defined. TEM image (Figure 4.7b-i) shows $[\text{AuCl}_4]^-/\text{ZnFe}$ (200 °C) are still in planar structure. The measurements of d-spacings of large-size crystals are majority ~ 0.27 nm (LDH structure). Partial conversion of charge-balance ion i.e. $[\text{AuCl}_4]^-$ to Au^0 was found. Metal oxide crystals like ZnO (0.24 nm) are observed, but were in minority. This result was consistent with the XRD result (Figure 4.6iii) where ZnO crystal peaks were not shown. Upon 300 °C calcination, as shown in the TEM images of Figure 4.7b-ii, and c-ii, all $[\text{AuCl}_4]^-$ converted to Au nanoparticles (0.23 nm), and LDH layers were dehydroxylated and converted to intimately mixed ZnO (0.24 nm) and Fe_2O_3 (0.21 nm). In addition, the TEM images shows that ZnO, Fe_2O_3 and Au particles co-existed as an intimately mixed unit (Figure 4.7c-ii), lower magnification TEM image (Figure 4.7c-i) shows that the intimately MMO units are well dispersed.

Based on the above obtained information, Figure 4.4b illustrates the morphology evolution of calcined $[\text{CO}_3]^{2-}/\text{ZnFe}$ LDH and $[\text{AuCl}_4]^-/\text{ZnFe}$ LDH. With $[\text{CO}_3]^{2-}$ intercalation, the anionic balancing ion decomposed and LDH layer merged at 200 °C calcination. Calcinations at 300 °C led the growth of MMO through inter-layer merging of metal ions. With $[\text{AuCl}_4]^-$ intercalation, the decomposition behavior is delayed. Gradual conversion of charge-balance ion ($[\text{AuCl}_4]^-$) to Au nanoparticles occurred before the growth of MMO. The partially converted Au nanoparticles were deposited on LDH layers as shown for $[\text{AuCl}_4]^-/\text{ZnFe}$ with 200°C calcination in Figure 4-4b. Due to the Au nanoparticle, inter-layer merging was inhibited during calcination. Growth of MMO took place mainly through intra-layer merging of metal ions instead of inter-layer merging as in the case of $[\text{CO}_3]^{2-}/\text{ZnFe}$ (300 °C). Based on this understanding, different morphology evolution of $[\text{CO}_3]^{2-}/\text{ZnFe}$ (300 °C) and $[\text{AuCl}_4]^-/\text{ZnFe}$ (300 °C) are explained in Figure 4.4b.

The differences of morphology change during crystallization and calcinations for $[\text{CO}_3]^{2-}/\text{ZnFe}$ LDH and $[\text{AuCl}_4]^-/\text{ZnFe}$ LDH are reflected in two aspects. Firstly, compared with $[\text{CO}_3]^{2-}/\text{ZnFe}$ (300 °C), the oxide particle size is smaller for $[\text{AuCl}_4]^-/\text{ZnFe}$ (300 °C) due to less Zn and Fe cations available during intra-layer merging process, compared with

during inter-layer merging growth. Applying Scherrer’s equation on ZnO (100) peak, smaller crystallite size (i.e. 10.8 nm) can be calculated for $[\text{AuCl}_4]^-/\text{ZnFe}(300\text{ }^\circ\text{C})$ as compared to that of $[\text{CO}_3]^{2-}/\text{ZnFe}(300\text{ }^\circ\text{C})$ (i.e. 15.4 nm). Secondly, the particle assembly is different as illustrated in Figure 4.4b. The top right graph illustrates the particle assembly for $[\text{CO}_3]^{2-}/\text{ZnFe}(300\text{ }^\circ\text{C})$ by inter-layer merging growth process. However, the intra-layer merging growth process, as in the case of $[\text{AuCl}_4]^-/\text{ZnFe}(300\text{ }^\circ\text{C})$, can lead to iron oxide existing with even smaller size than surrounding zinc oxide particle, as illustrated in Figure 4.4b (bottom right graph). Existence of iron oxide is supported by (i) EDX spectrum that shows Zn to Fe ratio of 3:1 (Figure 4.8), and (ii) d-spacing of HRTEM of 0.21 nm that belongs to Fe_2O_3 (Figure 4.7b-ii, c-ii). While the lack of FeO or Fe_2O_3 detected by XRD further prove their smaller size (Figure 4.6-iv).

Figure 4.8 EDX spectrum of $[\text{AuCl}_4]^-/\text{ZnFe}(300\text{ }^\circ\text{C})$. The inset table shows weight % and atomic % of FeK, ZnK, and AuL element. The inset bright field TEM image shows the scanned region of EDX spectrum.

4.3.3 Photocatalytic ability of $[\text{CO}_3]^{2-}/\text{ZnFe}$ LDH, and $[\text{AuCl}_4]^-/\text{ZnFe}$ LDH based samples

Zn/Fe-LDH had been reported to be very useful for photo-degradation of azo dyes.^[17] Zn/Fe MMO also showed good potential for photocatalytic degradation of dyes and H₂ evolution.^[18] In this work, the [CO₃]²⁻/ZnFe LDH and [AuCl₄]⁻/ZnFe LDH based samples had been employed for photocatalytic degradation of MB. MB was typically used in studies of waste water treatment relevant to organic dyes pollution. Bubbling of O₂ is needed for (i) producing O• and OH• which promote the degradation of the MB, and (ii) help to homogenize the reaction solution. The results of the photocatalytic degradation of MB in the presence of [CO₃]²⁻/ZnFe LDH and [AuCl₄]⁻/ZnFe LDH based samples are presented in Figure 4.9. The UV-vis spectra of dye degradation are shown in Appendix B Figure B.3.

Figure 4.9 Absorbance change of methylene blue dye solutions which shows the photocatalytic ability of the [CO₃]²⁻/ZnFe LDH and [AuCl₄]⁻/ZnFe LDH based samples, k is the reaction rate constant of pseudo-first order kinetics.

It can be observed in Figure 4.9 that both as-prepared and calcined [CO₃]²⁻/ZnFe LDH exhibited poor photocatalytic ability. For as-prepared [AuCl₄]⁻/ZnFe LDH, improved photocatalytic ability can already be achieved without calcination. Calcination at 300 °C significantly improved their photocatalytic ability. The photocatalysis rate was estimated using the slope of the normalized intensity curves at zero time. Using the slope of as-

prepared $[\text{CO}_3]^{2-}/\text{ZnFe}$ LDH as baseline, 3.5 and 5 times enhancements could be achieved for $[\text{CO}_3]^{2-}/\text{ZnFe}(200\text{ }^\circ\text{C})$ and $[\text{CO}_3]^{2-}/\text{ZnFe}(300\text{ }^\circ\text{C})$, respectively. For as-prepared $[\text{AuCl}_4]^-/\text{ZnFe}$ LDH, $[\text{AuCl}_4]^-/\text{ZnFe}(200\text{ }^\circ\text{C})$ and $[\text{AuCl}_4]^-/\text{ZnFe}(300\text{ }^\circ\text{C})$, up to 32, 33, and 43 times enhancements were achieved, respectively. The pseudo-first order kinetics $\ln(A_0/A) = kt$ have also been applied for them and the results are shown inside Figure 4.9. Higher calcination temperature ($> 300\text{ }^\circ\text{C}$) for $[\text{AuCl}_4]^-/\text{ZnFe}$ LDH is believed to be detrimental to the photocatalytic ability due to the uncontrolled growth and agglomeration of mixed oxides.

The UV-Vis absorption is one of the major factors that determine the efficiency of electron-hole pair generation. Figure 4.10 shows the absorption spectra of $[\text{CO}_3]^{2-}/\text{ZnFe}$ LDH and $[\text{AuCl}_4]^-/\text{ZnFe}$ LDH based samples. For both $[\text{CO}_3]^{2-}/\text{ZnFe}$ LDH and $[\text{AuCl}_4]^-/\text{ZnFe}$ LDH based samples, calcination result in clearer characteristic ZnO band-edge absorption. Furthermore, the $[\text{AuCl}_4]^-/\text{ZnFe}(200\text{ }^\circ\text{C})$ and $[\text{AuCl}_4]^-/\text{ZnFe}(300\text{ }^\circ\text{C})$ exhibited improved visible-light absorption that is beneficial for photocatalytic application. Bear in mind that an AM1.5G solar simulator was used in our photocatalytic tests.

Figure 4.10 Absorption spectra of different $[\text{CO}_3]^{2-}/\text{ZnFe}$ LDH and $[\text{AuCl}_4]^-/\text{ZnFe}$ LDH based samples. An improved absorbance in high wavelength region can be achieved with the incorporation of Au species after calcination.

Au is known to improve photocatalytic reaction. The SPR effect created electron excitation upon plasmonic band absorption¹, enhance the visible light absorption of low band gap semiconductor³¹ and UV light absorption of high band gap semiconductor^[19]. Besides that, the favored electron capture by Au species suppressed electron-hole recombination. The latest reported photocatalytic enhancement of TiO₂ by noble metals was 29 times^[4], whereas, up to 32, 33, and 43 times of enhancement was achieved in our system. In addition to the reasons mentioned above, it is necessary to emphasize that the manifestation of greatly enhanced photocatalytic ability in our system critically relied on the intimately mixed morphology created.

Figure 4.11a illustrates the charge transfer across the band potentials of MMO. This band energy configuration favors charge transfer within MMO. With light absorption, the excited electrons can be transferred from Fe₂O₃ to ZnO, and finally captured by Au nanoparticles to create O₂⁻· free radical. Photo generated holes is transferred to Fe₂O₃ and finally captured to generate OH· that degrade the MB dye.

Figure 4.11 Schematic representation of (a) charge transfer across the band gap structure; and (b) synergistic interactions between metal oxides of [AuCl₄]/ZnFe(300 °C)

Figure 4.11b illustrated the synergistic interactions within metal oxides as well as Au nanoparticle in [AuCl₄]/ZnFe(300 °C). The SPR of Au nanoparticles improve the light absorption of Fe₂O₃ and ZnO. Excited electrons are efficiently transferred from the excitation sites to avoid recombination, and finally captured by Au nanoparticles for photocatalytic reactions. Intimately mixed morphology improved the efficiency of the whole processes and maximized the number of reaction site.

4.4 Summary

In this work, $[\text{AuCl}_4]^-$ was directly intercalated into ZnFe LDH structure by a co-precipitation method. During low temperature calcinations, the intercalated charge-balance ion $[\text{AuCl}_4]^-$ was converted to Au nanoparticles before decomposition of LDH layers, and prevented the inter-layer merging. Further calcination led to MMO growth through intra-layer merging growth mechanism. Comparing with $[\text{CO}_3]^{2-}/\text{ZnFe}$ LDH, low temperature calcined $[\text{AuCl}_4]^-/\text{ZnFe}$ LDH at 300 °C exhibited 43 times improvement in photocatalytic activities. The significant improvement of photocatalytic property is attributed to the novel morphology created, which ensures the synergetic interactions between metal oxides and greatly manifested the role of Au nanoparticles.

References

- 1 Gomes Silva, C. u., Juárez, R., Marino, T., Molinari, R. & García, H. *Journal of the American Chemical Society* **2010**, 133, 595-602.
- 2 Wang, N., Tachikawa, T. & Majima, T. *Chemical Science* 2011, 2, 891-900.
- 3 Ismail, A. A., Bahnemann, D. W., Bannat, I. & Wark, M. *The Journal of Physical Chemistry C* 2009, 113, 7429-7435.
- 4 Bian, Z., Tachikawa, T., Zhang, P., Fujitsuka, M. & Majima, T. *Journal of the American Chemical Society* 2013, 136, 458-465.
- 5 Kawahara, T., Konishi, Y., Tada, H., Tohge, N. & Ito, S. *Langmuir* 2001, 17, 7442-7445.
- 6 Uddin, M. T. et al. *Inorganic Chemistry* 2012, 51, 7764-7773.
- 7 Choudary, B. M., Madhi, S., Chowdari, N. S., Kantam, M. L. & Sreedhar, B. *Journal of the American Chemical Society* 2002, 124, 14127-14136.
- 8 Basile, F. et al. *Chemical Communications* 1996, 2435-2436.
- 9 Takehira, K. & Shishido, T. *Catal Surv Asia* 2007, 11, 1-30.
- 10 Beaudot, P., De Roy, M. E. & Besse, J. P. *Journal of Solid State Chemistry* 2004, 177, 2691-2698.
- 11 Varade, D. & Haraguchi, K. *Journal of Materials Chemistry* 2012, 22, 17649-17655.
- 12 Zhao, J. et al. *Journal of Materials Chemistry* 2011, 21, 13926-13933.
- 13 Chmielarz, L. et al. *Applied Catalysis B: Environmental* 2013, 130-131, 152-162.
- 14 Basile, F., Fornasari, G., Gazzano, M. & Vaccari, A. *Applied Clay Science* 2000, 16, 185-200.
- 15 Tsyganok, A. I. et al. *Applied Catalysis A: General* 2004, 275, 149-155.
- 16 Valente, J. S., Rodriguez-Gattorno, G., Valle-Orta, M. & Torres-Garcia, E. *Materials Chemistry and Physics* 2012, 133, 621-629.
- 17 Parida, K. M. & Mohapatra, L. *Chemical Engineering Journal* 2012, 179, 131-139.
- 18 Pradhan, G. K., Martha, S. & Parida, K. M. *ACS Applied Materials & Interfaces* 2011, 4, 707-713.

- 19 Awazu, K. et al. Journal of the American Chemical Society 2008, 130, 1676-1680.

Chapter 5

NiFe MMO and CNT Hybrid

Besides noble metals as discussed in the previous chapter, MMO could also be coupled with nanocarbons, like CNT or graphene, to improve their functional properties. This chapter will discuss the strategy of utilizing LDH mediated synthesis route to prepare intimately mixed NiFe MMO and CNT hybrids. Well-defined NiFe LDH nano-plates were first synthesized on CNT as precursor. After controlled calcination, NiFe LDH is converted into intimately mixed NiFe MMO nano-particles, 5 to 10 nm. Further growth of the size and agglomerations are inhibited due to the spatial confinement on the CNT surface. Results showed that the MMO particles are not only uniformly deposited on the CNT surfaces but also in-grow into the subsurface of CNT resulting strong interfacial coupling. The intimately mixing morphology of MMO and unique in-grown structure with CNT offers an excellent synergetic interaction for the hybrid. This leads to an outstanding electrochemical OER performance with onset potential of 1.43 V vs RHE and tafel slope of 45 eV/dec.

Page intentionally left blank

5.1 Introduction

Oxygen evolution reaction (OER) is an electrochemical oxidation process to convert water into O_2 , in which form energy is stored.^[1,2] It plays a very important role in applications of energy conversion and energy storage, e.g., water splitting and rechargeable metal air batteries.^[3-5] Research for more efficient OER catalysts has received considerable attention in the field of energy related applications.

So far, RuO_2 and IrO_2 are reported to be the most active catalyst for OER process, but they are expensive and scarce.^[6,7] Transition metals such as Ni, Co, Fe, Mn, Sn, Ti, V hydroxide or oxides are studied as an alternative replacement.^[8-11] Among them, Ni based catalyst, such as NiO ^[12,13] and $Ni(OH)_2$ ^[12,14], has been intensively studied because of its high catalytic activity, stability and low cost. However, the poor electrical conductivity limits their electrochemical performance. In the literature, Fe has been used to improve the conductivity of Ni based catalysts, such as Ni-Fe oxyhydroxide ($Ni_{1-x}Fe_xOOH$)^[15-17] and NiFe layered double hydroxide (LDH)^[18-21]. Trotochaud et al. reported that, besides improving the electrical conductivity, loading of Fe could modify the electronic structure of $NiOOH$, and make it highly reactive for electrochemical performance.^[17] To further enhance the conductivity of NiFe based catalyst, electrically conducting materials such as Ni foam^[11,18], graphene^[22-24], carbon nanotube (CNT)^[25,26], and carbon quantum dots^[27] have been used to form hybrid materials together with NiFe LDH. A superlattice hybrid structure of exfoliated NiFe LDH and graphene was reported to exhibit excellent OER performance.^[23] Gong et al. reported that better OER activity and stability could be obtained from the hybrid material of NiFe LDH and CNT than that of commercial Ir catalyst, even though NiFe LDH is physically adsorbed on oxidized CNT surface through electro static force.^[25]

LDH can be considered as a molecular solid state precursor, where different metal ions are uniformly distributed at atomic level. We previously reported ZnFe MMO via in-situ intercalation of LDH, and the plasmonic of Au nanoparticles substantially enhanced the reactivity of the MMO.^[28] There are several reported studies on NiFe MMO for OER

application.^[29-32] However, NiFe MMO coupled with CNT, especially derived from LDH precursor, have not been reported before.

In this study, we report the synthesis of intimately mixed NiFe metal oxide in-grown into CNT structure via LDH mediated synthesis route. The in-grown structure leads to strong interfacial bonding between CNT and NiFe oxide catalyst instead of physical adsorption by organic ligand, which promotes the charge transfer during electrochemical process. The unparalleled degree of mixing magnifies the role of Fe in improving the conductivity and modifying the electronic structure of NiO towards favorable OER activity.

5.2 Experiments

5.2.1 Materials and synthesis

Materials: The pristine multi-walled carbon nanotubes (MWNTs) with diameter of 20 nm (purchased from Shenzhen Nanotech Por Co. Ltd) were firstly refluxed in nitric acid (65 wt%) at 140 °C for 6 hours before use. Reagent grade nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), iron (III) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), and sodium carbonate (Na_2CO_3) were purchased from Sigma Aldrich and used without further purification.

For NiFe LDH synthesis, the following procedure is taken:

- 100 ml aqueous mixture solution of 0.015 M $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.005 M $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were co-precipitated in an aqueous solution containing 0.01 M Na_2CO_3 , and the reaction solution was maintained at pH 10 by titrating 1M NaOH solution.
- After all the precursors were added, the reaction solution was sealed and stirred for 24 hours at 80 °C.
- The as-prepared solid products were then washed with DI water, separated through centrifugation, and this process is repeated several times until pH = 7, and finally freeze dried. The final product obtained is about 80 ~ 100 mg. This sample is denoted as NiFe LDH.

For CNT-NiFe LDH synthesis, the following procedure is taken:

- 0.1 mg/mL oxidized CNT aqueous solution (100 ml) was ultrasonically treated for 6 hours to achieve a good dispersion.

- 10 mL mixture of 0.015 M $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.005 M $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ solution were loaded into CNT solution.
- The solution was then moved into oil bath of 80 °C and allowed for stirring for 30 min.
- After that, the pH was tuned to pH 10 by titrating mixture of 1 M NaOH and 0.01 M Na_2CO_3 solution.
- The reaction solution was then sealed and stirred for 24 hours at 80 °C.
- The as-prepared solid products were washed with DI water, separated through centrifugation, and this process is repeated several times until pH = 7, and finally freeze dried. The final product is about 15 ~ 20 mg. The sample was denoted as CNT-LDH.

For CNT-MMO synthesis: The CNT-LDH catalyst was annealed in a tube furnace with Ar gas flow. Different temperature setting was used, including 500 °C for 2 hours (denoted as CNT-MMO), 500 °C for 0.5 hours (denoted as CNT-MMO-0.5 hr), 500 °C for 3 hours (denoted as CNT-MMO-3 hr), and 600 °C for 1 hour (denoted as CNT-MMO-600 °C). NiFe LDH was calcined at 500 °C for 2 hours for comparison study and denoted as calcined LDH.

5.2.2 Characterizations

Morphology of synthesized products were observed using transmission electron microscopy (TEM) (JEOL 2100F), and scanning electron microscopy (SEM) (FESEM 7600F). The scanning transmission electron microscopy (STEM) is done using JEOL 2100F. Powder X-ray diffraction (XRD) was performed by XRD Bruker D8 Powder with Cu-K α radiation source ($\lambda = 1.54 \text{ \AA}$) using measurement step-size of 0.02 ° and scan-rate of 2 °/min. Thermo-gravimetric analysis (TGA) was carried out using TA Q500, which provided information on weight loss during constant-rate heating test (heating rate = 10 °C/min) under atmosphere of synthetic air or N₂ gas. X-Ray Photoelectron Spectroscopy (XPS) were done by VG ESCALAB 220I-XL instrument equipped with a monochromatic Al K α X-ray source (1486.7 eV photons). The binding energy was calibrated according to C (1s) neutral carbon peak at 285.0 eV.

5.2.3 Electrochemical performance test

Ink preparation: The preparation method of the working electrode is as following. In brief, 4 mg catalyst was dispersed in a solution consisting of 768 μL water, 200 μL ethanol and 32 μL nafion solution (5 wt%, Sigma Aldrich). The mixture was then ultrasonicated for about 0.5 hr to obtain a homogeneous ink. After that, 5 μL of the dispersion was transfer onto the glassy carbon disk (3 mm in diameter), based on the catalyst loading of about 0.28 mg/cm^2 . Finally, the as prepared catalyst film was dried at room temperature.

Electrochemical measurement: The electrochemical studies were carried out in a standard three electrode system controlled by an autolab electrochemistry workstation. Catalyst powders cast on the glass carbon electrode was used as the working electrode, and rotating at 1600 rpm to get rid of generated oxygen. Pt foil and Ag/AgCl (4 M KCl) were used as the counter electrode and the reference electrode, separately. The reference was calibrated and converted to reversible hydrogen electrode (RHE), $E(\text{RHE}) = E(\text{Ag/AgCl}) + 0.059\text{pH}$. Linear sweep voltammetry was carried out at 5 mV/s for the polarization curve and tafel plot measurement. The hybrid catalyst was cycled ~ 50 times by cyclic voltammetry (CV) until a stable CV curve was developed before measuring the polarization curves. All polarization curves were corrected with iR compensation. Chronopotentiometry was carried out under a constant current density of 10 mA/cm^2 .

5.3 Results and Discussion

5.3.1 Preparation and properties of NiFe MMO and CNT hybrid

In this work, Ni^{2+} and Fe^{3+} metal ions were co-precipitated in well dispersed CNT solution at pH 10, and the NiFe LDH were adsorbed on oxidized CNT surface through electro-static interaction. Transmission electron microscopy (TEM) image shows that NiFe LDH nanoplates with diameter of $\sim 3 \text{ nm}$ are successfully deposited on CNT surface (Figure 5.1A). To obtain CNT-MMO catalyst, CNT-LDH catalyst was calcined at 500°C under Ar atmosphere for 2 hr. After calcination, the particle diameters are increased to 5-

10 nm, as shown in Figure 5.1B. Further growth of MMO nanoparticles are inhibited due to the spatial confinement on CNT surface that inhibits merging of LDH nano-plates in large scale. More interestingly, an in-grown structure is generated after calcination, i.e. some holes can be clearly observed at the CNT wall and are filled up with NiFe MMO nanoparticles. The in-grown structure is resulted from the following carbon reduction reaction between CNT and NiFe MMO nanoparticles:

Figure 5.1 TEM image of (A) CNT-LDH catalyst; (B) CNT-MMO catalyst, where some CNT outside fringe discontinuity is clearly shown as highlighted.

The low magnification TEM images of CNT-LDH (Figure 5.2A) and CNT-MMO (Figure 5.2B) as well as the scanning electron microscopy (SEM) images (Figure 5.2C for CNT-LDH and Figure 5.4D for CNT-MMO) show that their morphology are generally uniform.

Figure 5.2 Low magnification TEM images of (A) CNT-LDH; (B) CNT-MMO; (C) SEM image of CNT-LDH; and (D) SEM image of CNT-MMO.

In order to investigate the reaction during calcination, thermo-gravimetric analysis (TGA) study is carried out (Figure 5.3). Comparing with that of the CNT and NiFe LDH, TGA study of CNT-LDH catalyst shows a significant weight loss from 500 °C. The simulated weight loss curve of CNT/LDH that based on the same composition as in CNT-LDH catalyst is shown as the dashed line in Figure 5.3. It is clear that there is no obvious weight loss at 500 – 600 °C if CNT and LDH are calcined separately. The weight loss is attributed to the chemical reaction between CNT and NiO nanoparticles, i.e. carbon reduction reaction.

Figure 5.3 TGA curves of CNT, CNT-LDH, LDH, simulated CNT/LDH (the simulated weight loss curve for CNT/LDH is the sum of weight loss for 30 wt% CNT and 70 wt% LDH, which is the same ratio as in CNT-MMO catalyst).

The chemical reaction between CNT and NiO generates Ni^0 and Ni_3C nanoparticles, which are evidenced by the x-ray photoelectron spectroscopy (XPS) of CNT-MMO catalyst as shown in Figure 5.4. The deconvolution of C 1s spectrum shows binding energy at 283.6 eV that corresponds to Ni_3C (Figure 5.4A),^[33] and the deconvolution of Ni 2p3/2 spectrum shows binding energy at 853.2 eV, which is Ni^0 nanoparticle (Figure 5.4B).^[34-36]

Figure 5.4 XPS spectrum of (A) C 1s of CNT-MMO, the deconvolution reveals 283.6 eV corresponding to Ni₃C bonding energy; (B) Ni 2p_{3/2} of CNT-MMO, the deconvolution reveals NiO and Ni⁰ binding energy; (C) Fe 2p_{3/2} for CNT-MMO, the binding energy at 709.9 eV is corresponding to FeO, and 711.9 eV binding energy is corresponding to FeOOH.

In addition, Ni₃C and Ni⁰ nanoparticles are also observed under TEM (Figure 5.5A and Figure 5.5B). Furthermore, when CNT-LDH catalyst was calcined at 600 °C for 1 hr, all

CNT are consumed and metal oxides grow along with CNT as template, as shown in the TEM image of Figure 5.5C. The chemical reaction is important in establishing strong coupling between NiFe MMO and CNT, and resulting an in-grown structure. Meanwhile, the in-grown structure also increased the contact area between NiFe MMO and CNT. Both of the above two factors favor the charge transfer process at the interface of NiFe MMO and CNT for electrochemical performance.

Figure 5.5 TEM images of (A) and (B) CNT-MMO catalyst; (C) CNT-MMO-600 °C.

The x-ray diffraction (XRD) spectrum of CNT-LDH is shown in Figure 5.6-i. CNT (002) peak is identified, with other peaks assignable to NiFe LDH, which is the same with those of NiFe LDH synthesized without CNT (Figure 5.6-ii). Figure 3-iii is the XRD spectrum of CNT-MMO catalyst, which shows CNT (002) peak and NiO peaks. Iron oxide or hydroxide is not revealed in the XRD spectra. By contrast, Fe_2O_3 XRD peaks are clearly shown in calcined NiFe LDH XRD spectrum (Figure 5.6-iv). In addition, comparing with calcined NiFe LDH spectra, NiO peaks in CNT-MMO catalyst shifted by 0.25° to the right, which is caused by Ni^0 interstitials.

Figure 5.6 XRD spectra of (i) CNT-LDH; (ii) NiFe LDH; (iii) CNT-MMO; and (iv) Calcined NiFe LDH.

The XPS analysis of CNT-LDH catalyst is shown in Figure 5.7. The inset table shows Ni/Fe atomic ratio to be 3:1, which is the same as the loaded precursor ratio further confirming the successful synthesis of NiFe LDH.

Figure 5.7 XPS spectrum of CNT-LDH, the inset table shows the details data for calculating of Ni/Fe atomic ratio.

The binding energy analysis of Ni 2p_{3/2} (Figure 5.8A) and Fe 2p_{3/2} (Figure 5.8B) reveals that Ni oxidation state is 2+, and Fe oxidation state is 3+, which is consistent with those of reported NiFe LDH.^[18,25,37]

Figure 5.8 XPS spectrum of (A) Ni 2p_{3/2}; and (B) Fe 2p_{3/2} for CNT-LDH.

The XPS analysis of Ni 2p_{3/2} for CNT-MMO is shown in Figure 5.4B, where NiO is also identified. These results obtained from XPS analysis are consistent with the XRD result. In addition, the XPS analysis of Fe 2p_{3/2} for CNT-MMO (Figure 5.4C) also demonstrates Fe element is in the state of FeOOH and FeO. FeOOH nanoparticles (3-5 nm) are observed under TEM (Figure 5.9). Furthermore, the elemental mapping of CNT-MMO in Figure 5.10 clearly shows the existence of Fe element. The invisibility of iron oxides or hydroxides in XRD spectra could be caused by the ultra-small size and well distribution within the NiO matrix, which is benefited from the LDH mediated synthesis route.

Figure 5.9 TEM image of CNT-MMO catalyst, showing the existence of FeOOH nanoparticle, and the size is about 3-5 nm.

The dark field image of CNT-MMO catalyst obtained through scanning transmission electron microscopy (STEM), is shown in Figure 5.10A and Figure 5.10B. They show the overlapped image of elemental mapping at this position, which evidenced the intimately mixing of Ni and Fe elements. (The single Ni, Fe, and O elemental mapping images are shown in Figure 5.10C, 5.10D, and 5.10E). The morphology is obtained via the LDH mediated synthesis route, as Ni and Fe are intimately mixed at atomic level in LDH. Additionally, the mild growth of MMO is a result of the spatial confinement on CNT surface during the calcination process at 500 °C.

Figure 5.10 (A) STEM dark field image of CNT-MMO; (B) The overlapped image of elemental mapping distribution, which shows the Ni, Fe, and O of CNT-MMO for the position corresponding to the image (A); and (C-E) Elemental mapping of Ni, Fe, and O for catalyst CNT-MMO.

The unparalleled degree of mixing is expected to be highly favorable for OER performance. On top of the conductivity improvement, Fe could also modify the electronic structure of NiO_x towards high electrochemical performance, contributed by the strong interaction between Fe and Ni element. The electronic structure modification of NiO is supported by the XPS binding energy analysis of CNT-MMO catalyst. In details, the distance between Ni 2p_{1/2} and Ni 2p_{3/2} as shown in Figure 5.11 is 17.8 eV, which is 1.2 eV smaller than typical reported value of NiO (19 eV).^[31] It is known that the binding energy of an atom depends on oxidation state as well as local chemical and physical environment. The chemical shift of 1.2 eV indicates that the local chemical environment of NiO changed because of the strong interaction with Fe. In another word, the electronic structure of NiO is modified.

Figure 5.11 XPS binding energy of Ni 2p for CNT-MMO catalyst, the distance between Ni 2p_{1/2} and Ni 2p_{3/2} is 17.8 eV.

5.3.2 Structure and morphology evolution study

In fact, the calcination duration used to obtain the in-grown structure of CNT-MMO catalyst is important. With 0.5 hr calcination at 500 °C, LDH were converted into mixed metal oxides as studied by the XRD spectrum in Figure 5.12A-i, in which the CNT (002) peak and NiO peaks are identified. However, the in-grown structure cannot be observed under TEM as shown in Figure 5.12B, and the nanoparticles can exist only on the CNT surface.

Figure 5.12 (A) XRD spectra of CNT-MMO-0.5 hr (i) and CNT-MMO-3 hr (ii); (B) TEM image of CNT-MMO-0.5 hr; and (C) TEM image of CNT-MMO-3 hr.

The TEM image at low magnification (Figure 5.13A) further shows the uniform distribution of this morphology. In addition, TGA result of CNT-LDH catalyst at Figure 5.3 shows weight loss at 280 °C, which corresponds to the conversion of LDH to MMO. This temperature is much lower than the reaction temperature with CNT (500 °C). Therefore, we can conclude that NiFe LDH is converted into MMO before forming the in-grown structure. With increased calcination duration up to 3 hr, NiO (200) peak in XRD spectrum shown in Figure 5.12A-ii became clearer and CNT (002) peak is also identified. However, the high magnification (Figure 5.12C) and low magnification (Figure 5.13B) TEM images show that the tubular structure of CNT is destroyed for CNT-MMO-3 hr, due to over-reaction with NiO.

Figure 5.13 Low magnification TEM images of (A) CNT-MMO-0.5 hr; and (B) CNT-MMO-3 hr.

Base on all of the above discussion, the growth mechanism of the in-grown structure is herein proposed and illustrated in Figure 5.14. Figure 5.14A represents the structure of as synthesized CNT-LDH catalyst. With 0.5 hr calcination, NiFe LDH is converted into MMO, but only on the surface of CNT (Figure 5.14B). After 2 hr calcination, the in-grown structure is formed, and NiO nanoparticles grow into CNT wall through chemical reaction with external CNT wall, i.e. the case of CNT-MMO catalyst (Figure 5.14C). With 3 hr calcination, CNT structure is destroyed due to the over reaction of CNT and NiO (Figure 5.14D).

Figure 5.14 Growth mechanism of CNT-MMO during calcination: (A) structure of CNT-LDH catalyst; (B) structure of CNT-MMO-0.5 hr, where NiFe LDH are converted to MMO, but only on the surface of CNT; (C) in-grown structure of CNT-MMO catalyst, where NiO growth into CNT wall through chemical reaction with external CNT wall; (D) structure of CNT-MMO-3 hr, where CNT structure is destroyed due to over-reaction of CNT and NiO.

5.3.3 Electrochemical performance measurement

The electrochemical performance of CNT-LDH and CNT-MMO hybrid catalyst were investigated in 1 M and 0.1 M KOH solution, the results are shown in Figure 5.15A. In 1 M KOH solution, the CNT-MMO hybrid catalyst shows an onset potential at ~ 1.43 V vs. RHE, which is much lower than at ~ 1.48 V vs. RHE of CNT-LDH catalyst. The potential difference at current density of 10 mA/cm^2 is about 0.07 V vs. RHE. In 0.1 M KOH solution, the onset potential of OER current for CNT-MMO is also much lower than that of CNT-LDH hybrid catalyst.

Figure 5.15 (A) iR corrected polarization curves of CNT-MMO and CNT-LDH catalysts in 1 M, 0.1 M KOH solution. The catalyst loading is 0.28 mg/cm²; (B) Schematic drawing of OER process for CNT-MMO catalyst; (C) The iR corrected polarization curves for CNT-LDH, CNT-MMO, CNT-MMO-0.5 hr, and CNT-MMO-3 hr hybrid catalyst under 1M KOH solution; (D) The iR corrected polarization curves of CNT-MMO, CNT-LDH, calcined CNT, calcined LDH, and physical mixture of calcined CNT with calcined LDH in 1M KOH solution.

The onset potential is measured based on interpolation of the electrochemical curve down to zero current density. Interestingly, the electrochemical curve of CNT-MMO catalyst in Figure 5.15A shows a small hump from ~1.37 V vs. RHE before the onset potential, this is because of the redox reaction of Ni(II)/Ni (III or IV), although the peak is not visible. The peak should be covered by the high current density for OER. This phenomenon is previously reported in the literature,^[17,21,32] which happens when the NiO is doped with high content of Fe (25%), causing the redox potential shifted to a higher value. This shift

is a strong evidence of modification of the electronic structure of NiO towards favorable of OER activity.^[17,21,32] In this work, NiO catalyst is not simply doped with 25% of Fe, but there exists a strong interaction of Ni and Fe. This is one of the contributing factors for the low OER onset potential of CNT-MMO catalyst.

Besides the intimately mixed morphology in NiFe MMO catalyst, the outstanding OER performance also benefits from the in-grown structure, which provides strong interfacial bonding between NiFe MMO and CNT. Comparing with physical adsorption by organic ligand, the strong interfacial bonding lowers the energy barrier for charge transfer. At the same time, the in-grown structure increases the contact area which means more reaction sites for the charge transfer process. The schematic draw at Figure 5.15B illustrates the enhanced OER process at CNT-MMO catalyst with in-grown structure. With efficient charge transfer process, the role of CNT in enhancing the overall conductivity of the hybrid is significantly magnified. Hence the electrochemical property of this featured hybrid catalyst is extraordinarily improved.

The polarization curves for CNT-LDH, CNT-MMO, CNT-MMO-0.5 hr, and CNT-MMO-3 hr hybrid catalyst under 1 M KOH solution are included in Figure 5.15C. CNT-MMO-0.5 hr without in-grown structure already shows lower onset potential than CNT-LDH catalyst. With the formation of in-grown structure, the OER activity is further significantly improved. Extended calcination duration (CNT-MMO-3 hr) destroyed the tubular structure of CNT, hence decreasing the overall conductivity of the hybrid catalyst, and reduced the OER activity as compared with that of CNT-MMO catalyst. The OER activities of calcined CNT, calcined LDH, and physical mixture of calcined CNT with calcined LDH in 1 M KOH solution are all far inferior to that of CNT-MMO catalyst as shown in Figure 5.15D. Some of the previously reported NiFe based catalysts are listed in Table 5.1 for comparison.

Table 5.1 Comparison of electrochemical performance of the previous reported relevant works.

Catalysts	Onset potential (V vs. RHE)	Tafel slope (mV/dec)	Linear sweep voltammetry for Tafel plot (mV/s)	Ref
NiFe MMO-CNT In-Grown structure	1.43	45	5	This work
NiFe LDH-CNT Physical adsorption	1.48	55	5	This work
NiFe LDH-CNT Physical adsorption	1.45	35	0.1	25
NiFe LDH-rGO Hybrid structure	1.45	40	NA	23
NiFe LDH-Carbon QDs Hybrid structure	1.44	30	NA	27
NiFe LDH-Nickel foam Hybrid structure	1.46	50	1	18

The tafel plots of CNT-LDH and CNT-MMO catalysts derived from the polarization curve measured in 1 M KOH are shown in Figure 5.16A. The calculated tafel slope for CNT-MMO catalyst is ~45 mV/dec, which is much smaller than that of CNT-LDH catalyst (~55 mV/dec). The low tafel slope directly demonstrates the excellent OER activity of CNT-MMO catalyst, contributed by both of the intimately mixed morphology and in-grown structure. Considering the stability, CNT-LDH hybrid catalyst exhibits good durability under current density of 10 mV/cm² in 1M KOH solution as shown in Figure 5.16B. Nevertheless, the degradation for CNT-MMO catalyst is almost negligible. It is generally known that metal oxide is more stable than hydroxide. More importantly,

comparing with coupling of organic ligand, the strong interfacial bonding between CNT and MMO catalyst could avoid the MMO nanoparticles detaching from CNT, and hence improves the durability performance.

Figure 5.16 (A) The tafel plot of CNT-LDH and CNT-MMO measured in 1M KOH solution at sweep rate of 5 mV/cm²; (B) The stability test of CNT-LDH and CNT-MMO under 1 M KOH solution. The dash lines are the horizontal straight line for comparison.

5.4 Summary

NiFe MMO and CNT hybrid catalyst (CNT-MMO) was synthesized via NiFe LDH-CNT intermediate or precursor. Upon calcination, NiFe LDH nano-plates were converted to intimately mixed NiFe MMO nanoparticles with the spatial confinement on CNT surface. More importantly, the NiFe nanoparticles are partially in-grown into CNT walls via carbon reduction reaction. The in-grown structure ensures strong interfacial bonding and increased contact area, which favors the charge transfer between CNT and MMO. The resultant CNT-MMO catalyst demonstrated excellent OER electrocatalytic activities (onset potential of 1.43 V vs. RHE) due to the high degree of mixing and strong interfacial bonding.

References

- 1 Walter, M. G. et al. Chemical Reviews 2010, 110, 6446-6473.
- 2 Cook, T. R. et al. Chemical Reviews 2010, 110, 6474-6502.
- 3 Cheng, F. & Chen, J. Chemical Society Reviews 2012, 41, 2172-2192.
- 4 Yadav, R. M. et al. ACS Applied Materials & Interfaces 2015, 7, 11991-12000.
- 5 He, H. et al. Small 2014, 10, 4671-4676.
- 6 Lee, Y., Suntivich, J., May, K. J., Perry, E. E. & Shao-Horn, Y. The Journal of Physical Chemistry Letters 2012, 3, 399-404.
- 7 Paoli, E. A. et al. Chemical Science 2015, 6, 190-196.
- 8 Subbaraman, R. et al. Nat Mater 2012, 11, 550-557.
- 9 Merrill, M. D. & Dougherty, R. C. The Journal of Physical Chemistry C 2008, 112, 3655-3666.
- 10 Zhang, C. et al. Journal of Materials Chemistry A 2015, 3, 756-761.
- 11 Lu, X. & Zhao, C. Nat Commun 2015, 6.
- 12 Stern, L.-A. & Hu, X. Faraday Discussions 2014, 176, 363-379.
- 13 Chekin, F., Tahermansouri, H. & Besharat, M. J Solid State Electrochem 2014, 18, 747-753.
- 14 Gao, M. et al. Journal of the American Chemical Society 2014, 136, 7077-7084.
- 15 Friebe, D. et al. Journal of the American Chemical Society 2015, 137, 1305-1313.
- 16 Chemelewski, W. D., Rosenstock, J. R. & Mullins, C. B. Journal of Materials Chemistry A 2014, 2, 14957-14962.
- 17 Trotochaud, L., Young, S. L., Ranney, J. K. & Boettcher, S. W. Journal of the American Chemical Society 2014, 136, 6744-6753.
- 18 Lu, Z. et al. Chemical Communications 2014, 50, 6479-6482.
- 19 Long, X., Xiao, S., Wang, Z., Zheng, X. & Yang, S. Chemical Communications 2015, 51, 1120-1123.
- 20 Gong, M. & Dai, H. Nano Res. 2015, 8, 23-39.
- 21 Louie, M. W. & Bell, A. T. Journal of the American Chemical Society 2013, 135, 12329-12337.
- 22 Long, X. et al. Angewandte Chemie International Edition 2014, 53, 7584-7588.

- 23 Ma, W. et al. *Acs Nano* 2015, 9, 1977-1984.
- 24 Yu, X., Zhang, M., Yuan, W. & Shi, G. *Journal of Materials Chemistry A* 2015, 3, 6921-6928.
- 25 Gong, M. et al. *Journal of the American Chemical Society* 2013, 135, 8452-8455.
- 26 Andersen, N. I., Serov, A. & Atanassov, P. *Applied Catalysis B-Environmental* 2015, 163, 623-627.
- 27 Tang, D. et al. *ACS Applied Materials & Interfaces* 2014, 6, 7918-7925.
- 28 Liang, Y. N. et al. *ACS Applied Materials & Interfaces* 2014, 6, 12406-12412.
- 29 Smith, R. D. L. et al. *Science* 2013, 340, 60-63.
- 30 Trotochaud, L., Ranney, J. K., Williams, K. N. & Boettcher, S. W. *Journal of the American Chemical Society* 2012, 134, 17253-17261.
- 31 Zhang, D. et al. *Electrochimica Acta* 2015, 169, 402-408.
- 32 Fominykh, K. et al. *ACS Nano* 2015.
- 33 Rosenthal, D., Ruta, M., Schlögl, R. & Kiwi-Minsker, L. *Carbon* 2010, 48, 1835-1843.
- 34 de Jesús, J. C., Pereira, P., Carrazza, J. & Zaera, F. *Surface Science* 1996, 369, 217-230.
- 35 Abellan, G., Coronado, E., Marti-Gastaldo, C., Ribera, A. & Sanchez-Royo, J. F. *Chemical Science* 2012, 3, 1481-1485.
- 36 Gong, M. et al. *Nat Commun* 2014, 5.
- 37 Zhao, J. et al. *Advanced Functional Materials* 2014, 24, 2938-2946.

Chapter 6

Conclusion and Future Work

Based on the previous discussions on the three connected works, this chapter summarizes the main findings and outcomes for this research. Some recommendations on future work are briefly discussed. In the end, this thesis comments on the potential impact of this layered double hydroxides mediated route.

Page intentionally left blank

6.1 Discussion

The works presented in this thesis were to develop the LDH mediated route to synthesize multifunctional hybrid materials, and to study how this strategy impacts the synergistic interactions of MMO hybrid material towards functional property enhancement. The major contributions and key findings are summarized as follows.

6.1.1 LDH intermediate synthesis route vs. solid state reaction method

To address the hypothesis, the first work systematically studies the advantage of LDH mediated synthesis route over non-LDH method (solid state reaction method) to obtain ternary metal oxides hybrid material. It is demonstrated that LDH mediated route is advantageous in creating well mixed morphology and enhancing metal to metal interactions for ternary MMO over solid state reaction method.

In details, the XRD spectra of ZnGaFe MMO obtained through LDH synthesis route shows only ZnO diffraction pattern with peak shift, unusual peak broadening and preferred crystal growth. The disappeared XRD diffraction peaks for high content of well crystallized gallium oxide and iron oxides crystals can clearly explain the well mixing morphology. Detailed analysis reveals that ZnO is not only doped, but also has high density of lattice defects due to the strong interaction with gallium oxide and iron oxide. Preferred crystal growth of ZnO (002) is also resulted from the effects of Fe^{3+} . In addition, the LDH synthesis route leads to redox interactions between Ga^{3+} and Fe^{3+} . The UV-Vis absorption study again reflects all the above discussions. The realization of these desirable attributes is contributed by the LDH mediated synthesis route.

For the morphology evolution in ZnGaFe MMO system, LDH acts as solid state molecular precursor to ensure the excellent synergistic interactions between metal oxides. Hence, favorable energy band alignment is built up at the interface. The excellent photocatalytic property of ZnGaFe MMO clearly shows the advantages of LDH mediated route over other method.

6.1.2 Direct intercalation of $[\text{AuCl}_4]^-$ ions into LDH and MMO growth from intra-layer merging

The second work reported in this thesis utilizes the strategy of direct intercalation of $[\text{AuCl}_4]^-$ ions into the ZnFe LDH precursor, and involves the study on how this strategy give rise to creating the intimately mixing morphology and synergistic interactions within ZnFe MMO and Au hybrid material.

Direct intercalation of $[\text{AuCl}_4]^-$ ions into LDH structure is feasible and facile. Study shows direct intercalation could result in disrupted layer stacking and layered crystal growth as compared with carbonate intercalated LDH structure. $[\text{AuCl}_4]^-$ intercalated LDH reveals a delayed decomposition behavior during the calcination process. During the heat treatment, Au nanoparticles firstly grow within the ZnFe LDH interlayer before the structure collapses, which inhibit the interlayer merging of metal ions during the ZnFe MMO growth. This results in the intra-layer growth mechanism. As compared to the $[\text{CO}_3]^{2-}$ intercalation, $[\text{AuCl}_4]^-$ ions intercalated LDH will result in MMO with an even higher degree of mixing through the intra-layer growth mechanism. The intimately mixed morphology not only enhances the charge transfer process between metal oxides, but also significantly magnified the role of Au nanoparticles. The photocatalytic ability is greatly enhanced by 43 times.

6.1.3 Spatial confinement for MMO growth and in-grown structure of MMO/CNT

In the third study, LDH mediated route is used to synthesize NiFe MMO and CNT hybrid catalyst for oxygen evolution reaction. Briefly, NiFe LDH nano-plates were firstly deposited on CNT surface through electro-static force. With a controlled calcination process, the LDH nano-plates were converted into intimately mixed metal oxide (5 to 10 nm). Due to the spatial confinement on CNT surface, merging of the LDH precursor during heat treatment is inhibited. As a result, intimately NiFe MMO nanoparticles are obtained with several nanometers (5 to 10 nm), and are well distributed on CNT surface.

In addition, the MMO nanoparticles strongly adhere to CNT wall exhibiting an interesting in-grown structure. This in-grown structure is formed through chemical reactions leading to strong bonding and chemical interaction at the interface. Comparing with the reported hybrid method via organic ligand aided adsorption, the strong coupling in this study favors charge transfer process during the electrochemical test (OER). More importantly, LDH acts as a solid state molecular precursor, where the metal cations (Ni and Fe) are mixed at atomic level. The NiFe MMO obtained from the LDH precursor shows unparalleled level of intimate mixing, which significantly magnifies the role of Fe in enhancing the OER performance. The OER performance measurement shows onset potential (1.43 V vs. RHE) which is very low in comparison to the reported values for other NiFe based OER catalysts.

6.2 Future works

6.2.1 Mixed metal oxide with spinel structure

Mixed metal oxide with spinel structure with a general formula of MM_2O_4 , is of low toxicity, low cost, and highly stable. It has been widely used in applications such as catalyst, photocatalyst, electrochemical, energy and environmental related areas.

In the literature, LDH approach has been used to synthesize spinels.^[1,2] However, several limitations make LDH approach not much explored in the context of spinel synthesis. Firstly, the post-synthesis heat treatment requires high temperature ($>500\text{ }^{\circ}\text{C}$), which could possibly lead to uncontrollable large size, undesirable structure, and agglomerations. Secondly, there is a concern about the stoichiometry. The lowest ratio of M^{2+}/M^{3+} is usually 2 for successful synthesis of LDH structures, whereas, the ratio of M^{2+}/M^{3+} is usually 0.5 for the spinel structure. The excess M^{2+} cations might negatively lead to a mixture of MO and MM_2O_4 .

With the above concerns, there are several suggested experimental methodologies.

Template: The LDH nano-plates could be synthesized on CNT or carbon fiber, graphene, carbon sphere, or hard template. The spatial confinement could lead to well controlled spinels with desired structure. For example, CNT or carbon fiber could lead to nanowires, graphene could lead to nano-sheet, carbon sphere could lead to hollow spheres, and hard template like Ni foam can also be used. In addition, spinel nanoparticles can also be grown on other metal oxide e.g. ZnO or TiO₂ nano-rod through pre-synthesis of the LDH precursor on the surface, and then subjected to calcination. The agglomerations of the spinel nanoparticles could be inhibited due to the spatial confinement. In addition, strong bonding could be built up between the metal oxide and spinel. Hence, it is very beneficial for the functional property. Furthermore, this strategy also opens the possibility of doping for spinels.

Stoichiometry: One of the options to tune the stoichiometry is through using transition metals like Ni and Co, which has both 2+ and 3+ oxidation state. During the heat treatment, M²⁺ can be oxidized to M³⁺ to form the spinel structure. Meanwhile, the stoichiometry of LDH opens the possibility to synthesize inverse spinel. In the inverse spinel, half of the M³⁺ position is replaced by M²⁺, making the general formula as M²⁺(M²⁺M³⁺)O₄. This stoichiometry can be the same as that of LDH.

6.2.2 Synthesis of gallium-zinc oxynitride solid solution

Gallium-zinc oxynitride, with a general formula of Ga_(1-x)N_(1-x)Zn_xO_x, is a semiconductor with proper band gap position and good visible light absorption for overall water splitting. The main issue to synthesize gallium-zinc oxynitride is the limited content of zinc doping and the nitridation process which requires long time and ultra-high temperature.^[3]

There are several advantages to use ZnGa LDH as a precursor to synthesize Ga_(1-x)N_(1-x)Zn_xO_x. Firstly, Zn and Ga metal ions are mixed at atomic level in LDH precursor. Well mixing of zinc and gallium is the most fundamental requirement for successful synthesis of gallium-zinc oxynitride. Secondly, high content of zinc can be loaded, so that the band gap of gallium-zinc oxynitride can be engineered through varied ratios of zinc and

gallium. These two aspects have been mentioned before in the literature.^[3] Besides them, the following additional aspects can be worked on:

Firstly, suitable counter ions can be intercalated into the LDH precursor to provide the nitridation source. This strategy could make the nitridation process more effective.

Secondly, $\text{Ga}_{(1-x)}\text{N}_{(1-x)}\text{Zn}_x\text{O}_x$ can be obtained in various structure, e.g. 0 D, 1 D, 2 D by depositing the LDH precursor on template.

Thirdly, appropriate co-catalyst can be strongly coupled with $\text{Ga}_{(1-x)}\text{N}_{(1-x)}\text{Zn}_x\text{O}_x$ through LDH approach, hence, the energy barrier for H_2 and O_2 evolution reaction can be lowered for effective water splitting.

6.2.3 Hybrid structure with functional polymers

Functional polymers, e.g. poly(3-thiophen-3yl-acrylic acid) which are soluble in aqueous solution, could be coupled with LDH in two aspects. Firstly, the functional polymer could be intercalated into the LDH interlayer. Secondly, LDH nanoplates could be synthesized on the main chain of functional polymer through coupling with the functional groups. Coupling with polymer could introduce new structural or functional properties. Polymers could act as a template to direct the growth of LDH and achieve a hierarchical structure. In addition, some functional polymers could self-assemble into 1D or 2D patterns depending on the concentration and pH. These could affect the conductivity and energy level.^[4] The strategy of in situ growth of LDH and functional polymer with desired polymer chain packing may open up new possibilities of designing hybrid material with unique electronic property or energy band structure.

6.3 Potential impact

From three research works discussed in this thesis, we learned that LDH can be considered as a platform to design multifunctional hybrid material with intimately mixing, strong coupling, various hierarchical structure, uniform morphology, high surface area,

high conductivity, and high stability. These unique properties could lead to excellent synergistic interactions from every component of the hybrid material. We believe that this LDH intermediated synthetic strategy can be extended to a library wide range of multifunctional hybrid materials.

References

- 1 Sun, G. et al. The Journal of Physical Chemistry B 2006, 110, 13375-13380.
- 2 Xu, Q. et al. Solid State Sciences 2009, 11, 472-478.
- 3 Adeli, B. & Taghipour, F. Ecs Journal of Solid State Science and Technology 2013, 2, Q118-Q126.
- 4 Yamamoto, T. NPG Asia Mater 2010, 2, 54-60.

Page intentionally left blank

Appendix A

Figure A.1 Photograph of the catalyst powder of Zn_3Ga_1 , $\text{Zn}_3\text{Ga}_{0.9}\text{Fe}_{0.1}$, $\text{Zn}_3\text{Ga}_{0.7}\text{Fe}_{0.3}$, and $\text{Zn}_3\text{Ga}_{0.5}\text{Fe}_{0.5}$ and $\text{Zn}_3\text{Ga}_{0.5}\text{Fe}_{0.5_SSR}$ from the left to the right

Figure A.2 Schematic draw of the experimental setup for photocatalytic reaction.

Appendix A

Figure A.3 SEM images of (A-i) Zn_3Ga , (B-i) $\text{Zn}_3\text{Ga}_{0.9}\text{Fe}_{0.1}$, (C-i) $\text{Zn}_3\text{Ga}_{0.7}\text{Fe}_{0.3}$, (D-i) $\text{Zn}_3\text{Ga}_{0.5}\text{Fe}_{0.5}$, and the particle size statistical measurement of (A-ii) Zn_3Ga , (B-ii) $\text{Zn}_3\text{Ga}_{0.9}\text{Fe}_{0.1}$, (C-ii) $\text{Zn}_3\text{Ga}_{0.7}\text{Fe}_{0.3}$, (D-ii) $\text{Zn}_3\text{Ga}_{0.5}\text{Fe}_{0.5}$.

Figure A.4 Molecular structure of methylene blue

Appendix A

Figure A.5 Photocatalytic degradation of MB by (A) Zn₃Ga₁; (B) Zn₃Ga_{0.9}Fe_{0.1}; (C) Zn₃Ga_{0.7}Fe_{0.3}; (D) Zn₃Ga_{0.5}Fe_{0.5}; (E) photolysis; (F) Zn₃Ga_{0.5}Fe_{0.5}_SSR.

Appendix A

Table A.1 Fraction of MB adsorbed by the catalysts in 30 ml solution with 10^{-5} M MB and 30 mg catalyst in the dark.

Catalyst	Intensity of light absorption at 665 nm for as-prepared MB solution	Intensity of light absorption at 665 nm for solution after equilibrium dye adsorption in the dark	Fraction of MB adsorbed
Zn_3Ga_1	1.22	0.86	30%
$\text{Zn}_3\text{Ga}_{0.9}\text{Fe}_{0.1}$	1.22	0.98	20%
$\text{Zn}_3\text{Ga}_{0.7}\text{Fe}_{0.3}$	1.22	0.90	26%
$\text{Zn}_3\text{Ga}_{0.5}\text{Fe}_{0.5}$	1.22	0.81	34%
$\text{Zn}_3\text{Ga}_{0.5}\text{Fe}_{0.5}\text{-SSR}$	1.22	0.82	33%

Appendix B

Figure B.1 Photographs of (A) $[\text{CO}_3]^{2-}/\text{ZnFe}(300\text{ }^\circ\text{C})$ and (B) $[\text{AuCl}_4]/\text{ZnFe}(300\text{ }^\circ\text{C})$.

Figure B.2 Schematic draw of the experimental set for photocatalytic reaction.

Appendix B

Figure B.3 Photocatalytic degradation of MB by (A) $[\text{CO}_3]^{2-}/\text{ZnFe}$ LDH; (B) $[\text{CO}_3]^{2-}/\text{ZnFe}(200\text{ }^\circ\text{C})$; (C) $[\text{CO}_3]^{2-}/\text{ZnFe}(300\text{ }^\circ\text{C})$; (D) $[\text{AuCl}_4]^-/\text{ZnFe}$ LDH; (E) $[\text{AuCl}_4]^-/\text{ZnFe}(200\text{ }^\circ\text{C})$; and (F) $[\text{AuCl}_4]^-/\text{ZnFe}(300\text{ }^\circ\text{C})$. 0