Multifunctional bismuth ferrite nanomaterials as a new-generation catalyst for water treatment

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**MULTIFUNCTIONAL BISMUTH FERRITE
NANOMATERIALS AS A NEW-GENERATION
CATALYST FOR WATER TREATMENT**

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SCHOOL OF CIVIL AND ENVIRONMENTAL ENGINEERING
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MULTIFUNCTIONAL BISMUTH FERRITE NANOMATERIALS AS A NEW-GENERATION CATALYST FOR WATER TREATMENT

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Abstract

Bismuth ferrite is one of the most promising ternary metal oxides with various functionalities. As compared with TiO_2 (P25, Evonik) catalyst, which can only be activated under the radiation of UV region, multifunctional bismuth ferrite can induce photocatalysis under visible-light irradiation and also exhibits magnetic property at room temperature. Therefore, it has the greatest potential for development of solar driven catalysis in water treatment, and meanwhile realizing catalyst recovery from the treated water by magnetic separation. The aims of this study are to fabricate a range of novel nanostructured bismuth ferrite catalysts and composites, and systematically investigate their performances in removal of recalcitrant pollutants in water.

In the first phase of this study, a single-crystalline mullite bismuth ferrite ($\text{Bi}_2\text{Fe}_4\text{O}_9$) nanopad was synthesized by a facile co-precipitation method under a low temperature of 95°C . The Bi/Fe precursor molar ratio and the reaction time were investigated for their influences on the resulting $\text{Bi}_2\text{Fe}_4\text{O}_9$ nanopad. The $\text{Bi}_2\text{Fe}_4\text{O}_9$ nanopad was formed via self-assembled crystal growth along the (001) plane, with an average thickness of 170 nm. The most well crystalline nanopad was produced at a reaction time of 36 h, beyond which the nanopad started to dissolve. The produced pure $\text{Bi}_2\text{Fe}_4\text{O}_9$ nanopad exhibited a high degree of elemental stoichiometry with uniform elemental distribution. The $\text{Bi}_2\text{Fe}_4\text{O}_9$ exhibited double bandgaps of 1.9 and 2.3 eV, and showed surface area of $5.8 \text{ m}^2 \text{ g}^{-1}$. It could be photoexcited by visible light of up to 656 nm. The $\text{Bi}_2\text{Fe}_4\text{O}_9$ could be used as a photocatalyst and Fenton catalyst. Its catalytic activities were evaluated using bisphenol A (BPA) as the model pollutant. Under visible-light irradiation from a solar simulator, 34% of BPA could be removed (compared to only ~3% with Evonik P25) via visible-light photocatalysis. With addition of H_2O_2 (16 mM), 54% and 73% of BPA could be removed within 1 h via dark Fenton-like and visible light photo-Fenton reactions, respectively. The $\text{Bi}_2\text{Fe}_4\text{O}_9$ also exhibited a weak magnetism of 0.99 emu g^{-1} .

In the second phase of this study, a delicate synthesis process was designed for the fabrication of a novel $\text{Bi}_2\text{Fe}_4\text{O}_9$ with the simultaneous realization of formation of nanostructured clusters and controllable morphologies. Through carefully controlling the entire synthesis processes, from co-precipitation at a lower temperature in water

system to hydrothermal treatment in methanol/water co-solvent system, nanostructured $\text{Bi}_2\text{Fe}_4\text{O}_9$ clusters with controllable morphologies which were composed of smaller $\text{Bi}_2\text{Fe}_4\text{O}_9$ crystals (~ 25 nm) could be obtained. The fast crystal growth of $\text{Bi}_2\text{Fe}_4\text{O}_9$ had been successfully hindered and a relatively pure $\text{Bi}_2\text{Fe}_4\text{O}_9$ with nanostructured clusters could be obtained. Their morphologies could be cube-, cuboid- and plate-like shapes. The resulted nanostructured $\text{Bi}_2\text{Fe}_4\text{O}_9$ clusters showed good crystallinity, uniform elemental distributions, high chemical stability, good dispersity, reusability, and a narrow bandgap of ~ 2.1 eV. They had remarkable multiplex catalytic activities in the degradation of methyl orange (MO) through visible light photo-Fenton oxidation, dark Fenton-like reaction and solar photocatalysis. Under visible light illumination, 99% of MO could be removed in 80 min. Without illumination, 96% of MO could be removed in 4 h.

To introduce a synergistic functional property to the $\text{Bi}_2\text{Fe}_4\text{O}_9$ catalyst, the third phase of this study was the synthesis of a graphene-supported $\text{Bi}_2\text{Fe}_4\text{O}_9$ nanoparticles (BFO249/rGO4.5) via a facile co-precipitation method under low temperature. BFO249/rGO4.5 had a 2D composite structure and the deposited $\text{Bi}_2\text{Fe}_4\text{O}_9$ nanoparticles (BFO249) had an average size of 5 nm. Fourier transform-infrared (FT-IR) analysis showed that the resulting BFO249/rGO4.5 catalysts were chemically bonded composites possibly with Fe-O-C and/or Bi-O-C bonds. Photoluminescence evaluation indicated that the reduced graphene oxide (rGO) can effectively suppress the recombination of e^-/h^+ pairs in BFO249. The adsorption and photocatalytic activity was evaluated using a hydrophobic pollutant, BPA. The adsorption capacity of BPA on BFO249/rGO4.5 was 4 mg g^{-1} , which was *ca.* 5.5 times higher than that of pristine BFO249. Under visible light region of full solar spectrum, BFO249/rGO4.5 showed a great synergistic adsorption-photocatalytic degradation efficiency of 62% after 3 h (~ 2 times higher than that of BFO249) and the corresponding mineralization is 47%. When BPA solution containing BFO249/rGO4.5 was exposed to the full solar spectrum, 76% and 80% of BPA can be removed at pH 6.5 and 5, respectively, in 3 h. The predominant reactive oxygen species (ROS) for BPA degradation was identified to be the $\text{O}_2^{\cdot -}$. The presence of bicarbonate induced moderate inhibitory effect on the photocatalytic degradation (PCD) of BPA by BFO249/rGO4.5 while sulfate, chloride or nitrate exhibited only minor effect.

In the fourth phase of this study, a cuboid-like $\text{Bi}_2\text{Fe}_4\text{O}_9/\text{Ag}$ with graphene-wrapping tribrid nanoarchitecture was fabricated using a delicate multi-step synthesis process. It was designed to further enhance the performance of the pristine $\text{Bi}_2\text{Fe}_4\text{O}_9$ (BFO) in organic pollutants removal through functional synergism among $\text{Bi}_2\text{Fe}_4\text{O}_9$, silver nanoparticles (AgNPs) and rGO. The challenges that inhibit catalytic degradation of pollutants, such as mass transfer of pollutants in water treatment, recombination of electrons/holes and rate of interconversion between $\text{Bi}_2\text{Fe}_4\text{O}_9(\text{Fe}^{3+})$ and $\text{Bi}_2\text{Fe}_4\text{O}_9(\text{Fe}^{2+})$ states within BFO, could be addressed effectively. The resulting sample (BFO/Ag/rGO) was assessed for methylene blue (MB) removal via visible-light photo-Fenton oxidation. The findings demonstrated the individual functions of AgNP (i.e., electrical conduction, enhanced interconversion of $\text{Bi}_2\text{Fe}_4\text{O}_9(\text{Fe}^{3+})$ and $\text{Bi}_2\text{Fe}_4\text{O}_9(\text{Fe}^{2+})$) and rGO (i.e., anti-recombination of electrons/holes, enhanced mass transfer of organic pollutants) within the $\text{Bi}_2\text{Fe}_4\text{O}_9/\text{Ag}/\text{rGO}$ composites.

Pristine bismuth ferrite usually possesses weak magnetic properties (e.g., saturation magnetization $M_s < 3 \text{ emu g}^{-1}$) for practical magnetic separation applications. Herein, the last phase of this study developed a superparamagnetic bismuth ferrite with coral-like hierarchical morphology (BFO-M) via methanol solvothermal treatment of the as-prepared $\text{Bi}_2\text{Fe}_4\text{O}_9$ nanoclusters (P-BFO). The BFO-M showed a higher M_s of $\sim 31 \text{ emu g}^{-1}$ compared to that of P-BFO treated in water (BFO-A), in ethanol (BFO-E) and in ethylene glycol (BFO-G). Compared to single-crystalline $\text{Bi}_2\text{Fe}_4\text{O}_9$ (PS) and $\text{Bi}_2\text{Fe}_4\text{O}_9$ clusters (NSP), BFO-M showed excellent organic pollutant removal rate by virtue of its high adsorption capacity and catalytic activity when MO was used as model organic pollutant. BFO-M also exhibited good visible light photo-Fenton oxidation rates for pharmaceuticals and pesticides. Even at a low catalyst load of 0.12 g L^{-1} (typically, $\geq 0.5 \text{ g L}^{-1}$), the removal rate of organic pollutants (e.g., 5-fluorouracil, isoproturon) could be $\sim 99\%$ in 100 min under visible-light irradiation. Besides, BFO-M was also a good adsorbent for different kinds of heavy metal ions (e.g., Pb(II) , Cd(II) , As(V) , Cr(III) , Cu(II) , Mn(II) , Ba(II) and Co(II)). For example, its maximal adsorption capacity for Pb(II) was 214.5 mg g^{-1} . The used BFO-M could be recovered via magnetic separation. The outstanding performances of BFO-M could be ascribed to its coral-like hierarchical morphology which consisted of self-assembled 1D nanowires ($\sim 6 \text{ nm}$ in diameter) and 2D ultrathin nanoflakes ($\sim 4.5 \text{ nm}$ in thickness).

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List of symbols and abbreviations

$A_xB_yO_z$	Ternary metal oxides
AFM	Atomic force microscope
AgNPs	Ag nanoparticles
AOPs	Advanced oxidation processes
AR	Analytical grade
AsA	Ascorbic acid
ATPES	3-aminopropyl trimethoxysilane
BET	Brunauer-Emmet-Teller
BFO	Bismuth ferrite (BiFeO_3 , $\text{Bi}_2\text{Fe}_4\text{O}_9$, or $\text{Bi}_{25}\text{FeO}_{40}$)
BPA	Bisphenol A
BQ	Benzoquinone
CB	Conduction band
CBE	Conduction band electrons
CHNS/O	Elementary analyzer for carbon, hydrogen, nitrogen, sulfur and oxygen
CNT	Carbon nanotube
DMSO	Dimethyl sulfoxide
DRS	Diffuse reflectance spectra
e^-/h^+	Photogenerated electron/hole pairs
EDS/EDX	X-ray energy dispersive/Energy dispersive X-ray spectroscopy
EG	Ethylene glycol
E_g	Bandgap of semiconductor
EIS	Electrochemical impedance spectroscopy
E°	Redox potential
ESR	Electron spin resonance
FE	Ferroelectric property
FESEM	Field emission scanning electron microscopy
FM	Ferromagnetic property
FT-IR	Fourier transform-infrared spectrum
FWHM	Full width at half maximum
GA	Glutaraldehyde
g- C_3N_4	Graphitic carbon nitride
GO/rGO	Graphene oxide/Reduced graphene oxide
H^+	Proton
$\text{HO}^\bullet$	Hydroxyl radical
$\text{HO}_2^\bullet$	Hydroperoxyl radical
HAOPs	Hybrid advanced oxidation processes
H_c	Coercivity
HPLC	High-performance liquid chromatograph

HRTEM	High-resolution transmission electron microscopy
$h\nu$	Photon energy
ICP-OES	Inductively coupled plasma-optical emission spectrometer
IPU	Isoproturon
K	Equilibrium constant
k	Reaction rate constants
K_{ads}	Langmuir adsorption constant
k_{app}	Apparent degradation rate constant
$k_{\text{HO}^\bullet}$	Reaction rate constant of hydroxyl radical
LMCT	Ligand-to-metal charge transfer
MB	Methylene blue
$\text{M}^{\text{n}+}$	Metal cations
MO	Methyl orange
M_r	Remanent magnetization
M_s	Saturation magnetization
ms	Millisecond
NHE	Normal hydrogen electrode
NMR	Nuclear magnetic resonance
NPs	Nanoparticles
ns	Nanoseconds
$^1\text{O}_2$	Singlet oxygen
$\text{O}_2^{\bullet-}$	Superoxide radicals
P25	Titanium dioxide (Evonik)
PCB	Polychlorinated biphenyl
PCD	Photocatalytic degradation
pH_{pzc}	Point of zero charge
PL	Photoluminescence
PLAL	Pulsed laser ablation in liquid
PLD	Pulsed laser deposition
PMRs	Photocatalytic membrane reactors
PV	Photovoltaic
PVP	Polyvinyl pyrrolidone
RhB	Rhodamine B
ROSs	Reactive oxygen species
SA	Self-activated
SAED	Selected area electron diffraction
SDA	Structure-directing agent
SHE	Standard hydrogen electrode
S_{max}	Maximum adsorption capacity
SPR	Surface plasmon resonance
SPV	Surface photovoltage spectroscopy

SR	Surface recombination
SSA	Specific surface area
STC	Solar-to-chemical
TAS	Transient absorption spectroscopy
TBAB	Tetrabutylammonium bromide
TEM	Transmission electron microscopy
TFA	Trifluoroacetic acid
TGA	Thermogravimetric analysis
T _N	Neél temperature
TOC	Total organic carbon
UV	Ultraviolet
VB	Valence band
VBH	Valence band holes
VR	Volume recombination
VSM	Vibrating sample magnetometer
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
λ	Wavelength
1D/2D/3D	One-/two-/three-dimensional
5-FU	5-fluorouracil

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Journal papers:

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Yu S., Liu J.*, Zhu W., **Hu Z.T.**, Lim T.T., Yan X.* (2015). Facile room-temperature synthesis of carboxylated graphene oxide-copper sulfide nanocomposite with high photodegradation and disinfection activities under solar light irradiation. *Scientific Reports* 5, 16369.

Hu Z.T.*, Lua S.K., Lim T.T.* (2015). Nanostructured hexahedron of bismuth ferrite clusters: delicate synthesis processes and an efficient multiplex catalyst for organic pollutant degradation. *RSC Advances* 5, 86891–86900.

Hu Z.T., Lua S.K., Lim T.T.* (2015). Cuboid-like $\text{Bi}_2\text{Fe}_4\text{O}_9/\text{Ag}$ with graphene-wrapping tribrid composite with superior capability for environmental decontamination: nanoscaled material design and visible-light-driven multifunctional catalyst. *ACS Sustainable Chemistry & Engineering* 3(11), 2726–2736.

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Lim T.T., **Hu Z.T.**, Liu J. Yan X. (2014). Synthesis of $\text{Bi}_2\text{Fe}_4\text{O}_9$ at low temperature for photocatalytic degradation of Bisphenol A under solar light. The 19th International Conference on Semiconductor Photocatalysis & Solar Energy Conversion (SPASEC-19), Crowne Plaza Hotel, San Diego, California, USA, November 16-20.

Chapter 1 Introduction

1.1 Background

Water pollution is causing unprecedented challenges worldwide. Tons of recalcitrant pollutants are entering into the natural water cycle from industrial manufacturers, agricultural irrigations, households and landfill leachates. They are present in groundwater and surface water threatening human health and environment. Conventional technologies for water treatment can not efficiently remove many of the recalcitrant pollutants. Solar energy is considered as one of the most promising renewable energy (Hernandez et al. 2014, Milbrandt et al. 2014, Twidell and Weir 2015). Therefore, a green water technology that shows effective removal of recalcitrant pollutants utilizing of solar light for water treatment is much desirable.

Advanced oxidation processes (AOPs) have been demonstrated to be the effective technology for degradation of recalcitrant organic pollutants in aqueous system (Hermosilla et al. 2015, Klavarioti et al. 2009, Rahim Pouran et al. 2015, Tsydenova et al. 2015). Among them, heterogeneous photocatalysis and photo-Fenton oxidation are favorable in water treatment because they are effective, economical and relatively clean technologies (Bahnemann 2004, Gaya and Abdullah 2008, Gernjak et al. 2005, Gogate and Pandit 2004, Rahim Pouran et al. 2015). Both of them can form different reactive oxygen species (ROSs), such as hydroxyl radical ($\text{HO}^\bullet$), which can oxidize and mineralize almost any organic pollutants except certain groups of perfluorinated chemicals (Herrmann 1999, Lim et al. 2011b). The redox potential of $\text{HO}^\bullet/\text{H}_2\text{O}$ couple is 2.27 V vs NHE at pH ~ 7 and its reaction rate constant ($k_{\text{HO}^\bullet}$) is usually in the order of 10^6 to $10^9 \text{ M}^{-1}\text{s}^{-1}$, which is the most powerful oxidant after fluorine (Fujishima and Zhang 2006, Litter 2005, Malato et al. 2009).

As an effective catalyst for AOPs, TiO_2 (e.g., Evonik P25) has appeared as the leading photocatalyst in the market for environmental decontamination. However, it is evident that P25 with a bandgap of ~ 3.2 eV has a low efficiency in utilizing solar energy because it can only be excited by UV radiation at $\lambda < 390$ nm (Hoffmann et al. 1995). Additionally, there is only 2-4% for UV in the composition of the solar energy reaching the earth's surface (AGGA 2012, Moniz et al. 2015). To improve utilization of solar light, solar driven catalysis is worth studying in different application aspects.

For application in water treatment, it is considered as a green route to degrade organic pollutants and to minimize energy consumption concurrently. However, solar driven catalysis needs to employ solar-responsive photocatalysts which shall induce photocatalysis and other photo-driven AOPs through absorbing UV radiation (≤ 400 nm), visible light (400-700 nm), or even infrared irradiation (≥ 700 nm), respectively.

Bismuth ferrite, as one of new-generation catalysts, is considered as a promising material for solar driven AOPs. At present, some published reports have revealed that bismuth ferrite with a narrow bandgap of ~ 2.2 eV can activate visible-light photocatalysis (Bharathkumar et al. 2015, Liu et al. 2012b, Mohan et al. 2014, Sarkar et al. 2015, Sun et al. 2013a, Zhu et al. 2011). In addition, bismuth ferrite might be separated from the treated water via magnetic separation technology because it has magnetic property (Das and Mandal 2012, Sun et al. 2013c, Tsai et al. 2012, Verma et al. 2015). Therefore, it has a potential to be used for water treatment through solar driven AOPs and then recovered via magnetic separation.

1.2 Motivation and knowledge gap

Due to the following advantages of bismuth ferrite, such as (1) visible light responsive catalyst, (2) magnetic material, and (3) multiferroic material with iron-containing characteristics (it has a potential to activate Fenton or photo-Fenton processes), it is worth developing bismuth ferrite (or -based) catalysts for water treatment.

The properties of materials can be influenced by their nanoparticle size, nanostructure, morphology, crystallinity, crystallographic orientation, crystal defect, crystal phase, etc. For examples, the free energy of a crystal varies with the crystallographic orientation (Kostiner and Shoemaker 1971, Murshed et al. 2013). A nanostructured material has attracted extensive attention because it is distinct from its bulk counterpart (Edelstein and Cammaratra 1998, Gao et al. 2007, Joo et al. 2012, Lu et al. 2011, Mann and Ozin 1996, Yang 2011). Morphology-controllable nanomaterial (1D, 2D, 3D) can exhibit enhanced/unique properties compared to their bulk counterparts due to the increase in surface area or the variation of surface feature (Han et al. 2006, Mo et al. 2005, Park et al. 2004, Wang et al. 2012, Zhong et al. 2006, Zhu and Deng 2015). Therefore, it is worth studying the effect of the fabricated bismuth ferrite with varied characteristics on its catalytic properties and magnetism.

Photo-Fenton oxidation can be induced under UV/vis illumination in the presence of $\text{Fe}^{3+}/\text{Fe}^{2+}$ and H_2O_2 (Gogate and Pandit 2004, Pignatello 1992b, Pignatello et al. 1999). Typically, the optimum pH is ~ 2.8 in order to maintain the dissolved state of $\text{Fe}^{3+}/\text{Fe}^{2+}$ ions (Benkelberg and Warneck 1995, Pignatello 1992a). Such a low pH leads to high chemical costs in pH adjustment and the post-treatment process. An alternative method has been reported that iron-containing bulk catalysts (e.g., hematite, goethite and magnetite, zero valent iron) can be used to drive heterogeneous photo-Fenton oxidation (Herney-Ramirez et al. 2010). Therefore, if bismuth ferrite could induce an effective heterogeneous photo-Fenton process at a higher pH (e.g., circumneutral pH), it would provide a solution for one of the major shortcomings associated with practical application of photo-Fenton oxidation in water treatment.

The recombination of photogenerated e^-/h^+ pairs is the main reason for causing a low photocatalytic activity of photocatalysts (Hoffmann et al. 1995). Previous investigations on TiO_2 /graphene have proved that graphene can efficiently suppress recombination of e^-/h^+ through transporting and storing e^- (Jiang et al. 2011, Lightcap et al. 2010, Perera et al. 2012, Zhang et al. 2009). Noble metal nanoparticles, e.g., Ag, Au and Pt, exhibit unique properties by virtue of their surface plasmon resonance (SPR) and electron conductivities, which have been used to enhance the photocatalytic activity of the pristine photocatalysts (Awazu et al. 2008, Basahel et al. 2014, Jiang et al. 2014, Zhang et al. 2011a). However, there are rare reports on the preparation of bismuth ferrite-based composites and its application into water treatment as a photocatalyst.

Photoreaction in slurry type has its advantages, but the post-treatment with membrane separation technologies, or photocatalytic membrane reactors (PMRs), has some of shortcomings. It possibly cause loss of catalysts, induce cross-contamination, block membranes, cause membrane fouling, or damage membranes (Mozia 2010, Zhao et al. 2002). Magnetic separation is one of the alternative methods that can be used to recover magnetic nanomaterials (Ambashta and Sillanpää 2010, Hu et al. 2005, Wang et al. 2010b). There is a possibility for recovery of bismuth ferrite from the treated water by magnetic separation (Li et al. 2010b, Wang et al. 2010c). However, bismuth ferrite has a weak magnetic property at room temperature (Hu et al. 2014, Park et al. 2007). Doping is an effective method to enhance its magnetic property, but it usually involves toxic metal ions and high-temperature processing (Das and Mandal 2012,

Jayakumar et al. 2010, Kan et al. 2010, Pradhan et al. 2010, Qian et al. 2010, Verma et al. 2015, Xi et al. 2014, Yang et al. 2010). Alternative approaches to improve the magnetic property of bismuth ferrites should be developed.

1.3 Objectives and scope of work

The objectives of this study are (i) to fabricate novel bismuth ferrite (-based) nanomaterials, (ii) to enhance their catalytic activities, and (iii) to enhance its magnetic property via tuning its synthesis method, crystal structure, nanostructure, morphology, or composite, and (iv) to investigate its application for the removal of recalcitrant pollutants in the aqueous system through visible-light photocatalysis, photo-Fenton oxidation and/or Fenton-like oxidation.

The scope of works are as listed below:

- 1) To synthesize single-crystalline $\text{Bi}_2\text{Fe}_4\text{O}_9$ nanopads, a facile co-precipitation method was conducted at a low temperature of 95°C . The application feasibility of $\text{Bi}_2\text{Fe}_4\text{O}_9$ nanopad in degradation of BPA in water was evaluated through examining visible-light photocatalysis, photo-Fenton oxidation, dark Fenton-like oxidation and magnetic property.
- 2) To fabricate nanostructured hexahedron of $\text{Bi}_2\text{Fe}_4\text{O}_9$ clusters, a delicate approach was developed combining co-precipitation in water system with hydrothermal treatment in methanol/water co-solvent system. The performances of nanostructured $\text{Bi}_2\text{Fe}_4\text{O}_9$ clusters in degradation of MO were assessed through varied AOPs (i.e., visible light photo-Fenton oxidation, dark Fenton-like oxidation and solar photocatalysis).
- 3) To prepare 2D graphene/ $\text{Bi}_2\text{Fe}_4\text{O}_9$ nanoparticles composites, an one-pot co-precipitation method was carried out. The photocatalytic activities of the fabricated composites in removal of BPA were evaluated under illumination at visible light region or full solar spectrum. The degradation kinetics was investigated by studying the different effects of parameters in aqueous system.
- 4) To synthesize cuboid-like $\text{Bi}_2\text{Fe}_4\text{O}_9/\text{Ag}/\text{rGO}$ multiphase composites, a delicate multi-step synthesis process was conducted. The performance of the fabricated composites in removal of MB was assessed through visible light photo-Fenton oxidation. The individual functions of AgNP and rGO within the $\text{Bi}_2\text{Fe}_4\text{O}_9/\text{Ag}/\text{rGO}$ composites were demonstrated.

- 5) To fabricate superparamagnetic Bi/Fe-based nanomaterial, a facile post-treatment using solvothermal synthesis was carried out. The product BFO-M both with coral-like hierarchical morphology and strong magnetic behavior was obtained. Its performance in water treatment was evaluated through using different pollutant models such as MO, 5-FU, IPU and heavy metal ions.
- 6) For all the catalysts fabricated, the effects of synthesis conditions were investigated, the physicochemical properties were characterized, and the mechanisms of structural evolution and catalytic removal of pollutants are proposed.

1.4 Organization of the report

This thesis comprises eight chapters. Chapter 1 presents an introduction of this research in terms of background, motivation, objectives and scope of work. Chapter 2 provides a literature review, including fundamentals of photocatalysis and photo-Fenton oxidation, introduction of bismuth ferrites and the optimization methods of materials. Chapter 3 presents the synthesis and characterization of single-crystalline $\text{Bi}_2\text{Fe}_4\text{O}_9$ nanopads, investigates its feasibility application in water treatment, and presents a plausible mechanism of hybrid advanced oxidation processes. Chapter 4 reports the fabrication and characterization of varied nanostructured $\text{Bi}_2\text{Fe}_4\text{O}_9$ clusters and evaluate their performance in degradation of MO through visible light photo-Fenton oxidation, dark Fenton-like oxidation and solar photocatalysis, respectively. Chapter 5 presents the preparation and characterization of 2D graphene/ $\text{Bi}_2\text{Fe}_4\text{O}_9$ composites and their efficiencies for BPA removal in the aqueous system through visible light (or solar) photocatalysis, studies the effects of wavebands of solar irradiation, pH, and anions, and illustrates a mechanism of a synergistic adsorption-photocatalytic pollutant degradation process. Chapter 6 reports the synthesis and characterization of $\text{Bi}_2\text{Fe}_4\text{O}_9/\text{Ag}/\text{rGO}$ multiphase composite and its high-efficiency in MB removal in water via visible light photo-Fenton oxidation, and presents a plausible mechanism of functional synergism among $\text{Bi}_2\text{Fe}_4\text{O}_9$, AgNPs and rGO. Chapter 7 presents the fabrication and characterization of a magnetically enhanced Bi/Fe-based nanomaterial and its performance in removal of MO dye, 5-FU pharmaceutical, and IPU pesticide. Chapter 8 presents conclusions derived from this study and several recommendations for future works.

Chapter 2 Literature review

2.1 Photocatalysis

Photocatalysis is the acceleration of a photoreaction in the presence of a catalyst. The photocatalytic activity depends on the ability of the catalyst to form electron/hole (e^-/h^+) pairs, which generate free radicals in the reaction medium for secondary reactions. Photocatalysis has been widely investigated since Fujishima and Honda (1972) discovered the phenomenon of photoelectrochemical water splitting on TiO_2 single-crystal electrode. Thereafter, Carey et al. (1976) reported that dechlorination of polychlorinated biphenyls (PCB) could take place on illuminated TiO_2 , which initiated the harbinger of application of photocatalytic degradation (PCD) technique in environmental decontamination. Heterogeneous photocatalysis has been reported to be able to degrade almost all organics except certain groups of perfluorinated chemicals (Blake 2001). Nowadays, visible light (or solar) responsive catalysts and their photocatalysis are widely investigated (Highfield 2015, Kanhere and Chen 2014, Moniz et al. 2015).

Heterogeneous photocatalysis involves five independent steps (Herrmann 1999, Herrmann 2005):

1. Transfer of pollutants from the bulk fluid phase to the surface of photocatalysts,
2. Adsorption of pollutants at the surface of photocatalysts,
3. Reaction in the adsorbed phase usually including oxidation and reduction,
 - 3.1. Photons will be absorbed by the photocatalyst.
 - 3.2. Generation of e^-/h^+ pairs which will be dissociated into photogenerated e^- and h^+ .
 - 3.3. e^- and h^+ transfer to the surface of photocatalyst and react with adsorbed species (e.g., water, oxygen, pollutants), or recombine (with heat release).
4. Desorption of the products,
5. Migration of the products into the bulk fluid phase.

The semiconductor photocatalysts of greatest interest, especially for visible light responsive catalysts at $\lambda > 400$ nm (with a bandgap < 3.1 eV), are listed in Table 2.1.

Table 2.1. Bandgap energies of various visible-light responsive semiconductor photocatalysts (Highfield 2015, Kanhere and Chen 2014, Moniz et al. 2015)

Semiconductor	Bandgap energy (eV)	Semiconductor	Bandgap energy (eV)
CuTiO ₃	3.00	GaP	2.25
FeTiO ₃	2.80	Fe ₂ O ₃	2.20
V ₂ O ₅	2.80	LaFeO ₃	2.10
PbTiO ₃	2.75	Sr ₂ FeNbO ₆	2.06
AgNbO ₃	2.70	KBiO ₃	2.04
NaBiO ₃	2.60	Cu ₂ O	2.00
AgSbO ₃	2.58	CuNbO ₃	2.00
AgBiO ₃	2.50	BiFeO ₃ /Bi ₂ Fe ₄ O ₉	1.90-2.70
YFeO ₃	2.43	CeSe	1.70
WO ₃	2.40	LiBiO ₃	1.63
CdS	2.40	CaCu ₃ Ti ₄ O ₁₂	1.27
BiVO ₄	2.40	MoS ₂	1.20

Heterogeneous photocatalysis is initiated when a photon with energy ($h\nu$) equal to or greater than the bandgap energy (E_g) of the semiconductor photocatalyst. A bulk of electron/hole (e^-/h^+) pairs will be generated after the semiconductor photocatalyst absorbs photons.

Figure 2.1. Schematic diagram of heterogeneous photocatalysis and the recombination pathways of the electron/hole pairs: (A) surface recombination, (B) volume recombination, (C) electron migration to the surface of semiconductor and reduction of electron acceptor, (D) hole migration to the surface of semiconductor and oxidation of electron donor and (E) photogeneration of electron/hole pair (modified from Linsebigler et al. (1995)).

As shown in Figure 2.1, the photogenerated electrons (e^-) will move to the conduction

band (CB) from the valence band (VB), while leaving behind holes (h^+) in the VB. The e^- and h^+ can dissipate by recombination with heat release in the bulk and/or on the surface of semiconductor photocatalyst in nanoseconds (ns). These phenomena are defined as volume recombination (VR) and surface recombination (SR) respectively (Herrmann 2005). The charge recombination is a major factor inhibiting the photocatalytic activity of the semiconductor photocatalyst. A fraction of e^- and h^+ can migrate to the surface of the semiconductor photocatalyst and induce the photocatalytic redox reactions. The recombination of e^-/h^+ is as fast as 10-100 ns, whereas the consumption of e^- by reduction on the surface of the semiconductor photocatalyst is very slow (ms) (Hoffmann et al. 1995, Lim et al. 2011b).

Typically, the photocatalytic redox reactions including a series of chemical reactions are described below:

All the above reactions are attributed to the presence of electron acceptor and donor, e.g., dissolved oxygen and water molecules (or OH^-) (Chong et al. 2010). The reactions between e^- and electron acceptors will produce superoxide radicals ($O_2^{\bullet -}$) (Eq. (2.2)) which can further protonate to form hydroperoxyl radicals ($HO_2^{\bullet}$) under an acid environment (Eq. (2.3)) followed by conversion to hydrogen peroxides (H_2O_2) (Eq. (2.4)). H_2O_2 can further interact with the e^- and protons (H^+) to form $HO^{\bullet}$ (Eq. (2.5)). The reactions between h^+ and electron donors will produce $HO^{\bullet}$ (Eqs. (2.6) and (2.7)). The singlet oxygen (1O_2) may be generated through reaction between h^+ and $O_2^{\bullet -}$ (Eq. (2.8)). Sometimes the reduction and oxidation cannot occur simultaneously, which depends on the type of semiconductor photocatalyst and pH value in the aqueous phase. At pH 0, the representative band positions of various semiconductor photocatalysts are shown in Figure 2.2.

Figure 2.2. Band positions of various semiconductor photocatalysts in contrast aqueous phase at pH 0 (V vs NHE) (Highfield 2015).

In general, the valence band holes (VBH) are powerful oxidants locating at +1.0 to +3.5 V vs normal hydrogen electrode (NHE), while the conduction band electrons (CBE) are good reductants between +0.5 to -1.5 V vs NHE (Hoffmann et al. 1995). Taking TiO₂ as an example, its VBH and CBH are located at +2.53 and -0.52 V vs the standard hydrogen electrode (SHE) at pH 7, respectively. It has a sufficient catalytic activity to generate various powerful ROSs such as HO[•] (the redox potential (E^0) of HO[•]/H₂O couple is +2.27 V vs SHE in pH 7) (Fujishima and Zhang 2006). Figure 2.3 show the potentials of various redox processes occurring on the surface of TiO₂.

Figure 2.3. Schematic diagram showing the potentials for various redox processes occurring on the TiO₂ surface at pH 7 (V vs SHE, SHE ≈ NHE) (Fujishima and Zhang 2006).

2.2 Fenton and photo-Fenton processes

Fenton process is another AOP that generates $\text{HO}^\bullet$ to oxidize organic pollutants in the presence of Fenton's reagent such as hydrogen peroxide and ferrous iron, while photo-Fenton process is similar to Fenton process but with light illumination (Ribeiro et al. 2015). As compared with Fenton reaction, photo-Fenton oxidation is easier to produce ROSs (e.g., $\text{HO}^\bullet$) through effectively accelerating the interconversion between ferric (Fe^{3+}) and ferrous (Fe^{2+}) ions. The principles of Fenton and photo-Fenton processes will be introduced later in this section.

The photo-Fenton oxidation can enhance the degradation rate of pollutants in the presence of $\text{Fe}^{3+}/\text{Fe}^{2+}$ ions, hydrogen peroxide (H_2O_2) and UV/vis illumination (Gogate and Pandit 2004, Ortega-Gómez et al. 2015, Pignatello 1992b, Pignatello et al. 1999, Ribeiro et al. 2015). Heterogenous photo-Fenton oxidation occurs at the interface between solid and water in nature (Faust and Hoffmann 1986), in which the solid commonly contain $\text{Fe}^{3+}/\text{Fe}^{2+}$ or fictitious ion of iron. Photo-Fenton oxidation can remove various pollutants from wastewater such as chlorophenol, pesticides, aromatic compounds, sulphites, dyes, and pharmaceuticals (Fallmann et al. 1999, Gernjak et al. 2004, Gogate and Pandit 2004, Huston and Pignatello 1999, Kavitha and Palanivelu 2015, Lan et al. 2015, Pera-Titus et al. 2004, Romero et al. 2016, Torrades et al. 2015, Venkatadri and Peters 1993). Moreover, it has been reported that photo-Fenton oxidation is more promising than photocatalysis in water treatment (Pignatello et al. 2006, Pouran et al. 2015). Photo-Fenton oxidation not only is flexible in the selection of light sources (i.e., UV, visible and solar light) but also uses high-active reagent. For examples, the $E^\circ(\text{H}_2\text{O}_2/\text{H}_2\text{O})$ is 1.8 V vs NHE at pH 0 (Fujishima and Zhang 2006, Neyens and Baeyens 2003).

Figure 2.4 shows the process of photo-Fenton oxidation which involves three steps. In the initial step, the Fe^{3+} /ligand complexes (e.g., aquocomplex (FeOH^{2+})) was photo-reduced to Fe^{2+} under UV radiation along with the formation of $\text{HO}^\bullet$. The Fe^{3+} will be regenerated through Fenton reaction in the step 2, while generating $\text{HO}^\bullet$. This circulation system continues until the H_2O_2 is exhausted. The $\text{HO}^\bullet$ generated will be used to mineralize organic compounds (Step 3). The formation of FeOH^{2+} is dependent on the pH and aqueous matrix species in the photo-Fenton oxidation system (De Laat

et al. 2004). It has been reported that the optimum pH for photo-Fenton oxidation is ~ 2.8 because it can avoid generation of ferric precipitate and maintain the dominance of FeOH^{2+} in the aqueous system (Pignatello 1992a). However, such a low pH leads to high chemical costs for pH adjustment during the pretreatment and post-treatment stages.

Figure 2.4. Reaction pathways of the photo-Fenton process (Gogate and Pandit 2004).

There is common presence of different dissolved species in an aqueous system especially for carbonate (CO_3^{2-}), phosphate (PO_4^{3-}), sulphate (SO_4^{2-}) and chlorine (Cl^-). These aqueous matrix species will influence the performance of catalysts because they can interact with Fe^{3+} (ionic state) and affect the pH value in the reaction system, resulting in reduction of the active species (Fe^{3+} and FeOH^{2+}) (Gernjak et al. 2005, Oliveros et al. 1997, Torrades et al. 2003). During the last ten years, a pillared clay-based catalyst for photo-Fenton oxidation has been developed through combining $\text{Fe}^{3+}/\text{Fe}^{2+}$ with clay, which can effectively reduce the inhibitory effect from aqueous matrix species and improve the performance of photo-Fenton oxidation (Herney-Ramirez et al. 2010). Unfortunately, the optimal pH for this heterogeneous photo-Fenton oxidation is pH 3. In recent years, a great deal of research effort has aimed to strive for the enhancement of Fenton and photo-Fenton processes at circumneutral pH (Conte et al. 2016, De Luca et al. 2015, Giannakis et al. 2016, Miralles-Cuevas et al. 2015a, Miralles-Cuevas et al. 2015b, Ortega-Gómez et al. 2016, Papoutsakis et al. 2015, Romero et al. 2016, Ruales-Lonfat et al. 2015).

The mechanism of photo-Fenton oxidation has not been clearly understood. Here the

author reviewed the foundation on Fenton reaction instead of photo-Fenton oxidation, while studied a plausible concept, ligand-to-metal charge transfer (LMCT), which is widely used to explain its relative photoredox reaction. This LMCT is developed based on the different species of Fe^{3+} /ligand complexes ($\text{Fe}^{3+}(\text{L}^-)$) which have different properties in terms of complexing abilities, range of absorption wavelength and absorption intensities. Typically, the $\text{Fe}^{3+}(\text{L}^-)$ contain organic and inorganic types. The representative investigated $\text{Fe}^{3+}(\text{L}^-)$ for photo-Fenton oxidation are listed in Table 2.2.

Table 2.2. A list of various Fe^{3+} /ligand complexes and their UV/vis absorption characteristics

Complexes	Maximum UV/Vis absorption (nm)	Absorption intensity	Log K_a of Fe^{3+} /ligands	Remarks
Fe^{3+}	< 280			&
Fe^{3+} /EDTA	409	0.391	25.0	#
Fe^{3+} /EGTA	456	0.619	20.5	#
Fe^{3+} /NTA	404	0.945	15.9	#
Fe^{3+} /CDTA	371	0.453	30.0	#
Fe^{3+} /Phytate	No shift			#
Fe^{3+} /EHPG	No shift		33.9	#
Fe^{3+} /DTPA	No shift		28.0	#
Fe^{3+} /Desferal	No shift		30.7	#
Fe^{3+} /ADP	347	0.940		#
	426	0.842		
Fe^{3+} /ATP	340	0.855		#
	443	0.789		
Fe^{3+} /Bleomycin	356	0.471		#
Fe^{3+} /DHBA	400	0.260	21.4	#
	490	0.314		
FeOH^{2+}	420		-2.17 (25°C)	&
$\text{Fe}(\text{OH})_2^+$			-6.40 (25°C)	&
$\text{Fe}(\text{O}_2\text{H})^{2+}$	650		-2.70	\$
Fe^{3+} /Oxalate	436	0.89		£

The complexes and the corresponding results on the maximum absorption peak positions and absorption intensities were obtained from differential spectroscopic scans of 0.3 mM Fe^{3+} , 5.0 mM ligands, 1.0 M NaN_3 , 50 mM Tris, pH 7.4, versus the same solution minus azide (Graf et al. 1984).

& The complexes and the corresponding results on the maximum absorption peak positions were tested by quantum yield based on 0.46 mM Fe^{3+} at pH 3 (Benkelberg and Warneck 1995).

\$ The complexes and the corresponding results on the maximum absorption wavelength were tested by absorption spectra based on 0.2 mM Fe^{3+} with 0.9 M H_2O_2 at pH 2.8 (Pignatello et al. 1999).

£ The complexes and the corresponding results on the maximum absorption wavelength were tested based on 0.02-0.06 M $\text{K}_3\text{Fe}(\text{C}_2\text{O}_4)_3$ and 0.18 M $\text{K}_2\text{C}_2\text{O}_4$ at neutral pH (Allmand and Webb 1929a, Allmand and Webb 1929b).

The systematical mechanism for Fenton reaction can be described by the following equations (Eqs. (2.9)-(2.18)) (Kitis et al. 1999, Lu et al. 2001, Yoon et al. 2001) along with the corresponding reaction rate constants (k).

Radical generation:

Radical consumption:

Organic degradation:

Where RH represents organic compounds; k_{10} and k_{11} depend on the type of organic compounds.

Fenton reaction can be classified into three stages: radical generation, radical consumption, and organic degradation. According to the values of k , the reactions of radical consumption predominate over that of the radical generation. Thus the generated radicals are mainly consumed in the reactions of radical consumption (Eqs. (2.12)-(2.16)) and only a small fraction of generated radicals could react with organic pollutants through Eqs. (2.17)-(2.18). On the other hand, the regeneration of Fe^{2+} from Fe^{3+} is a rate-limiting step. As shown in Eq. (2.10), k_2 is only $0.001\text{-}0.01 \text{ M}^{-1} \text{ s}^{-1}$. To enhance the degradation efficiency in Fenton reaction, the reaction constants (k_2 , k_3 , k_{10} and k_{11}) need to be improved. The k_{10} and k_{11} depend on the type of the targeted pollutants. These are fixed values in k_{10} and k_{11} when an experiment designed is to remove a certain organic pollutants in water treatment (Walling 1975). It has been reported that photo-Fenton can efficiently promote the interconversion between Fe^{3+}

and Fe^{2+} , as well as enhance the value of k_2 and k_3 through Eq. (2.19) (Benkelberg and Warneck 1995, Faust and Hoigne 1990, Gogate and Pandit 2004, Koppenol et al. 1978, Pignatello et al. 1999).

Moreover, LMCT works based on the $\text{Fe}^{3+}(\text{L}^-)$, in which an overall equation can be described as Eq. (2.20). The concept of LMCT is based on electron transfer which is distinguished from the hydrogen abstraction and electrophilic addition to π -systems (aromatic pollutants) (Bahnemann and Robertson 2013).

2.3 Nanomaterials for removal of heavy metal ions

Nanomaterials in various morphologies/nanostructures, such as nanoparticles, single-crystal, hierarchical nanostructures etc., function as adsorbents are used for the removal of a wide range of contaminated heavy metals (e.g., lead, chromium, copper, arsenic, cadmium, cobalt, manganese, barium, mercury, etc.). Nanomaterials show a better performance than other conventional techniques because of their high surface area (surface-to-volume ration) and their associated high reactivity (surface energy) (Khin et al. 2012). In general, adsorption is a mass transfer process by which a substance is transferred from the liquid phase to the surface of a solid material and becomes bound by physical and/or chemical interactions (Sen Gupta and Bhattacharyya 2011). Therefore, the impact of the surface properties of solid materials on the removal of heavy metal ions is an important consideration. For instances, the surface characteristics of nanomaterials can be altered by adding surfactants due to the introduction of new functional groups, which influences the adsorption capacity of nanomaterials on the removal of heavy metal ions (Sadeghi et al. 2012). The presence of functional groups on the adsorbent surface can exhibit chemical interactions or physical adsorption between adsorbent and adsorbate (Stumm 1992). The net surface charge of nanomaterials is influenced by the pH value in aqueous systems. The surface charge is neutral at pH_{pzc} (point of zero charge). Below the pH_{pzc} , the surface charge of nanomaterials is positively charged. When the pH level of the solution increases, the heavy metal ions adsorption usually increase due to the electrostatic interactions. On the other hand, ionic forms of the heavy metal ions can be reformed in aqueous

solutions due to hydrolysis reactions (Elliott et al. 1986). Hydrolysis of metal ions can be interpreted as progressive replacement of coordinated water molecules by hydroxide groups. In aqueous solutions, metal ions and protons compete with each other for the available bases. Brønsted proposed that multivalent metal ions (e.g., Fe^{3+}) may participate in a series of consecutive proton transfers:

Hydrolysis reaction are usually written without the coordinated water (Eqs 2.22-2.25). The existing ionic form in aqueous solutions is influenced by pH value.

2.4 Bismuth ferrites

Bismuth ferrite (BFO) is a ternary metal oxide consisting of Bi, Fe and O elements. It is a Bi-based multiferroic material. Royen and Swars (1957) are the first to successfully synthesize perovskite bismuth ferrite (i.e., BiFeO_3) using solid state reactions in the 1950s. Since BFO is sensitive to temperature and oxygen pressure during synthesis, the fabricated product easily contained impurity phases (e.g., mullite or sillenite BFO). Achenbach et al. (1967) prepared single-phase BiFeO_3 by removing the impurity phases using HNO_3 and then Kubel and Schmid (1990) successfully conducted research on BiFeO_3 using X-ray diffraction technique. Thereafter, BFO as one of the most promising multiferroic materials has been widely investigated. Many investigations have revealed that BFO possesses outstanding magnetic, electronic and dielectric properties (Hur et al. 2004, Wang et al. 2003, Zhang et al. 2005). In recent years, researchers discovered that BFO also has a remarkable optical property, which makes it capable of utilizing ~40% of solar energy reaching on the earth's surface due to its narrow bandgap of ~2.2 eV (Sun et al. 2013c, Tiwari et al. 2015, Tsai et al. 2012). Some of the previous studies have reported that BFO exhibited photocatalytic degradation of organic pollutants through visible-light photocatalysis (Liu et al. 2012b, Sun et al. 2013a, Zhu et al. 2011).

While BFO can be used to fabricate ceramic capacitors (Quickel et al. 2015), ferroelectric memory cells (Lines and Glass 2001), information storage devices (Cheong and Mostovoy 2007, Filippetti and Hill 2002), spintronic devices (Kimura et al. 2003), sensors (Catalan and Scott 2009), and ferroelectric ultrafast optoelectronic devices (Takahashi et al. 2006), it also can be used as catalyst (Luo et al. 2010, Mao et al. 2005, Sun et al. 2013c, Tsai et al. 2012). More recently, some of efforts in BFO-based optoelectrochemical conversion have been reported in respects of photovoltaic (PV) devices, solar-to-chemical (STC) conversion, CO₂ reduction, and catalytic degradation of organic pollutants. For examples, BFO, which was prepared by a solution-based method, was reported as an absorber layer in a thin-film solar cell configuration. It exhibits higher photoconversion efficiency compared with other all-oxide photovoltaic devices prepared via solution-based approaches (Sarkar et al. 2016, Sarkar et al. 2015, Tiwari et al. 2015). BFO, as a n-type (or p-type revealed by some of published reports), also can be applied for ferroelectric-photovoltaic (FE-PV) devices in which the polarization electric field (or spontaneous electric polarization) is the driving force for the photocurrent (Butler et al. 2015, Chen et al. 2014, Fei et al. 2015, Nechache et al. 2016, Puli et al. 2014, Sarkar et al. 2016, Yuan et al. 2014). Moreover, BFO can be used as a solar driven photocatalyst for solar energy conversion including H₂ generation by water splitting, conversion of CO₂ to hydrocarbons (e.g., CH₄) (Gao et al. 2015a, Kanhere and Chen 2014, Moniz et al. 2015), CO₂ reduction with the formation of carbohydrate and oxygen gas via artificial photosynthesis (Highfield 2015), or degradation of organic pollutants via solar driven catalysis (Bharathkumar et al. 2015, Gao et al. 2015b, Hu et al. 2015b, Hu et al. 2015c, Soltani and Entezari 2014, Tan et al. 2015, Wang et al. 2015).

2.4.1 Crystal structure

BFO has three structures such as perovskite BiFeO₃, mullite Bi₂Fe₄O₉ and sillenite Bi₂₅FeO₄₀. This phenomenon is known as polymorphism. Among them, BiFeO₃ is the most widely studied by researchers followed by Bi₂Fe₄O₉, whereas Bi₂₅FeO₄₀ is rarely investigated. As shown in Figure 2.5a, BiFeO₃ belongs to distorted rhombohedral structure with *R3c* space group (Ravindran et al. 2006). The unit cell of BiFeO₃ can be described as a pseudo cube. In this structure, Fe³⁺ coordinates with 6 oxygen anions forming a FeO₆ octahedron while Bi³⁺ coordinates with 12 oxygen anions, occupying

the center of the pseudo cube. Figure 2.5b shows the mullite structure of BFO. $\text{Bi}_2\text{Fe}_4\text{O}_9$ has orthorhombic structure with $Pbam$ space group (Kostiner and Shoemaker 1971). In the standard crystal unit cell, it is composed of FeO_6 octahedra, FeO_4 tetrahedra and approximate BiO_6 octahedra (Friedrich et al. 2010). Columns formed via edge-sharing FeO_6 octahedra are connected by apex-sharing FeO_4 tetrahedra, while Bi^{3+} located between the columns are surrounded by 6 oxygen anions. Eventually, Bi^{3+} is surrounded by 8 oxygen anions via attracting another 2 oxygen from the other polyhedra centered by Fe^{3+} . Therefore, mullite $\text{Bi}_2\text{Fe}_4\text{O}_9$ is a distorted structure as well (the detailed crystal structure information is shown in **Appendix I**). The crystal structure of BFO is sensitive to temperature and oxygen pressure during synthesis. It requires careful tuning of growth parameters in order to prevent formation of impurity phases including Bi_2O_3 (Gattow and Schutze 1964), hematite Fe_2O_3 (Catti et al. 1995), and magnetite Fe_3O_4 (Okudera et al. 1996). For instance, it is not uncommon to obtain BFO with mixed phases at temperature of $> 550^\circ\text{C}$ (Fischer et al. 1980, Mukherjee and Wang 1971, Murshed et al. 2013, Safi and Shokrollahi 2012).

Figure 2.5. Crystal structure of BFO: (a) BiFeO_3 (modified from Hatt et al. (2010) and (b) $\text{Bi}_2\text{Fe}_4\text{O}_9$ (modified from Kann et al. (2012)).

2.4.2 Properties

Various interesting properties of BFO, including photochemical effects under visible light (or solar light), spontaneous polarization, piezoelectric effect, switchable ferroelectric diode characteristics, resistive switching, and ferromagnetic/ferroelectric behaviors, have been investigated, because BFO is one of the few multiferroic materials at room temperature with ferromagnetism, ferroelectricity and optical bandgap which is commonly located between 1.9 to 2.7 eV (Catalan and Scott 2009,

Sun et al. 2013c, Tsai et al. 2012). The ferroelectricity is an intrinsic nature of ferroelectrics which has an asymmetry in ionic charge and/or electronic charge, whereas ferromagnetism is associated with ferromagnet which has an asymmetry in the electronic spin and a net angular momentum (Cheong and Mostovoy 2007). In BFO (e.g., BiFeO_3), the ferroelectric instability is contributed by Bi $6s^2$ lone pair (A-site) since the polarization mainly come from the Bi-O orbital hybridization, while the magnetization ascribes to the canting moment of Fe-O-Fe (B-site) because of antisymmetric Dzyaloshinskii-Moriya interaction (Filippetti and Hill 2002, Hill 2000). The ferroelectric properties can be utilized to enhance the electron-hole separation and improve the photocatalytic activities of BFO (Kanhare and Chen 2014). As a typical BFO, BiFeO_3 shows antiferromagnetic or week ferromagnetic properties below a Néel temperature (T_N) of 643 K, while $\text{Bi}_2\text{Fe}_4\text{O}_9$ possesses paramagnetic properties at room temperature due to the existence of net magnetic moment and will be converted to an antiferromagnetic state below the T_N at 264 K (Mao et al. 2005, Zhang et al. 2007). The net magnetic moment is ascribed to the slightly distorted crystal structure of BFO and can be adjusted via tuning the distortion/asymmetry of crystal structure. In the lattice of BFO, the number of oxygen vacancies or Fe^{2+} states has an effect on the asymmetry of crystal structure (Safi and Shokrollahi 2012), which will further affect BFO with respect to its ferromagnetic, ferroelectric properties and catalytic activities. With the excessive existence of Fe^{2+} in BFO, it will trap h^+ , leading to a large current leakage, and inducing further distortion/asymmetry of crystal structure of BFO (Cheng et al. 2010, Dutta et al. 2010, Khomchenko et al. 2008, Kumar and Yadav 2006). Moreover, the doping method widely adopted is an efficient method for tuning oxygen vacancies and Fe^{2+} state in semiconductors. In BFO, A-site doping (i.e., replace Bi) is helpful to generate oxygen vacancies and lead to the suppression of the spiral spin structure, resulting in the presence of net magnetization (Khomchenko et al. 2009, Khomchenko et al. 2008), while B-site substitution (i.e., replace Fe) by a higher valence ions (e.g., Ti^{4+}) has an inhibitive effect on Fe^{2+} generation. Both A-site and B-site dopings increase the distortion of Fe-O-Fe bonds that leads to improve magnetic moment (Cheng et al. 2010).

2.4.3 Optimization

Material optimization can be attempted through: (1) tuning the crystal structure of a

material, including crystallinity, crystallographic orientation, crystalline defect, crystal phase, single crystalline/polycrystalline state, etc., which have been shown to influence the properties of a material due to the variation of free energy (e.g., surface energy, interfacial energy); (2) controlling of nanoparticle size, nanostructure, or morphology of a material, which have been demonstrated to optimize the properties of a material because of the quantum size effect, the increase in surface area, or the difference in surface feature (e.g., roughness), etc.; (3) fabricating composites (or heterojunction materials), which is artificially produced multiphase (or two-phase) materials having a desirable combination of the best properties of the constituent phase. The influence of synthesis conditions on a material, such as reaction temperature, reaction time, reaction system, stoichiometric ratio of raw materials, use of additive agents, synthesis methods, etc., need to be carefully controlled. The effect of weak interactions, including crystal-face attractions, hydrogen bonds, *van der Waals* forces, π - π interactions, and/or electrostatic attractions, etc., are worthy to be examined.

Crystal structure

Some of the properties of crystalline solids depend on the crystal structure of the material, the manner in which atoms, ions, or molecules are spatially arranged. For semiconductors, the atomic bonding is either partially or purely ionic. Most crystal structures of semiconductors may be thought of as being composed of electrically charged ions instead of atoms. Their crystal structures are generally more complex and their properties have more variability because semiconductors are composed of two or more elements. With the alteration of reaction conditions in the synthesis process, the array of ions will change, which affects the crystal structure with the variation of crystallinity, crystallographic orientation, crystalline defect, crystal phase, or single crystalline/polycrystalline state. Those alterations have influences on the properties of resultant materials. Many researches on the relationship between crystal structure and properties of materials were reported previously (Bakardjieva et al. 2005, Chen et al. 2011, Hosono et al. 2009, Jiang et al. 2007, Kuang and Yang 2013, Li et al. 2008, Tian et al. 2009, Yan et al. 2005, Yu and Xu 2007, Zhang et al. 2008). Single-crystal SrTiO_3 exposed the facet (001) showed enhanced photocatalytic hydrogen evolution (Kuang and Yang 2013). Single crystalline LiMn_2O_4 nanowire, which was fabricated by a novel reaction using $\text{Na}_{0.44}\text{MnO}_2$ nanowires, exhibited higher thermal stability and rate of charge-discharge due to its nanowire morphology, crystallinity, and high quality of

the single crystalline state (Hosono et al. 2009). Moreover, the crystal phase of a material is an important factor that influences the photocatalytic activity. Zhang et al. (2008) have demonstrated that the photocatalytic activity of TiO_2 nanoparticles for photocatalytic H_2 evolution is directly related to the composition ratio of anatase and rutile TiO_2 . Similarly, TiO_2 with different anatase/rutile ratios was prepared by a microemulsion-mediated hydrothermal method. The reported results indicated that TiO_2 containing 74.2% anatase showed the highest photocatalytic activity for degradation of MO (Yan et al. 2005). Furthermore, it has been reported that BFO crystallites tend to grow along the plane of (001), (110) and $(\bar{1}10)$ (Kostiner and Shoemaker 1971, Liu et al. 2012b, Murshed et al. 2013, Zhang et al. 2011b). However, there is few reports on the effect of crystal facets on the photocatalytic activity of BFO in the degradation of organic pollutants.

Nanostructure

Development (or fabrication) of nanostructured materials is always a hot research area because the properties and application of a material can be effectively optimized via nanostructurization (Edelstein and Cammaratra 1998, El-Sayed 2004, Gao et al. 2007, Joo et al. 2012, Liu et al. 2011, Liu et al. 2013, Lu et al. 2013, Lu et al. 2011, Mann and Ozin 1996, Mao et al. 2005, Modeshia and Walton 2010, Wu et al. 2012a, Yang 2011). Some of published reports are discussed below. Hollow TiO_2 , which was prepared by the combination of trifluoroacetic acid (TFA)-assisted Ostwald ripening process and thermal treatment at 450°C , showed a better photocatalytic activity for degradation of Rhodamine B (RhB) than its bulk counterpart (Li et al. 2013b). Porous Fe_3O_4 flower-like nanostructures, which were synthesized by decomposition of iron alkoxide precursors that were prepared by heating up the solution of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, urea, and surfactant (tetrabutylammonium bromide, TBAB) in ethylene glycol, showed different electromagnetic properties with variation of its nanostructurization (Li et al. 2011b). Moreover, ZnO hierarchical nanoarchitecture with dense nanosheet-built networks, which was synthesized by a facile solvothermal procedure, exhibited enhanced photocatalytic activity for degradation of MO (Lu et al. 2008). More and more reports released the effects of nanostructurization on the performance of materials and demonstrated nanostructured semiconductor materials exhibited outstanding properties in electrochemical fields (Lu et al. 2013, Wang et al. 2013a, Wu et al. 2012a). For BFO, it with the existence of polymorphism are sensitive to

temperature and oxygen pressure during synthesis. In order to prevent formation of impurity phases, the preparation of pure BFO requires carefully tuning of synthesis parameters, introducing of organic additives, or selecting of synthesis methods (Fischer et al. 1980, Mukherjee and Wang 1971, Murshed et al. 2013, Safi and Shokrollahi 2012). BFO nanostructures have not been well studied, especially in the field of heterogeneous catalysis.

Morphology

Morphology-controllable materials (e.g., 1D, 2D, 3D) exhibit enhanced or unique properties compared to their bulk counterparts. Previous researches have demonstrated the phenomena of morphology-dependent properties of materials (Clavel et al. 2007, Dujardin and Mann 2002, Han et al. 2006, Li et al. 2010a, Li et al. 2011b, Mo et al. 2005, Park et al. 2004, Ruan and Zhang 2009, Wang et al. 2012, Wang et al. 2010a, Wu et al. 2010b, Xiao et al. 2010, Zhang et al. 2011b, Zhong et al. 2006, Zhu and Deng 2015). For examples, flower-like α -Fe₂O₃ prepared using 3D ion-carving process exhibited enhanced electrochemical and magnetic properties compared to its single-crystalline sphere-like precursor (Zhu and Deng 2015). Nickel-based materials with varied morphology (urchin-, ring-, or hexagon-like), which were synthesized at 85°C with addition of polyvinyl pyrrolidone (PVP) and control of reaction time, showed different electromagnetic properties (Wang et al. 2010a). Cu materials with varied morphology (spindle-, flower-, or hexagon-like), which were fabricated using surfactant-assisted hydrothermal method with addition of cetyltrimethylammonium chloride (CTAC), cetyltrimethylammonium bromide (CTAB), and polyethylene glycol (PEG-200) respectively, displayed different optical properties (Jing et al. 2014). Other reviews also revealed that the properties of gold nanorods in optical and electronic properties were affected by their shape and size (Gao et al. 2011, Vigderman et al. 2012). Additionally, a comparison experiment between TiO₂ nanobelts and nanospheres under fixed conditions, such as same phase structure, similar specific surface area and similar photoadsorption efficiency, was designed by Wu et al. (2010b) who demonstrated that nanobelts possessed higher photocatalytic activity due to their higher charge carrier mobility. For BFO, much effort has been undertaken to tune their morphology into fibre-, sheet-, cube-, flower-, octahedron-, rod- and groove-like shapes using different synthesis methods (Bharathkumar et al. 2015, Chen et al. 2011, Chybczyńska et al. 2014, Gao et al. 2015b, Joshi et al. 2008, Liu et al. 2014, Sun et al.

2013a, Sun et al. 2009, Wang et al. 2015, Zhang et al. 2007). However, most of the previously synthesized bismuth ferrites had the micrometer-sized ($\geq 1 \mu\text{m}$) morphologies in at least one of their dimensions, which might lead to BFO exhibiting limited enhanced catalytic activities through morphology tuning.

Composites

A composite is considered to be any multiphase material that exhibits a combination of properties that makes the composite superior to each of the component phases. According to this principle of combined action, the composites that produce better property are fashioned by the judicious combinations of two or more distinct materials. The distinct material can be metals, semiconductors, polymers or carbon materials. Noble metal nanoparticles (NPs), e.g., Ag, Au, Pt, exhibit unique properties on account of their surface plasmon resonance (SPR) and electron conductivities, which was successfully used to enhance the photocatalytic activity of the pristine semiconductors (Awazu et al. 2008, Jiang et al. 2014, Sun et al. 2013b, Zhang et al. 2013a, Zhang et al. 2011a). For a carbon material, the properties of graphene oxide (GO) contains large specific surface area ($\sim 2630 \text{ m}^2 \text{ g}^{-1}$) with a micro-scale 2D structure (Stoller et al. 2008, Zhou et al. 2010), high electrical conductivity and mobility of charge carriers ($\sim 200 \text{ 000 cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) (Bolotin et al. 2008), high optical transmittance ($\sim 97.7\%$) (Nair et al. 2008), excellent thermal conductivity ($\sim 5000 \text{ W m}^{-1} \text{ K}^{-1}$) (Balandin et al. 2008) and Young's modulus ($\sim 1.0 \text{ TPa}$) (Lee et al. 2008). The preparation of GO usually use Hummers method (Hummers and Offeman 1958) or other costly approaches such as organic synthesis route (Yan et al. 2010, Yan and Li 2011), longitudinal “unzipping” of carbon nanotube (CNTs) (Jiao et al. 2009, Kosynkin et al. 2009), epitaxial growth (de Heer et al. 2007, Shivaraman et al. 2009), chemical vapor deposition (CVD) technique (Mattevi et al. 2011, Reina et al. 2009) and micromechanical exfoliation method (Novoselov et al. 2004, Novoselov et al. 2005). Reduced GO (rGO) can be prepared through reduction of GO using chemical reduction method (i.e., NaBH_4 , N_2H_6 or others as reducing agents), thermal reduction technique, electrochemical method, photoirradiation, bacterial respiration, etc. (Bai and Shen 2012).

Extensive efforts for the fabrication of noble metal-decorated photocatalyst have been reported, in which different synthesis methods were used (e.g., pulsed laser ablation in liquid (PLAL), two-step method in wet chemistry, etc.) (Basahel et al. 2014, Deng

et al. 2012, Zhang et al. 2013a). The enhanced photocatalysis could be attributed to the enhanced light harvesting due to the plasmonic properties of noble metal NPs and the enhanced charge separation efficiency by their serving as an electron reservoir. However, although noble metal NPs can be used to enhance charge separation and light harvesting, they also act as a recombination center. In addition, some of studies have revealed that carbon-based materials, including activated carbon (AC), carbon nanotube (CNT), graphene oxide (GO), and graphitic carbon nitride (g-C₃N₄), can enhance photocatalytic degradation efficiency of the pristine semiconductors on organic pollutants via suppression of recombination of photogenerated e^-/h^+ through transporting and storing electrons, as well as enhance adsorption capacity of pollutants on the composites (Chen et al. 2010, Eder 2010, Gao et al. 2009, Lam et al. 2014, Lim et al. 2011a, Liu et al. 2012a, Perera et al. 2012, Pradhan et al. 2013, Wang et al. 2014, Wang et al. 2015, Wu et al. 2013, Yap et al. 2012, Zhang et al. 2009, Zhang et al. 2013b, Zhou et al. 2014). For example, an experiment with the observation of color change in the presence of TiO₂, GO and silver nitrate was designed by Lightcap et al. (2010) who demonstrated the mechanism of enhanced photocatalytic efficiency of TiO₂ by GO. Besides, many researches based on GO-based composites have been reported for enhanced photocatalytic degradation of organic pollutants (Akhavan 2011, Bai and Shen 2012, Chen et al. 2010, Guo et al. 2014, Hou et al. 2013, Li et al. 2013a, Liu et al. 2010a, Lv et al. 2013, Pradhan et al. 2013, Rani et al. 2013, Wang et al. 2013b, Wang et al. 2014, Xiao et al. 2014, Zhang et al. 2009).

Chapter 3 Single Crystals — Single-crystalline $\text{Bi}_2\text{Fe}_4\text{O}_9$ nanopad synthesized via low-temperature co-precipitation: performance as photo- and Fenton catalysts

3.1 Introduction

As presented in Chapter 2, heterogeneous photocatalysis has the ability to degrade almost all organics with the exception of perfluorinated chemicals. The widely used TiO_2 (P25, Evonik) has a large bandgap which renders it photo-excitable by UV only. Furthermore, the dispersed nanocatalysts are difficult to separate from the treated water. These two disadvantages have hindered a large-scale application of photocatalysis in water and wastewater treatment.

To overcome these shortcomings, a novel catalyst which can be photoexcited by solar light or indoor illumination, and meanwhile can be easily recovered from the treated water is much sought after. In recent years, much attention has been paid on the use of bismuth ferrites (BFO) in water treatment due to its narrow bandgap of ~ 2.2 eV and its magnetic property at room temperature (as mentioned in Chapter 2) (Catalan and Scott 2009, Gao et al. 2007). These two properties allow efficient utilization of solar energy and possible catalyst recovery via a magnetic separation technique.

Since 1950s, many synthesis methods have been attempted to produce BFO. Royen and Swars (1957) are the first to successfully synthesize perovskite bismuth ferrites using solid state reactions. Thereafter, different methods such as electrospinning (Wang et al. 2013c), microwave (Joshi et al. 2008), sol-gel (Yan et al. 2013), hydrothermal (Wu et al. 2012b), spark plasma sintering (Dai and Akishige 2010), rapid liquid phase sintering (Wang et al. 2004) and rapid two-stage solid state reaction method (Khomchenko et al. 2008) were reported. In recent years, the hydrothermal method with or without the assistance of microwave became popular for preparation of BFO. Liu et al. (2012b) investigated the effect of NaOH concentration and reaction time on the synthesis of mullite bismuth ferrites and found that a highly crystalline BFO nanoplates with exposing crystal faces (001) could be synthesized in 12 M NaOH at 160°C for 2 h using a microwave hydrothermal method. Sun et al. (2013c) reported that perovskite and sillenite bismuth ferrites could be prepared by a hydrothermal

method while adjusting the reaction temperature at 120 and 100°C, respectively. Zhang et al. (2011b) discovered that the crystal growth direction of mullite bismuth ferrites could be tuned through adjusting the concentration of NaOH and successfully synthesized mullite bismuth ferrite with varied morphologies using a hydrothermal synthesis at 200°C. It was proved that nanoplate-like catalysts with exposing facets (001) achieved a higher photodegradation performance for methyl orange than that of other morphologies. However, the hydrothermal method still has some challenges for scale-up because of the use of higher pressure and temperature and the detrimental scale-up effect on the resulting product (e.g., easier phase separation, worse element distribution).

In this study, the author developed a facile co-precipitation method to synthesize BFO nanopads and nanoparticles under a lower temperature (i.e., 95°C) than that of typical hydrothermal methods. To the knowledge of the author, this is the first report on the synthesis of BFO using co-precipitation method at such a low temperature. The effects of synthesis parameters for the mullite BFO ($\text{Bi}_2\text{Fe}_4\text{O}_9$) and its catalytic performance for organic degradation in the aqueous system were evaluated. The crystal growth of $\text{Bi}_2\text{Fe}_4\text{O}_9$ was investigated through adjusting the molar ratio of Bi/Fe and reaction time. The characteristics of $\text{Bi}_2\text{Fe}_4\text{O}_9$ were investigated systematically using various characterization techniques including XRD, TEM, SEM, EDS, BET, ICP-OES, FT-IR and DRS. The evolution mechanism for the self-assembled growth of $\text{Bi}_2\text{Fe}_4\text{O}_9$ crystallite is proposed. The efficiencies of bisphenol A (BPA) removal through photocatalysis, dark Fenton-like reaction and visible-light photo-assisted Fenton-like oxidation were examined. A proposed reaction mechanism is presented to depict the high-efficient catalytic performance of the $\text{Bi}_2\text{Fe}_4\text{O}_9$ in BPA removal. At last, the magnetic property of $\text{Bi}_2\text{Fe}_4\text{O}_9$ was evaluated using VSM.

3.2 Experimental

3.2.1 Materials

All the chemicals were of analytical grade and used without further purification. Bismuth (III) nitrate pentahydrate ($\geq 98\%$, VWR), ferric (III) nitrate nonahydrate ($\geq 99\%$, Merck), sodium hydroxide (pellet, Schedelco), nitric acid (1N, Merck), absolute ethanol (99.9%, Fisher chemical), bisphenol A (AR, Merck), hydrogen peroxide (35%,

Alfa Aesar), and acetonitrile (HPLC grade, TEDIA) were used in this study. Milli-Q ultrapure water (18.2 MΩ cm) was used for all the experiments.

3.2.2 Synthesis

Bi₂Fe₄O₉ nanopads were prepared via the co-precipitation method under low temperature (co-precipitation/low-temperature dehydration route). Typically, a mixture of Bi(NO₃)₃·5H₂O and Fe(NO₃)₃·9H₂O at individual stoichiometric proportions, such as 0.5:1, 0.48:1 and 0.46:1 by molar ratio, was dissolved in 20 ml of 1 M HNO₃ by ultrasonication for 5 min. Then, 73 ml of 1 M NaOH was instantly added into the solution to adjust the pH to ~8 with rapid stirring. The reaction was carried out at room temperature and ended after 20 min. A brown suspension was obtained and the corresponding cake (noted as “precursor”) was collected by centrifugation at 10 000 rpm for 5 min followed by washing with 100 ml of water to remove the residual of nitrate ions. Thereafter, the precursor was dispersed into 80 ml of 12 M NaOH. Then the suspension was transferred into a Teflon vessel and heated at 95°C with constant stirring for 48 h in an oil bath. For further study on the effect of the reaction time, several precursors were prepared at the Bi/Fe molar ratio of 0.48:1 and dispersed into 12 M NaOH following the above mentioned procedure but the reactions were carried out in the oil bath for varied reaction times of 6, 12, 36 and 48 h. The formation of Bi₂Fe₄O₉ can be depicted as follows:

After the dehydration process was completed, the reaction was cooled down to room temperature under ambient environment. The precipitate was filtered and then washed with water, followed by rinsing with 10 ml of absolute ethanol twice. At last, the final product was dried using a vacuum freeze dryer at -44°C overnight.

3.2.3 Characterization

The crystal growth was investigated using field emission scanning electron microscopy (FESEM, JEOL JSM-7600F) and X-ray diffraction (XRD, Bruker D8 Advance) with Cu-Kα (λ = 1.5418 Å) operated at 40 kV and 40 mA in a 2θ range of 10-70° with a step size of 0.0266° and a scan speed of 1.05 s per step. The purity of

products was analyzed by XRD pattern associated with Match software (version 2.1.3). Moreover, the chemical composition and elemental distribution were examined by X-ray Energy Dispersive Spectroscopy (EDS, Oxford Xmax80 LN2 Free). The corresponding cationic stoichiometry was determined by acid digestion followed by analysis of the digestate with inductively coupled plasma-optical emission spectrometer (ICP-OES, Perkin Elmer Optima 2000DV). The $\text{Bi}_2\text{Fe}_4\text{O}_9$ powder were further characterized using transmission electron microscopy (TEM, JEOL JEM-2010), Fourier transform-infrared spectra (FT-IR), UV-vis diffuse reflectance spectra (DRS, Perkin Elmer Lambda 35) and vibrating sample magnetometer (VSM, LakeShore 7400). The specific surface area was calculated using the Brunauer-Emmet-Teller (BET) equation through N_2 adsorption-desorption measurements (Quantachrome Autosorb-1).

3.2.4 Catalytic evaluation

The resulted $\text{Bi}_2\text{Fe}_4\text{O}_9$ was evaluated for its performance in heterogeneous photocatalysis, Fenton-like reaction and photo-assisted Fenton-like oxidation of bisphenol A (BPA) used as the model compound. The pH of the reaction system throughout the reactions was rather constant at circumneutral value. Typically, the desired amount of the catalyst, which corresponded to 1.5 g L^{-1} , was added into 100 mL of solution containing 15 mg L^{-1} of BPA followed by continuous stirring for 1 h in dark to achieve adsorption-desorption equilibrium. Thereafter, for the heterogeneous photocatalytic reaction, the suspension was illuminated with visible light (420-630 nm) using a solar simulator (Newport, 150 W Xenon arc lamp, one sun) equipped a polycarbonate filter for UV cut-off. A small amount of solution was drawn out from the reaction vessel at each designated time interval, filtered using $0.45 \text{ }\mu\text{m}$ cellulose acetate membrane syringe filter, and then determined for BPA concentration. For the Fenton-like reaction, the experiment was carried out in dark with the assistance of 1.63 mmol of H_2O_2 (16.3 mM). For the photo-assisted Fenton-like oxidation, the reaction was carried out with visible-light irradiation and addition of 16.3 mM of H_2O_2 . A high-performance liquid chromatograph (HPLC, Perkin Elmer Series200) equipped with Hypersil GOLD C18 column and Series 200 UV/Vis detector was used to determine the concentration of BPA. The conditions were set at 220 nm of detector

wavelength, a mobile phase of acetonitrile/water (60/40, v/v) and a flow rate of 0.75 mL min⁻¹.

3.3 Results and discussion

3.3.1 Effect of the Bi/Fe molar ratio on crystal growth

In the standard crystal unit cell of mullite bismuth ferrites, as described in Chapter 2, it is composed of FeO₆ octahedra, FeO₄ tetrahedra and approximate BiO₆ octahedra, simultaneously (Friedrich et al. 2010). Eventually, Bi³⁺ is surrounded by eight O via attracting another two O from the other polyhedra centered by Fe³⁺. This special structure results in the polyhedral shape with a slight distortion, especially for the BiO₆ octahedra. Through this kind of dragging structures, the BFO crystallites tends to grow along the plane of (001), (110) and ($\bar{1}10$), individually. Among them, the crystal growth orientation favors along the (001) plane since it has the lowest surface energy (Kostiner and Shoemaker 1971, Liu et al. 2012b, Murshed et al. 2013, Zhang et al. 2011b).

Herein, to investigate the influence of the relative amounts of Bi and Fe sources on the crystal growth, the experiments with the varied molar ratios of Bi/Fe were performed. A series of reactions were carried out while maintaining other conditions such as 12 M NaOH at 95°C for 48 h. Figure 3.1 shows the XRD patterns of the as-prepared BFO with different initial Bi/Fe molar ratios of 0.50, 0.48 and 0.46. According to the standard XRD pattern of mullite bismuth ferrite (JCPDS PDF 04-009-6352), it indicates that all the as-prepared samples are mullite bismuth ferrites (this will be discussed in detail later) and have no obvious evidence of impurities while tuning the Bi/Fe molar ratio from 0.50 to 0.46. In addition, the high intensities of diffraction peaks exhibit that the as-prepared BFO have high crystallinity. The main diffraction peaks are attributed to different facets such as (001), (121), (211), (002), (112), (022), (131), (212), (003), (330), (332), and (004). Among them, it is worth noting that the diffraction intensities along the particular facets (*ab* planes, marked as *) have a significant change while altering the molar ratio of Bi/Fe. As shown in Figure 3.1, when the molar ratio of Bi/Fe is 0.50 (scan 2), the maximum diffraction peak is located at 2 θ of 28.2° corresponding to the crystal face (121). As Bi/Fe molar ratio decreases to 0.48, the highest diffraction intensity is replaced and the corresponding

facet has shifted to (001) (scan 3). It suggests that the dominating orientation of the crystal growth has changed or the crystal is more favorable to grow along the (001) plane, which is beneficial to form a crystal with a large facet (001). With the Bi/Fe molar ratio further reduces to 0.46, the diffraction intensity of facet (001) becomes stronger and the crystal growth along the other *ab* planes are more active, indicating that the lower Bi/Fe molar ratio not only promotes the crystal growth along the (001) plane, but also causes it to grow along the [001] direction. It will lead to an increase in thickness of crystals. According to a previous report, photocatalytic activities of mullite bismuth ferrites with exposing facet (001) have the order of significance following nanosheet > nanoplate > nanocube (Zhang et al. 2011b). The following discussion will be based on the Bi/Fe molar ratio of 0.48, with crystal formula of $\text{Bi}_2\text{Fe}_4\text{O}_9$.

Figure 3.1. XRD patterns of standard mullite structure of $\text{Bi}_2\text{Fe}_4\text{O}_9$ (1) and $\text{Bi}_2\text{Fe}_4\text{O}_9$ samples synthesized at various Bi/Fe molar ratio of 0.50 : 1 (2), 0.48 : 1 (3) and 0.46 : 1 (4) (* highlights *ab* planes).

3.3.2 Effect of reaction time on crystal growth

Since the crystal growth is a slow process under a normal atmospheric pressure, the reaction time becomes very important. Through controlling the reaction time, the morphology and size of crystallites can be tuned. Thus, it is worthy to study the influence of reaction time to reveal the evolution of the crystal growth of $\text{Bi}_2\text{Fe}_4\text{O}_9$.

crystallites. Figure 3.2 exhibits SEM images of the $\text{Bi}_2\text{Fe}_4\text{O}_9$ synthesized with varied reaction times of 6, 12, 36 and 48 h. With increase of the reaction time, it is obvious that the particle size of $\text{Bi}_2\text{Fe}_4\text{O}_9$ increased from nanometers to micrometers and the morphology changes from sphere-like nanoparticles to square nanopads. As shown in Figure 3.2a, uniform nanoparticles of $\text{Bi}_2\text{Fe}_4\text{O}_9$ formed in 6 h had a typical size of ~ 6 nm. In Figure 3.2b, it is evident that there were various coexisting morphologies of $\text{Bi}_2\text{Fe}_4\text{O}_9$ in 12 h reaction time along with the formed nanopads, while some of them were undergoing formation of nanopads. Figure 3.2c shows that regular $\text{Bi}_2\text{Fe}_4\text{O}_9$ nanopads with flat surfaces were formed after 36 h. The crystallite had the side length of ~ 1.5 μm and thickness of ~ 170 nm. With the reaction time further extended to 48 h, the flat nanopads turned into broken nanopads with fragmented pieces and uneven surfaces (Figure 3.2d).

Figure 3.2. SEM images of $\text{Bi}_2\text{Fe}_4\text{O}_9$ samples at different reaction times of 6 h (a), 12 h (b), 36 h (c) and 48 h (d).

Based on the above results, a self-assembled evolution of the crystal growth along the plane is proposed. In general, the crystal growth is random along with different orientations and rates due to their different surface energies (Chen et al. 2011). However, there is a lower surface energy while $\text{Bi}_2\text{Fe}_4\text{O}_9$ crystallites grow along the particular crystal faces in the synthesis process, which may contribute to the self-assembled growth of $\text{Bi}_2\text{Fe}_4\text{O}_9$ along a specific plane. Moreover, adjusting the molar ratio of Bi/Fe can help the $\text{Bi}_2\text{Fe}_4\text{O}_9$ crystallites to grow along facet (001).

Hence, it is possible to synthesize $\text{Bi}_2\text{Fe}_4\text{O}_9$ nanopads that grow along the (001) plane. As illustrated in Figure 3.3, the evolution mechanism of $\text{Bi}_2\text{Fe}_4\text{O}_9$ crystallites includes 4 steps: nucleation and nanoparticle formation, crystal growth with self-assembly, crystal densification and crystal dissolution. In the nucleation and nanoparticle formation stage, the concentration of precursor reaches the critical supersaturation state to nucleate. Nucleation and growth of small crystallites happen simultaneously to result in forming $\text{Bi}_2\text{Fe}_4\text{O}_9$ nanoparticles. With the increase of the reaction time, $\text{Bi}_2\text{Fe}_4\text{O}_9$ nanoparticles tend to aggregate together along with spontaneous self-organization. This kind of self-organization is going on with the main way of epitaxial extension while subsequently attracting the surrounding $\text{Bi}_2\text{Fe}_4\text{O}_9$ nanoparticles. It will not end until $\text{Bi}_2\text{Fe}_4\text{O}_9$ nanoparticles are exhausted. This kind of crystal growth is similar to self-epitaxy of BFO which was reported by Wang et al. (2003). In contrast with pulsed laser deposition (PLD), the facile co-precipitation method adopted in this study is low cost, low energy consumption and easy scale-up. The $\text{Bi}_2\text{Fe}_4\text{O}_9$ nanopads composed of nanoparticles will be formed into dense and flat $\text{Bi}_2\text{Fe}_4\text{O}_9$ nanopads. If further prolonged reaction time, the $\text{Bi}_2\text{Fe}_4\text{O}_9$ nanopads will dissolve and recrystallize. The flat surfaces are damaged while generating a lot of pores and forming some fragmented pieces. Thus, the following discussion will be based on the Bi/Fe molar ratio of 0.48 and reaction time of 36 h.

Figure 3.3. Schematic illustration of the evolution mechanism of $\text{Bi}_2\text{Fe}_4\text{O}_9$ crystallites included nucleation and nanoparticle formation (1), crystal growth with self-assembly (2), crystal densification (3) and crystal dissolution (4).

3.3.3 Phase purity analysis of $\text{Bi}_2\text{Fe}_4\text{O}_9$ nanopads

Figure 3.4 shows XRD patterns of the as-prepared $\text{Bi}_2\text{Fe}_4\text{O}_9$ and different standard samples. Herein, Match software as a fast phase purity analysis is used to characterize the phase compositions of the as-prepared samples. As shown in the figure, it has many crystal plane diffraction peaks marching well with the standard mullite bismuth ferrites ($\text{Bi}_2\text{Fe}_4\text{O}_9$, JCPDS PDF 04-009-6352) (Kostiner and Shoemaker 1971), indicating the as-prepared $\text{Bi}_2\text{Fe}_4\text{O}_9$ belongs to the space group of orthorhombic crystal system ($Pbam$) along with many crystal faces and the corresponding diffraction peaks. The main characteristic peaks are located at 2θ of 14.8, 26.9, 28.2, 28.9, 29.8, 30.9, 33.6, 33.7, 39.1 47.3 and 56.7° .

Figure 3.4. Phase purity analysis of $\text{Bi}_2\text{Fe}_4\text{O}_9$ sample. The XRD pattern is an experimental sample (1). The standard XRD patterns correspond to mullite $\text{Bi}_2\text{Fe}_4\text{O}_9$ (2), perovskite BiFeO_3 (3), sillenite $\text{Bi}_{25}\text{FeO}_{40}$ (4), Bi_2O_3 (5), hematite Fe_2O_3 (6) and magnetite Fe_3O_4 (7).

Obviously, it is hard to match with the other standard patterns such as perovskite bismuth ferrites (BiFeO_3 , 04-014-1679) (Ravindran et al. 2006), sillenite bismuth ferrites ($\text{Bi}_{25}\text{FeO}_{40}$, 01-073-9538) (Infante and Carrasco 1986), Bi_2O_3 (01-074-2351) (Gattow and Schutze 1964), hematite Fe_2O_3 (01-088-2359) (Catti et al. 1995) and magnetite Fe_3O_4 (04-009-8443) (Okudera et al. 1996), respectively. For examples, the main diffraction peaks at 2θ for BiFeO_3 are 22.6, 31.8 and 32.5° and for $\text{Bi}_{25}\text{FeO}_{40}$ are 27.7, 30.4, 32.9 and 52.4° . The possible separated phases of Bi_2O_3 , Fe_2O_3 and Fe_3O_4 are also shown in Figure 3.4. Bi_2O_3 has main 2θ of 27.9, 32.7 and 46.3° , Fe_2O_3 has

23.9, 32.9 and 35.1°, and Fe_3O_4 has 30.0, 35.3 and 62.2°, respectively. Thus, through the fast phase purity analysis by Match software, it has been shown that the as-prepared sample synthesized using a facile co-precipitation method under low temperature fits well with the standard mullite structure of BFO.

3.3.4 Structure and composition

TEM micrographs of $\text{Bi}_2\text{Fe}_4\text{O}_9$ nanopads at low and high magnifications are shown in Figure 3.5a and b. The inset is the corresponding selected area electron diffraction (SAED) pattern along the zone axis [001], confirming the main exposing facets is (001) plane. The TEM image (Figure 3.5a) reveals that $\text{Bi}_2\text{Fe}_4\text{O}_9$ nanopads have a regular square morphology with the side length of 1.5 μm , which confirms with the result of SEM (Figure 3.2c). Moreover, the sharp diffraction spots shown in SAED pattern (Figure 3.5a) indicates that the as-prepared $\text{Bi}_2\text{Fe}_4\text{O}_9$ nanopads are single-crystalline (Joshi et al. 2008, Wu et al. 2012b), while the $\text{Bi}_2\text{Fe}_4\text{O}_9$ nanoparticles with electron diffraction ring-patterns are poly-crystalline (Figure 3.5c). Furthermore, the high-resolution TEM (HRTEM) image (Figure 3.5b) displays clear lattice fringes with d -spacing of 0.36 nm, which corresponds to the mullite $\text{Bi}_2\text{Fe}_4\text{O}_9$ crystal plane (210) based on JCPDS PDF 04-009-6352.

Figure 3.5. TEM images of $\text{Bi}_2\text{Fe}_4\text{O}_9$ nanopad and the corresponding SAED pattern (a) and HRTEM image (b); TEM images of $\text{Bi}_2\text{Fe}_4\text{O}_9$ nanoparticle and the corresponding SAED pattern (c).

In order to analyze the presence of chemical elements and their distribution within $\text{Bi}_2\text{Fe}_4\text{O}_9$ nanopads, X-ray Energy Dispersive Spectroscopy (EDS) equipped to the SEM was used to analyze the as-prepared $\text{Bi}_2\text{Fe}_4\text{O}_9$ (Figures 3.6 and 3.7). The chemical elements of Bi, Fe and O are shown in Figure 3.6 (whereby the element of C mainly originates from the carbon tape). It reveals that the stoichiometric ratio of Bi/Fe is 0.47, which is similar to the result obtained from digestion of the sample (i.e.,

0.476) and is close to the experimental dosage ratio of 0.480. The absolute error (ϵ) is less than 0.005.

Figure 3.6. EDS of $\text{Bi}_2\text{Fe}_4\text{O}_9$ nanopads and the corresponding table of elemental contents (the inset).

The elemental distributions of Bi, Fe and O within the $\text{Bi}_2\text{Fe}_4\text{O}_9$ nanopads are very uniform as revealed through profiling their elemental distribution mapping (Figure 3.7b-d). Thus, it can be concluded that the $\text{Bi}_2\text{Fe}_4\text{O}_9$ nanopad prepared using co-precipitation has the Fe-rich single-crystalline mullite structure along with the uniform elemental distribution.

Figure 3.7. SEM image of $\text{Bi}_2\text{Fe}_4\text{O}_9$ nanopads (a) and the corresponding element distribution mapping of Bi (b), Fe (c) and O (d).

3.3.5 Surface area and surface property

The photocatalytic activity of a catalyst is directly proportional to its specific surface area because a catalyst with higher surface area possesses more active sites and possibly promotes the separation of electron-hole pairs (Bell 2003). Figure 3.8 shows the nitrogen sorption isotherm of $\text{Bi}_2\text{Fe}_4\text{O}_9$ nanopads. The specific surface area as calculated using the Brunauer-Emmet-Teller (BET) equation is $5.8 \text{ m}^2 \text{ g}^{-1}$ which is larger than that of the bulk $\text{Bi}_2\text{Fe}_4\text{O}_9$ ($0.53 \text{ m}^2 \text{ g}^{-1}$) synthesized by solid state reaction (Park et al. 2005). It is also larger than the $\text{Bi}_2\text{Fe}_4\text{O}_9$ of $4.32 \text{ m}^2 \text{ g}^{-1}$, which was prepared using a hydrothermal method (Sun et al. 2009). It indicates that a co-precipitation method is beneficial to prepare catalyst with a higher surface area.

Figure 3.8. Nitrogen adsorption-desorption isotherm of $\text{Bi}_2\text{Fe}_4\text{O}_9$.

The chemical bonds of $\text{Bi}_2\text{Fe}_4\text{O}_9$ nanopads were characterized for FT-IR spectroscopy. As shown in Figure 3.9, the FT-IR transmittance spectrum of $\text{Bi}_2\text{Fe}_4\text{O}_9$ shows three band groups in the 900-800, 800-600 and 600-400 cm^{-1} regions. The single sharp peak at 811 cm^{-1} is assigned to Fe-O stretching vibration of the FeO_4 tetrahedral unit. Moreover, a very broad band from 722-555 cm^{-1} centered at 634 cm^{-1} is attributed to Fe-O stretching vibration of the FeO_4 tetrahedra at 648 cm^{-1} , Fe-O-Fe bending stretching with Fe on both FeO_4 tetrahedral sites at 600 cm^{-1} and Bi-O stretching vibration of the BiO_6 octahedra at 570 cm^{-1} . In general, wavelengths at 524 and 494 cm^{-1} are noted as O-Fe-O bending vibrations of the FeO_4 tetrahedral sites. Furthermore,

the other broad absorption band from 478-410 cm^{-1} centered at 448 cm^{-1} is possibly combined by two Fe-O stretching vibrations of the FeO_6 octahedra at 471 cm^{-1} and 437 cm^{-1} , respectively. All of the peak positions shown above are similar to ones reported previously for bismuth ferrites (Aroyo et al. 2006, Murshed et al. 2013, Voll et al. 2006), which further confirms that Fe-rich mullite bismuth ferrites have been successfully prepared via the facile co-precipitation method under low temperature and indicates the polyhedra present in $\text{Bi}_2\text{Fe}_4\text{O}_9$ crystallites still consist of tetrahedral FeO_4 , octahedral FeO_6 and octahedral BiO_6 groups.

Figure 3.9. FT-IR transmittance spectra in the 1000-400 cm^{-1} of $\text{Bi}_2\text{Fe}_4\text{O}_9$.

3.3.6 Optical property

As shown in Figure 3.10, the UV-vis diffuse reflectance spectra (DRS) of $\text{Bi}_2\text{Fe}_4\text{O}_9$ nanopads and TiO_2 (P25, Evonik) exhibit the different absorption spectra in the wavelength range of 300-700 nm. The result shows that TiO_2 only exhibits photoresponse at wavelengths < 400 nm with an optical bandgap of 3.13 eV. For $\text{Bi}_2\text{Fe}_4\text{O}_9$, the absorbance of visible light in the range of 400-656 nm becomes stronger coupling with two edges of the absorption bands at ~ 544 and ~ 656 nm. The corresponding optical bandgaps for $\text{Bi}_2\text{Fe}_4\text{O}_9$ are 2.3 and 1.9 eV (calculated by the Kubelka-Munk function). The result reveals that $\text{Bi}_2\text{Fe}_4\text{O}_9$ is a unique semiconductor with double bandgaps and the corresponding postulation is the d-d transitions of Fe (Sun et al. 2009). This implies that $\text{Bi}_2\text{Fe}_4\text{O}_9$ can be a visible-light responsive

photocatalyst. All physicochemical properties of BFO, including the as-prepared $\text{Bi}_2\text{Fe}_4\text{O}_9$ and the reported previously, are summarized in Table 3.1 for comparison.

Figure 3.10. UV-vis absorption spectra and the corresponding Kubelka-Munk transformed reflectance spectra of $\text{Bi}_2\text{Fe}_4\text{O}_9$.

Table 3.1. Physicochemical properties of BFO for the as-prepared sample and the previous reported

Characteristics	Experiment results	Ref. Results	Ref.
Morphology ^a (nm)	Nanopads with the thickness of 170	Nanoparticle (10-150 nm) Nanoplate (100-200 nm) Nanocube (400-800 nm) Nanofiber (220-480 nm)	(Da Silva et al. 2011, Joshi et al. 2008, Liu et al. 2010c, Liu et al. 2012b, Sun et al. 2009, Wang et al. 2013c, Zhang et al. 2011b)
SSA ^b ($\text{m}^2 \text{g}^{-1}$)	5.8	0.53	(Park et al. 2005)
E_g^c (eV)	1.9, 2.3	1.68 - 2.2	(Fischer et al. 1980, Gao et al. 2007, Sun et al. 2013c)
D-spacing ^d (nm)	0.357	0.23 - 0.42	(Da Silva et al. 2011, Joshi et al. 2008, Zhang et al. 2011b)
Bi/Fe ^e (by mole)	0.476	0.5, 1.0, 25.0	(Murshed et al. 2013, Selbach et al. 2009, Sun et al. 2013a)
M_s^f (emu g^{-1})	0.99	0.13 - 3.17	(Kothai and Ranjan 2012, Park et al. 2007, Sun et al. 2013c, Tan et al. 2012, Wang et al. 2013c)

^a Particle size was measured through FE-SEM.

^b Specific surface area was determined by the BET equation.

^c Band gap energy was derived using Kubelka-Munk function.

^d Crystal lattice spacing was measured by HRTEM.

^e Molar ratio of Bi/Fe was analyzed by ICP-OES.

^f Magnetization was measured by VSM.

Figure 3.11. Photocatalytic performance of $\text{Bi}_2\text{Fe}_4\text{O}_9$ nanopad (a) and $\text{Bi}_2\text{Fe}_4\text{O}_9$ nanoparticle (b) for degradation of BPA. (c) Performance of $\text{Bi}_2\text{Fe}_4\text{O}_9$ nanopads for degradation of BPA via Fenton-like reaction and photo-assisted Fenton oxidation.

3.3.7 Evaluation of the potential applications

3.3.7.1 Visible-light driven photocatalysis

Figure 3.11a shows the degradation of BPA through photolysis and photocatalysis under visible-light irradiation. During 4 h of visible-light irradiation at the wavelength region of 420-630 nm, the removal efficiency of BPA can be negligible ($\leq 0.4\%$) in the absence of $\text{Bi}_2\text{Fe}_4\text{O}_9$ because BPA has an excellent photostability. Photocatalytic degradation with P25 shows only 3% of the initial removal rate of BPA after 1 h (and 5% for 4 h) because of its limited photoresponse at $\lambda \geq 420$ nm. As compared to P25 at the same catalyst loading, $\text{Bi}_2\text{Fe}_4\text{O}_9$ nanopad exhibits a significant enhancement in the photocatalytic degradation (PCD) rate with 34% of the BPA removed in the same period (and 47% for 4 h). In addition, $\text{Bi}_2\text{Fe}_4\text{O}_9$ nanoparticle ($\text{Bi}_2\text{Fe}_4\text{O}_9$ 6h) shows the

visible photocatalytic activity with lower degradation of BPA compared with that of $\text{Bi}_2\text{Fe}_4\text{O}_9$ nanopad with exposed facet (001) ($\text{Bi}_2\text{Fe}_4\text{O}_9$ 36h) (Figure 3.11b). As shown in Figure 3.11a, the PCD rate of BPA slows down after 1 h. It could be that the intermediates produced and the products would compete with BPA for active sites on the surface of catalysts. Another plausible postulation is that $\text{Bi}_2\text{Fe}_4\text{O}_9$ shows a lower yield of hydroxyl radicals ($\text{HO}^\bullet$) under visible-light irradiation, which will be discussed later.

3.3.7.2 Fenton-like and photo-assisted Fenton reaction

Figure 3.11c shows the degradation of BPA through Fenton-like reaction and photo-assisted Fenton-like oxidation. As shown in the figure, the removal efficiency of BPA by H_2O_2 in the dark is only 5% without $\text{Bi}_2\text{Fe}_4\text{O}_9$, whereas it reaches 54% through Fenton-like reaction in the presence of $\text{Bi}_2\text{Fe}_4\text{O}_9$ and H_2O_2 at 1 h (67% for 4 h). Furthermore, it is evident that the removal efficiency of BPA has a significant improvement with the introduction of visible-light irradiation ($420 \leq \lambda \leq 630 \text{ nm}$) as compared with that of Fenton-like reaction in dark. Through photo-assisted Fenton-like oxidation, 73% of BPA can be removed within 1 h (more than 97% after 2.5 h). Commonly, Fenton-like reactions can be induced under an aqueous system containing iron ions at low pH ~ 2.8 (as mentioned in Chapter 2) and it can be negligible for iron ions under circumneutral pH (Babuponnusami and Muthukumar 2013). During the entire reaction process, the pH measured was consistently within the range of 6.3-6.5, which suggests the occurrence of Fenton-like reaction induced by fictitious $\text{Bi}_2\text{Fe}_4\text{O}_9(\text{Fe}^{3+})$ cations. The fictitious $\text{Bi}_2\text{Fe}_4\text{O}_9(\text{Fe}^{3+})$ would be used to discuss the high-efficient photo-assisted Fenton-like oxidation rather than the conventional concept of photodissolution of iron oxides. This is due to the fact that iron oxides are photostable at longer wavelengths ($\geq 420 \text{ nm}$) at pH ~ 7 (Litter and Blesa 1988) and the iron concentrations as detected in the solution are quite low (e.g., $< 0.3 \text{ mg L}^{-1}$) in the reaction solution during the process.

In summary, $\text{Bi}_2\text{Fe}_4\text{O}_9$ could exhibit visible-light photocatalysis, Fenton-like reaction and photo-Fenton oxidation, or hybrid advanced oxidation processes (HAOPs). The corresponding reaction mechanisms of HAOPs will be discussed later.

3.3.7.3 Magnetic property

For the application of heterogeneous catalytic advanced oxidation processes (AOPs) in water treatment, a catalyst with magnetic property has attracted considerable interest in recent years (Marichy et al. 2012). BFO as a kind of multiferroic oxides have more than one property. It has been reported that BiFeO_3 shows a saturation magnetization (M_s) ranging from 0.13 to 1.55 emu g^{-1} (Park et al. 2007, Wang et al. 2013c), while $\text{Bi}_{25}\text{FeO}_{40}$ exhibits a larger M_s of about 2.6-3.17 emu g^{-1} (Sun et al. 2013c, Tan et al. 2012). However, there are only a few studies on the magnetism of $\text{Bi}_2\text{Fe}_4\text{O}_9$. This study investigated the magnetic property of the as-prepared $\text{Bi}_2\text{Fe}_4\text{O}_9$. The M-H hysteresis loop of the $\text{Bi}_2\text{Fe}_4\text{O}_9$ nanopads was measured at $T = 300 \text{ K}$ under an appropriate applied field of 14.5 kOe. As shown in Figure 3.12, the result exhibits that the M_s is $\sim 0.99 \text{ emu g}^{-1}$, indicating that $\text{Bi}_2\text{Fe}_4\text{O}_9$ nanopads have ferromagnetic properties at room temperature. The magnetic intensity of $\text{Bi}_2\text{Fe}_4\text{O}_9$ is between those of BiFeO_3 and $\text{Bi}_{25}\text{FeO}_{40}$. Although the pristine magnetic intensity of BFO is not strong enough, it still implies that it has a potential for catalyst recovery from the treated water using magnetic separation technology.

Figure 3.12. M-H hysteresis loop of $\text{Bi}_2\text{Fe}_4\text{O}_9$ nanopads measured at $T = 300 \text{ K}$.

3.3.8 Proposed mechanism

Figure 3.13 shows the schematic illustration of reactive oxygen species (ROSs) generation through $\text{Bi}_2\text{Fe}_4\text{O}_9$ -based HAOPs which includes enhanced photocatalysis

by auxiliary H₂O₂, Fenton-like reaction and photo-Fenton oxidation. Typically, during the photocatalytic process using Bi₂Fe₄O₉ under visible-light irradiation at pH 6.3-6.5, the mechanism of generation of HO• ($E^0(\text{H}_2\text{O}_2/\text{HO}\bullet) = 0.8 \text{ V vs NHE at pH 7}$) (Wardman 1989) by conduction band electrons (CBE) can be depicted in Eqs. (3.3)-(3.8). The process involves formations of the corresponding ROSs such as superoxide radicals ($E^0(\text{O}_2/\text{O}_2^{\bullet-}) = -0.28 \text{ V}$) (Fujishima and Zhang 2006), hydroperoxyl radicals (HO₂•, Eq. (3.5)) (Bielski et al. 1985) and autogenerated hydrogen peroxide through termination reactions (Eq. (3.6)) (Hoffman et al. 1994) and/or through Eq. (3.7) ($E^0(\text{O}_2^{\bullet-}/\text{H}_2\text{O}_2 = 0.92 \text{ V, pH 7}$) (Wardman 1989). Here a limited amount of HO• was formed under such conditions of both a weak acidic solution and a lower valence band hole about 1.3 V vs NHE (conduction band electron is -1.0 V) for Bi₂Fe₄O₉ (Sun et al. 2009), resulting in a lower degradation rate of BPA (Figure 3.11a). The reasons are summarized as follow: (1) the amount of autogenerated H₂O₂ is limited by that of HO₂• and O₂•⁻ formed; (2) it is thermodynamically impossible for the generation of HO• through photogenerated h⁺ because of $E^0(\text{HO}\bullet/\text{H}_2\text{O}) = 2.27 \text{ V at pH 7}$ (Fujishima and Zhang 2006). Nevertheless, the h⁺ might contribute to continuous production of O₂ and stability of pH in the photoreactor (Eq.(3.9)), where the $E^0(\text{O}_2/\text{H}_2\text{O}) = 0.83 \text{ V at pH 7}$ (Fujishima and Zhang 2006). Interestingly, an enhanced photocatalysis might improve BPA degradation with the assistance of auxiliary H₂O₂ (Figure 3.13).

Another plausible reaction can be the Fenton-like reaction, which can be induced by Bi₂Fe₄O₉ in dark at pH 6.3-6.5 (Velichkova et al. 2013). Herein, fictitious Bi₂Fe₄O₉(Fe³⁺) cations are introduced to explain reaction mechanisms, which have a similar function as Fe³⁺ (ionic state), and possibly caused by oxygen vacancies and interactions between Fe and Bi atoms. The interconversion between Bi₂Fe₄O₉(Fe³⁺) and Bi₂Fe₄O₉(Fe²⁺) can be described by Eqs. (3.10)-(3.11). Similar as a conventional Fenton-like reaction, the fictitious Bi₂Fe₄O₉(Fe³⁺) cations will be transformed to

$\text{Bi}_2\text{Fe}_4\text{O}_9(\text{Fe}^{3+})(\text{HO}_2^-)$ complexes through Eq. (3.10a) followed by generation of $\text{HO}_2^\bullet$ via Eq. (3.10b). The corresponding iron-like cycle is shown in the dotted line square (Figure 3.11). However, Eq. (3.10) is a rate-limiting step during the entire Fenton-like process since the reaction rate constant (k) for Eq. (3.10a) is much lower ($k_{10} = 0.001\text{-}0.01 \text{ M}^{-1} \text{ s}^{-1}$ for formation of $\text{Fe}(\text{HO}_2)^{2+}$ at pH 2.8) than that of Eq. (3.11) ($k_{11} = 70 \text{ M}^{-1} \text{ s}^{-1}$) (Rigg et al. 1954, Walling and Goosen 1973), which leads to retardation of the BPA degradation rate (Fenton-like in Figure 3.11b).

Furthermore, it has been proved that photo-Fenton oxidation can enhance the regeneration rate of Fe^{2+} at pH 2.8 efficiently and can be induced by irradiation with wavelength up to 650 nm (λ_{max}) in the presence of H_2O_2 (Koppenol et al. 1978, Pignatello 1992b, Pignatello et al. 1999). Here an overall equation of the $\text{Bi}_2\text{Fe}_4\text{O}_9$ -based photo-Fenton reaction can be described as Eq. (3.12) (details are shown in **Appendix II**). The generated $\text{Bi}_2\text{Fe}_4\text{O}_9(\text{Fe}^{2+})$ can also drive Fenton reaction (Eq. (3.11)). Thus, an iron-like cycle will be activated between Eqs. (3.11) and (3.12), which is shown in the bottom right-hand corner of Figure 3.13. It also contributes to the control of the concentration of dissolved O_2 and pH value in the entire system.

Hence, with the presence of both visible light (420-630 nm) and H_2O_2 , the resulting HAOPs can exhibit an enhanced efficiency of $\text{Bi}_2\text{Fe}_4\text{O}_9$ in BPA degradation (photo-assisted Fenton-like in Figure 3.11b) that is ascribed to the interaction among enhanced photocatalysis, photo-Fenton oxidation and Fenton-like reaction. In this HAOPs system, H_2O_2 can be autogenerated via photocatalysis and initiated Fenton-like reaction, while the solar-driven self-renewal of O_2 also can be used to promote HAOPs (Figure 3.13). In the absence of visible light, the auxiliary H_2O_2 needs to be introduced to ensure continuity of AOP in this system, albeit at a slow reaction rate. Nevertheless, it is expected to realize a continuous treatment of wastewater at all hours of the day and night through alternation of these AOPs.

Figure 3.13. Schematic illustration of ROSs generation through $\text{Bi}_2\text{Fe}_4\text{O}_9$ -based HAOPs (Note: reactions of BPA with ROSs are not shown and simulated visible light at a range of 420-630 nm with UV/IR cut-off).

3.4 Conclusions

This study has successfully developed a facile low-temperature co-precipitation method to prepare self-assembled $\text{Bi}_2\text{Fe}_4\text{O}_9$ nanopads with exposing facet (001). Through investigation of synthesis parameters, it was found out that the molar ratio of Bi/Fe and the reaction time have significant effects on the crystal growth. A corresponding mechanism of morphological evolution is proposed. The resulting $\text{Bi}_2\text{Fe}_4\text{O}_9$ has single-crystalline structure with double bandgaps, and possesses a high degree of phase purity, crystallinity, elemental stoichiometry and uniform elemental distributions, and exhibit a relatively higher surface area. It shows its multifunctionality in respect of visible-light photocatalysis, dark Fenton-like reaction and photo-Fenton oxidation. In the presence of both visible light and H_2O_2 , a plausible mechanism of hybrid advanced oxidation processes (HAOPs) is illustrated to explain the high efficiency of $\text{Bi}_2\text{Fe}_4\text{O}_9$ in BPA degradation. $\text{Bi}_2\text{Fe}_4\text{O}_9$ also exhibits a weak magnetism at room temperature. This study has a great significance in the synthesis of highly efficient $\text{Bi}_2\text{Fe}_4\text{O}_9$ by a up-scalable method with low cost and energy saving. It

is expected to realize a continuous treatment of wastewater at all hours of the day and night through alternation of solar-driven HAOPs and dark Fenton-like reaction, and catalyst recovery from the treated water by magnetically-enhanced gravity separation.

Chapter 4 Nanostructures — Nanostructured hexahedron of $\text{Bi}_2\text{Fe}_4\text{O}_9$ clusters: development of a delicate synthesis process and efficient multiplex catalyses for pollutant degradation

4.1 Introduction

In Chapter 3, a facile low-temperature co-precipitation method was developed to prepare single-crystalline $\text{Bi}_2\text{Fe}_4\text{O}_9$ nanopads with exposing facet (001). It exhibited multifunctionality in respect of visible-light photocatalysis, dark Fenton-like reaction, and photo-Fenton oxidation, as well as a weak magnetic property. Unlike the conventional homogeneous/heterogeneous photo-Fenton or Fenton-like oxidation mentioned in Chapter 2 which is only operational at $\text{pH} < 3.0$, the as-prepared $\text{Bi}_2\text{Fe}_4\text{O}_9$ can induce heterogeneous photo-Fenton and Fenton-like oxidation at circumneutral pH. The findings indicate that the as-fabricated $\text{Bi}_2\text{Fe}_4\text{O}_9$ can be practically applied for a continuous treatment of wastewater without downtime.

As mentioned in Chapter 2, morphology-controllable fabrication is one of the effective approaches for enhancing performance of catalysts, since morphology-controllable nanomaterials (e.g., 1D, 2D, 3D) exhibit enhanced properties compared to their bulk counterparts (Han et al. 2006, Li et al. 2010a, Ruan and Zhang 2009, Wang et al. 2012). Much effort has been undertaken to tune the morphology of BFO into sheet-, cube-, flower-, octahedron-, rod- and groove-like shapes (Chen et al. 2011, Chybczyńska et al. 2014, Joshi et al. 2008, Liu et al. 2014, Sun et al. 2013a, Sun et al. 2009, Zhang et al. 2007). However, most of the previously synthesized BFO had the micrometer-sized ($\geq 1 \mu\text{m}$) morphologies in at least one of their dimensions, and thus they exhibited limited enhanced catalytic activities. To address this problem, development of a novel nanostructured BFO could be the overarching strategy (Mao et al. 2005). Nanostructured materials have attracted extensive attention, which are distinct from their bulk counterparts and from the atomic or molecular precursors (Edelstein and Cammarata 1998, El-Sayed 2004, Gao et al. 2007, Joo et al. 2012, Liu et al. 2011, Lu et al. 2011, Mann and Ozin 1996, Yang 2011). Unfortunately, since BFO with the existence of polymorphism are sensitive to temperature and oxygen pressure during

synthesis, they require careful tuning of synthesis parameters, introduction of organic additives, or selection of synthesis methods in order to prevent formation of impurity phases (Fischer et al. 1980, Mukherjee and Wang 1971, Murshed et al. 2013, Safi and Shokrollahi 2012). The previous study reported in Chapter 3 (Section 3.3) has demonstrated that $\text{Bi}_2\text{Fe}_4\text{O}_9$ has the ability of self-assembly with fast crystal growth. Those are the daunting challenges in synthesis of nanostructured BFO.

The study presented in this chapter was aimed to develop a delicate method for synthesizing nanostructured $\text{Bi}_2\text{Fe}_4\text{O}_9$ with varied morphologies via combining co-precipitation at a lower temperature (95°C) in the aqueous system with hydrothermal treatment under mild conditions in methanol/water co-solvent system. The nanostructured $\text{Bi}_2\text{Fe}_4\text{O}_9$ obtained would be characterized using the techniques described in Chapter 3. A plausible formation mechanism of the nanostructured $\text{Bi}_2\text{Fe}_4\text{O}_9$ clusters is proposed. The catalytic activity of the nanostructured $\text{Bi}_2\text{Fe}_4\text{O}_9$ clusters were evaluated for visible-light photo-Fenton oxidation, dark Fenton-like oxidation and solar photocatalysis of methyl orange (MO) as the model pollutant. Finally, a mechanistic insight into the multiplex catalytic degradation of a pollutant by the nanostructured $\text{Bi}_2\text{Fe}_4\text{O}_9$ clusters is proposed.

4.2 Experimental

4.2.1 Materials

The materials used in this study have been described in Chapter 3. Additionally, citric acid ($\geq 99.5\%$, Merck), urea (99% , Sigma), methanol (LC grade, Merck), and methyl orange (85% , Sigma) were also used in this study. All the chemicals were of analytical grade and used without further purification.

4.2.2 Synthesis of nanostructured bismuth ferrite clusters

$\text{Bi}_2\text{Fe}_4\text{O}_9$ clusters with cuboid-like shape were prepared via combining low-temperature co-precipitation with hydrothermal treatment, as illustrated in Figure 4.1. Typically, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (1.21 g) and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (2.02 g) were completely dissolved in 2 mL of 2 M HNO_3 and citric acid (3.2 g) was dissolved in 5 mL of water, respectively. A transparent solution could be obtained after mixing them together in a

Teflon vessel. Then, 33 mL of 12 M NaOH was instantly added into the solution with vigorous stirring. After stirring for 1 h, the Teflon vessel containing the deep-brown slurry was transferred to an oil bath and heated at 95°C with constant stirring. After 12 h, the reaction was cooled down naturally to room temperature. The precipitate (BFO nanoparticles) was collected and washed using water until pH ~10, followed by re-suspended into 6 mL of methanol/water (1:1 v/v) co-solvent by ultrasonication for 10 min. Thereafter, the suspended precipitate was surface-modified by addition of citric acid solution (0.6 g dissolved into 3.5 mL of the co-solvent) to promote its dispersion (noted as “precursor”). Then, 3.82 g of urea was dissolved in 7 mL of the co-solvent at 65°C in water bath, which was then added slowly into the precursor with continuous stirring at room temperature. After 120 min, the dispersion was transferred into a 50-mL Teflon-lined stainless steel autoclave and heated at 200°C for 20 min in an electric oven. After the autoclave reaction chamber was cooled down naturally to room temperature, the product was collected and washed thoroughly with water followed by absolute ethanol. At last, the final product was dried in a vacuum oven at 65°C overnight followed by calcination at 250°C for 1 h under N₂ atmosphere to remove the residual citric acid. For comparison, Bi₂Fe₄O₉ clusters with cube-like shape and plate-like shape were also prepared through adjusting the reaction time of the hydrothermal treatment to 10 min and 60 min, respectively. Additionally, the as-prepared BFO nanoparticles were used to prepare Bi₂Fe₄O₉ via conventional calcination method. The reactions conditions are the ramping rate of 5°C min⁻¹, and temperature of 200-700°C, and holding time of 20 min to 24 h.

4.2.3 Characterization

The material characterization techniques have been introduced in Chapter 3. In addition, the materials were further characterized using X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra Spectrometer, Al-Ka at 1486.7 eV, 15 kV voltage, 10 mA emission current) and UV-vis diffuse reflectance spectroscopy (DRS, UV-9000, Metash). The specific surface area was calculated using the Brunauer-Emmet-Teller (BET) equation through N₂ adsorption-desorption isotherm (Quantachrome, Quadrasorb SI).

Figure 4.1. Schematic illustration of the evolution mechanism of cuboid-like nanostructured $\text{Bi}_2\text{Fe}_4\text{O}_9$ clusters through a delicate synthesis included a low-temperature co-precipitation in water system and a hydrothermal treatment in co-solvent system: (1)-(2) formation of Bi/Fe-citrate complexes; (2)-(3) formation of Bi/Fe hydroxide; (3)-(4) formation of BFO NPs; (4)-(5) removal of excessive citrate and formation of citrate-stabilized BFO NPs; (5)-(6) formation of cuboid-like $\text{Bi}_2\text{Fe}_4\text{O}_9$ clusters

4.2.4 Catalytic evaluation

The catalytic performances of the resulted $\text{Bi}_2\text{Fe}_4\text{O}_9$ clusters were evaluated through visible-light photo-Fenton oxidation, Fenton-like reaction (dark) and solar photocatalysis, respectively. Methyl orange (MO) is used as the model pollutant. Throughout the experimental runs, the pH of the reaction system was rather constant at circumneutral value (~ 6.5). Typically, the desired amount of the catalyst (0.5 g L^{-1}) was added into 50 mL of solution containing 5 mg L^{-1} of MO followed by continuous

stirring for 1 h in dark to achieve adsorption-desorption equilibrium. Thereafter, for the visible-light photo-Fenton oxidation experiment, the suspension was added with 1 mmol of H_2O_2 (20 mM) and then illuminated with visible light (420-630 nm) using a solar simulator (Newport, 150 W Xenon arc lamp, one sun, polycarbonate filter for UV cut-off). A certain amount of solution was drawn out from the reaction vessel at each designated time interval. After the catalysts were separated, the supernatant solutions were analyzed for UV-vis absorption at ~ 464 nm using UV-vis spectrometer (SHIMADZU, UV-1800). For the Fenton-like reaction, the experiments were carried out in dark with addition of 3 mmol H_2O_2 . The reactions for the solar photocatalysis were carried out with solar irradiation from the solar simulator without adding H_2O_2 .

Figure 4.2. SEM image of BFO nanoparticles.

4.3 Results and discussion

4.3.1 Formation process of nanostructured $\text{Bi}_2\text{F}_4\text{O}_9$ clusters

A plausible evolution of $\text{Bi}_2\text{Fe}_4\text{O}_9$ clusters with a regular morphology is depicted in Figure 4.1. Previous study as reported in Chapter 3 has demonstrated that $\text{Bi}_2\text{F}_4\text{O}_9$ has the ability of self-assembled growth. In the present study, citric acid was introduced to control the crystal growth of $\text{Bi}_2\text{F}_4\text{O}_9$ through the induced steric hindrance effect. As shown in Figure 4.1 (water system), Bi/Fe mixed solution (transparent light yellow) will form trinuclear Bi/Fe-citrate complexes (transparent brown) through interaction between citric acid and Bi/Fe ions, followed by transformation to Bi/Fe hydroxides (dark brown) after adding the strong base (NaOH). The resulted hydroxides with abundant citrate surfactants will undergo a dehydration process at a low temperature of

95°C. Due to the steric hindrance effect induced by citrate ions, yellow-brown BFO nanoparticles (BFO NPs) without self-assembled growth could be formed (Figure 4.1(4)), as revealed by the SEM and XRD analyses (Figure 4.2 and 4.3 respectively).

Figure 4.3. XRD pattern of BFO nanoparticles with perovskite and mullite crystalline phases.

Figure 4.4. SEM images of $\text{Bi}_2\text{Fe}_4\text{O}_9$ at different ratios of methanol/water by volume for hydrothermal treatment processes (conditions: holding 20 min at 200°C). (a) 100:0 v/v, (b) 0:100 v/v, (c) 1:4 v/v, (d) 1:1 v/v, (e) 4:1 v/v

In order to promote the crystal growth or self-assembled aggregation of BFO NPs to form an unique morphology or nanostructure, it is crucial that the citrate-stabilized BFO NPs further undergo hydrothermal treatment in the methanol/water co-solvent system. In this treatment process, the effect of the different solvent ratios (methanol/water) on the preparation of BFO was investigated as well. As shown in

Figure 4.4, the prepared $\text{Bi}_2\text{Fe}_4\text{O}_9$ could be cube-like and pad-like shape with the reaction system of methanol and water, respectively. When the reaction system was replaced by co-solvent systems with the different ratios of methanol to water (i.e., 1:4, 1:1, or 4:1 v/v), the prepared $\text{Bi}_2\text{Fe}_4\text{O}_9$ will become cuboid-like shapes with a minor particle size change. As shape-directing agents, the citric acid plays an important role in tuning nanostructured morphologies. As shown in Figure 4.1 (co-solvent system), the citrate-stabilized BFO NPs will undergo small-group self-assembled aggregation under the control of the amount of citrate surfactants (Figure 4.1(5)). Subsequently, in the presence of urea under hydrothermal conditions at 200°C , the aggregated BFO NPs can be further reformed into nanoplates (~ 25 nm) after undergoing crystal dissolution and re-growth processes. The formed nanoplates tend to aggregate together through subsequent decomposition of citrate surfactants and their self-organization. Finally, unlike previous studies which commonly used hard templates (Liu et al. 2013, Vigderman et al. 2012), the well-suspended deep-yellow $\text{Bi}_2\text{Fe}_4\text{O}_9$ clusters with a regular morphology were obtained under mild conditions in the presence of citrate acid (Figure 4.1(6)).

Figure 4.5. SEM images of nanostructured $\text{Bi}_2\text{Fe}_4\text{O}_9$ clusters with different morphologies of cube-like (a and b), cuboid-like (c and d) and plate-like (e and f) shapes.

4.3.2 Characteristics of nanostructured $\text{Bi}_2\text{Fe}_4\text{O}_9$ clusters

The as-prepared nanostructured $\text{Bi}_2\text{Fe}_4\text{O}_9$ can form different morphologies through changing the aging time of their hydrothermal treatment with delicate control of the

entire synthesis processes (Figure 4.5). A plausible reason is that the effect of citrate molecules on the different crystal faces could change during the hydrothermal process, which contributed to the final morphologies/nanostructures of materials (Chen et al. 2011, Zhang et al. 2007). As shown in Figure 4.5, the SEM images show three regular morphologies such as “cube-like” (a and b), “cuboid-like” (c and d), and “plate-like” (e and f) shapes. Figure 4.5a and b exhibit well synthesized cube-like $\text{Bi}_2\text{Fe}_4\text{O}_9$ and its size has the side length of around 400-450 nm. In Figure 4.5c and d, a standard cuboid-like morphology has the side length of ~ 230 nm and height of ~ 600 nm with great uniformity and narrow size distribution. In Figure 4.5e and f, the morphology of $\text{Bi}_2\text{Fe}_4\text{O}_9$ displays a square plate-like shape. This structure has the typical length of ~ 380 nm and thickness of ~ 80 nm. It seems that $\text{Bi}_2\text{Fe}_4\text{O}_9$ with regular morphologies are composed of subunits (Figure 4.5b, d and f). For the detailed information, further investigations were carried out via transmission electron microscopy (TEM).

Figure 4.6. TEM images and corresponding SAED patterns (inset) for nanostructured $\text{Bi}_2\text{Fe}_4\text{O}_9$ clusters of cube-like (a), cuboid-like (b) and plate-like (c) shapes.

The corresponding TEM images further confirm the morphologies for the as-prepared $\text{Bi}_2\text{Fe}_4\text{O}_9$ (Figure 4.6). In addition, the TEM images display a mass-thickness contrast observed as the dark and light around the edge of the as-prepared samples, implying that the as-prepared $\text{Bi}_2\text{Fe}_4\text{O}_9$ with regular morphologies are consisted of smaller units (crystals). The selected area electron diffraction (SAED) patterns of the as-prepared samples are shown in Figure 4.6 (inset). The SAED patterns reveal that the as-prepared $\text{Bi}_2\text{Fe}_4\text{O}_9$ are the poly-crystalline materials, indicating the obtained $\text{Bi}_2\text{Fe}_4\text{O}_9$ with different morphologies are present as clusters. The as-prepared $\text{Bi}_2\text{Fe}_4\text{O}_9$ clusters with nanostructured cube-like, cuboid-like and plate-like morphologies are hereafter referred as NSC- $\text{Bi}_2\text{Fe}_4\text{O}_9$, NSCC- $\text{Bi}_2\text{Fe}_4\text{O}_9$ and NSP- $\text{Bi}_2\text{Fe}_4\text{O}_9$, respectively.

Figure 4.7. UV-vis absorption spectra and Kubelka-Munk transformed reflectance spectra of NSC- $\text{Bi}_2\text{Fe}_4\text{O}_9$, NSCC- $\text{Bi}_2\text{Fe}_4\text{O}_9$ and NSP- $\text{Bi}_2\text{Fe}_4\text{O}_9$ samples, and the representative well suspension of nanostructured $\text{Bi}_2\text{Fe}_4\text{O}_9$ clusters (NSCC- $\text{Bi}_2\text{Fe}_4\text{O}_9$) in ethanol/water co-solvent (a). Nitrogen adsorption-desorption isotherms (b). XRD patterns of NSC- $\text{Bi}_2\text{Fe}_4\text{O}_9$, NSCC- $\text{Bi}_2\text{Fe}_4\text{O}_9$ and NSP- $\text{Bi}_2\text{Fe}_4\text{O}_9$ samples (c).

The optical properties of $\text{Bi}_2\text{Fe}_4\text{O}_9$ clusters were investigated by using UV-vis diffuse reflectance spectroscopy (DRS). As shown in Figure 4.7a (inset), well-suspended $\text{Bi}_2\text{Fe}_4\text{O}_9$ in ethanol/water (1:1 v/v) co-solvent exhibit deep-yellow color. The color of the as-prepared sample implies that $\text{Bi}_2\text{Fe}_4\text{O}_9$ clusters have the capability of visible light absorption. Additionally, Figure 4.7a displays that the as-prepared samples (i.e., NSC- $\text{Bi}_2\text{Fe}_4\text{O}_9$, NSCC- $\text{Bi}_2\text{Fe}_4\text{O}_9$ and NSP- $\text{Bi}_2\text{Fe}_4\text{O}_9$) exhibit similar photo-absorption abilities in the visible-light region from 400 to 700 nm. It further confirmed that $\text{Bi}_2\text{Fe}_4\text{O}_9$ clusters have a remarkable light absorption in the visible-light region. The corresponding optical bandgaps are calculated by the Kubelka-Munk function shown in Figure 4.7a (inset). The results show that the as-prepared samples have a similar optical bandgap about 2.1 eV, implying that $\text{Bi}_2\text{Fe}_4\text{O}_9$ clusters can function as visible-light photocatalysts. The above results indicate that nanostructured $\text{Bi}_2\text{Fe}_4\text{O}_9$

clusters with various morphologies have remarkable photoresponse properties under visible-light irradiation. On the other hand, the surface areas of the as-prepared samples (i.e., NSC-Bi₂Fe₄O₉, NSCC-Bi₂Fe₄O₉ and NSP-Bi₂Fe₄O₉) were investigated using nitrogen adsorption-desorption measurements (Figure 4.7b). All three samples exhibit type III isotherms with a hysteresis loop. The corresponding BET surface areas are 2.21, 3.31 and 8.55 m² g⁻¹, respectively. The surface area of the NSP-Bi₂Fe₄O₉ sample (8.55 m² g⁻¹) is larger than that of the bulk (0.53 m² g⁻¹) and flower-like (4.3 m² g⁻¹) BFO (Park et al. 2005, Sun et al. 2009).

The crystalline phases of Bi₂Fe₄O₉ clusters were confirmed by XRD analysis. As shown in Figure 4.7c, the XRD patterns of the as-prepared NSC-Bi₂Fe₄O₉, NSCC-Bi₂Fe₄O₉ and NSP-Bi₂Fe₄O₉ samples with high intensities of diffraction peaks indicate that the as-prepared samples are ternary BFO with high crystallinity. They are mainly composed of mullite BFO (Bi₂Fe₄O₉, JCPDS PDF 04-009-6352) (Kostiner and Shoemaker 1971). In particular, the NSC-Bi₂Fe₄O₉ and NSP-Bi₂Fe₄O₉ samples also contained a small fraction of perovskite BFO (BiFeO₃, JCPDS PDF 04-014-1679) (Ravindran et al. 2006). It is estimated by Rietveld analysis that the BiFeO₃ were present at the percentages of 7.04, 1.28 and 9.40% in NSC-Bi₂Fe₄O₉, NSCC-Bi₂Fe₄O₉ and NSP-Bi₂Fe₄O₉ samples respectively (TOPAS V4.1). All of them have no observable characteristic diffraction peaks corresponding to sillenite BFO (Bi₂₅FeO₄₀, JCPDS PDF 01-073-9538) (Infante and Carrasco 1986). There are no obvious evidences of impurities such as separated phases, i.e., Bi₂O₃ (01-074-2351) (Gattow and Schutze 1964), hematite Fe₂O₃ (01-088-2359) (Catti et al. 1995) and magnetite Fe₃O₄ (04-009-8443) (Okudera et al. 1996). The phase purity analysis of BFO has been discussed in detail in Chapter 3 (see Figure 3.4). Without the hydrothermal treatment, the composition for crystalline phases of BFO becomes different. As compared with the samples treated with hydrothermal, BFO formed without hydrothermal treatment was mainly consisted of BiFeO₃ (Figure 4.3).

Figure 4.8a shows that pure Bi₂Fe₄O₉ could be prepared via pretreatment of BFO NPs with calcination temperature set at 700°C. There is some minor effect of the holding time on synthesis of Bi₂Fe₄O₉ using a longer reaction time when the temperature was controlled under 700°C (Figure 4.8b). However, the prepared Bi₂Fe₄O₉ have the poor morphology and particle size distribution with micro-scaled sizes (Figure 4.9). Besides, a relatively pure Bi₂Fe₄O₉ could not be formed when the holding time was decreased

to 20 min (see Figure 4.8b, there is coexisting BiFeO_3 phase). In contrast to the above results, there is clear indication that the proposed delicate synthesis method with hydrothermal treatment is beneficial to produce $\text{Bi}_2\text{Fe}_4\text{O}_9$ with nano-scaled sizes under mild conditions as discussed in section 4.3.1. However, it must be treated with caution using hydrothermal treatment because BFO phase is changeable easily among its different crystalline phases (Catalan and Scott 2009). As shown in Figure 4.7c, the relative pure $\text{Bi}_2\text{Fe}_4\text{O}_9$ (i.e., the NSCC- $\text{Bi}_2\text{Fe}_4\text{O}_9$ sample) could be obtained in well-controlled conditions in which the aging time of hydrothermal treatment should be set at 10 to 60 min under this delicate synthesis process.

Figure 4.8. XRD patterns marked with major characteristic peaks of the prepared BFO under different thermal pretreatment temperatures with conditions of ramping rate of 5°C min^{-1} and holding time of 24 h (a). XRD patterns of the prepared BFO under the different thermal pretreatment holding times with conditions of ramping rate of 5°C min^{-1} and temperature of 700°C (b).

Figure 4.9. SEM image of the prepared $\text{Bi}_2\text{Fe}_4\text{O}_9$ at temperature of 700°C for 24 h.

The properties of $\text{Bi}_2\text{Fe}_4\text{O}_9$ clusters were further investigated by energy dispersive X-ray (EDX) microanalysis and X-ray photoelectron spectroscopy (XPS) analyses. Figure 4.10 shows the EDX elemental distribution mappings of Bi, Fe and O within the NSCC- $\text{Bi}_2\text{Fe}_4\text{O}_9$ sample. As compared with the SEM image of NSCC- $\text{Bi}_2\text{Fe}_4\text{O}_9$, it clearly shows that the elemental distributions of Bi, Fe and O within the as-prepared NSCC- $\text{Bi}_2\text{Fe}_4\text{O}_9$ are uniform. The EDX analysis indicates a high degree of uniformity in elemental distributions for NSCC- $\text{Bi}_2\text{Fe}_4\text{O}_9$, and implies that the nanostructured $\text{Bi}_2\text{Fe}_4\text{O}_9$ clusters with different morphologies could be produced using the synthesis processes adopted in this study.

Figure 4.10. SEM image of NSCC- $\text{Bi}_2\text{Fe}_4\text{O}_9$ sample (a) and the corresponding EDX elemental distribution mappings of Bi (a1), Fe (a2) and O (a3).

Figure 4.11a exhibits the full XPS spectra of the as-prepared NSCC-Bi₂Fe₄O₉. It is clearly shown that all the standard photoelectron peaks of the NSCC-Bi₂Fe₄O₉ sample, i.e., Fe 2p, Bi 4p, O 1s, Bi 4d, C 1s and Bi 4f, are present. These results match well with that of the EDX analysis in which the C1s peak probably come from the residual carbon in the organic compound. High resolution spectra of Bi 4f, Fe 2p and O 1s are shown in Figure 4.11bi to biii. The Thermo Advantage V5.945 is used to analyze XPS deconvolution. The characteristic peaks of Bi 4f_{5/2} and Bi 4f_{7/2} at ~163.8 eV and ~158.5 eV (Figure 4.11bi) are attributed to the spin-orbit splitting of the Bi 4f components, which are in good agreement with the Bi³⁺ species. Figure 4.11bii presents the characteristic peaks of Fe 2p such as Fe 2p_{1/2} (~725.44 eV) and Fe 2p_{3/2} (~711.43 eV), corresponding to Fe³⁺ species. There are no obvious reduced states of Fe such as Fe²⁺ and Fe⁰. The as-prepared NSCC-Bi₂Fe₄O₉ shows that the characteristic peak of O 1s is located at ~530.22 eV, which can be attributed to the O 1s binding energy of O²⁻ in the lattice. All of them are consistent with the reported literature (An et al. 2013, Sun et al. 2013a, Wu et al. 2010a).

Figure 4.11. XPS survey scan spectra of NSCC-Bi₂Fe₄O₉ (a) and its high resolution spectra of Bi4f (bi), Fe2p (bii) and O1s (biii).

4.3.3 Performance of nanostructured Bi₂Fe₄O₉ clusters in degradation of MO

Heterogeneous catalysis is beneficial for catalyst separation and recovery, thus avoiding production of the secondary waste stream in the treated water. However commonly the degradation efficiency of heterogeneous catalysis is relatively weaker compared to the homogeneous system (Contentin et al. 2013, Gawande et al. 2013). To improve heterogeneous catalysis, a novel catalyst which possesses multiplex catalytic activities is required in water treatment. Herein, the performances of the as-prepared nanostructured Bi₂Fe₄O₉ samples with multiplex catalytic activities in heterogeneous visible-light photo-Fenton oxidation, Fenton-like reaction in the dark and solar photocatalysis are investigated. The investigations on the degradation of MO as a model organic pollutant were carried out at pH ~6.5. Figure 4.12a shows the degradation of MO as a function of irradiation time with the three as-prepared samples in the presence of H₂O₂ and visible-light illumination (420-630 nm). In the absence of the catalysts, the degradation of MO was insignificant (< 3% over 3 h) even with H₂O₂ addition and visible-light illumination. In contrast, a rapid decrease in the concentration of MO was observed in the presence of the catalysts (i.e., NSC-Bi₂Fe₄O₉, NSCC-Bi₂Fe₄O₉ and NSP-Bi₂Fe₄O₉), indicating that the nanostructured Bi₂Fe₄O₉ samples can effectively promote visible-light photo-Fenton oxidation. Figure 4.12a (inset) displays the discoloring of MO solution as the reaction proceeds in the presence of the NSP-Bi₂Fe₄O₉ sample and H₂O₂, suggesting that the chromophoric structure of MO was effectively decomposed. The degradation efficiencies of MO in 80 min and the corresponding apparent degradation rate constants (k_{app}) are summarized in Table 4.1. Typically, the kinetics of the degradation process follows a pseudo-first-order kinetic model, $\ln(C/C_0) = -k_{app}t$, where k_{app} is the apparent degradation rate constant, and C_0 and C are the concentrations of MO at initial and at a certain reaction time t , respectively. As shown in Table 4.1, the degradation efficiencies of MO reach 92, 99 and 99% for the as-prepared NSC-Bi₂Fe₄O₉, NSCC-Bi₂Fe₄O₉ and NSP-Bi₂Fe₄O₉ samples, respectively. According to the corresponding k_{app} values, the catalytic activities for visible-light photo-Fenton oxidation are significantly influenced by the Bi₂Fe₄O₉ morphologies, in the order of NSP-Bi₂Fe₄O₉ > NSCC-Bi₂Fe₄O₉ > NSC-Bi₂Fe₄O₉.

Figure 4.12. Performance of nanostructured $\text{Bi}_2\text{Fe}_4\text{O}_9$ clusters for degradation of MO through (a) visible-light photo-Fenton oxidation, (b) dark Fenton-like oxidation and (c) solar photocatalysis. Efficiency of reused nanostructured $\text{Bi}_2\text{Fe}_4\text{O}_9$ clusters in degradation of MO through different catalytic oxidation processes (d).

Table 4.1. Kinetic constants and removal efficiencies using nanostructured $\text{Bi}_2\text{Fe}_4\text{O}_9$ at various catalytic oxidation processes

AOPs	Photo-Fenton oxidation (visible)			Fenton-like reaction (dark)			Solar photocatalysis		
Sample	R^a (%)	k_{app} ($\times 10^{-3} \text{ min}^{-1}$)	R^2	R^b (%)	k_{app} ($\times 10^{-3} \text{ min}^{-1}$)	R^2	R^b (%)	k_{app} ($\times 10^{-3} \text{ min}^{-1}$)	R^2
NSC- $\text{Bi}_2\text{Fe}_4\text{O}_9$	92	22.7	0.981	96	13.6	0.997	54	3.5	0.982
NSCC- $\text{Bi}_2\text{Fe}_4\text{O}_9$	99	36.2	0.963	77	6.7	0.971	60	4.2	0.972
NSP- $\text{Bi}_2\text{Fe}_4\text{O}_9$	99	41.2	0.995	78	7.1	0.968	56	3.9	0.961

^a Removal rate of MO at 80 min.

^b Removal rate of MO at 240 min.

Figure 4.12b shows the degradation of MO through heterogeneous Fenton-like reaction in the dark. In the absence of nanostructured $\text{Bi}_2\text{Fe}_4\text{O}_9$ samples, the degradation efficiency of MO is insignificant ($\leq 2\%$ in 4 h) even with H_2O_2 addition. In contrast, a rapid decrease in the MO concentration was observed in the presence of the nanostructured $\text{Bi}_2\text{Fe}_4\text{O}_9$ samples. The degradation efficiencies of MO are 96, 77

and 78% for the Fenton-like reaction with NSC-Bi₂Fe₄O₉, NSCC-Bi₂Fe₄O₉ and NSP-Bi₂Fe₄O₉, respectively (Table 4.1). These results demonstrate that the nanostructured Bi₂Fe₄O₉ samples exhibit remarkable catalytic performance in Fenton-like reaction even at pH ~6.5, which can be more economical and eco-friendly than that of traditional Fenton/Fenton-like catalysis which has to be applied at pH ≤ 3.

Figure 4.12c shows that the degradation efficiency of MO can be negligible (≤ 0.5%) in the absence of the catalysts through solar photolysis. In contrast, with the presence of the NSC-Bi₂Fe₄O₉, NSCC-Bi₂Fe₄O₉ and NSP-Bi₂Fe₄O₉, 54, 60 and 56% of MO could be degraded, respectively. The results suggest that the nanostructured Bi₂Fe₄O₉ samples are photocatalytic and their photocatalytic activities are similar, regardless of their morphologies.

Chemical stability of a catalyst is important for its practical application. The corresponding investigation was carried out and the results show that the nanostructured Bi₂Fe₄O₉ clusters exhibit good reusability potential (Figure 4.12d). The slight reduction in the efficiencies of the degradation of MO might be due to the residual MO (or by-products) accumulated on the catalyst surface. During the processes of visible-light photo-Fenton oxidation, dark Fenton-like reaction and solar photocatalysis, small amounts of the reaction solutions were also drawn out and analyzed with inductively coupled plasma-optical emission spectrometer (ICP-OES, Perkin Elmer Optima 2000DV). The results display that the concentrations of the ion species (i.e., Bi³⁺, Fe³⁺/Fe²⁺) are quite low (< 0.1 mg L⁻¹ or corresponding to < 0.02% (w/w) of the added amount of catalysts). The above results indicate that the as-prepared Bi₂Fe₄O₉ clusters have good chemical stability and reusability.

4.3.4 Proposed mechanism

Figure 4.13 illustrates a plausible mechanism of catalytic degradation of organic pollutants by the nanostructured Bi₂Fe₄O₉ clusters. The interconversion between fictitious Bi₂Fe₄O₉(Fe³⁺) and Bi₂Fe₄O₉(Fe²⁺) cations takes place within the nanostructured Bi₂Fe₄O₉ clusters along with both formation of reactive oxygen species (ROSs) and consumption of H₂O₂. For the concept of fictitious Bi₂Fe₄O₉(Fe³⁺) and Bi₂Fe₄O₉(Fe²⁺) cations within as-prepared samples, it has been discussed in Chapter 3 and will be further demonstrated in this chapter. Without solar illumination (night time), ROSs such as HO₂[•] and HO[•] are formed in which the reaction pathway can be

described by Eqs (4.1)-(4.2).

Figure 4.13. Schematic illustration of multiplex catalytic activities for nanostructured $\text{Bi}_2\text{Fe}_4\text{O}_9$ clusters.

Typically, the reaction as shown by the dash-dotted blue line has a lower reaction rate constant because of the rate-limiting step (Eq (4.1a)) with a reaction rate constant of $0.001\text{-}0.01 \text{ M}^{-1} \text{ s}^{-1}$ (Rigg et al. 1954, Walling and Goosen 1973). Under solar illumination, $\text{HO}^\bullet$ instead of the $\text{HO}_2^\bullet$ will be formed (day time, $\lambda < 420 \text{ nm}$). This reaction pathway (Eq (4.3)) is shown below:

The reaction is defined as photo-Fenton oxidation, which can be successfully excited under visible-light irradiation and effectively enhance the interconversion between $\text{Bi}_2\text{Fe}_4\text{O}_9(\text{Fe}^{3+})$ and $\text{Bi}_2\text{Fe}_4\text{O}_9(\text{Fe}^{2+})$ along with the abundant formation of $\text{HO}^\bullet$ (Hu et al. 2014, Koppenol et al. 1978, Pignatello 1992b, Pignatello et al. 1999). The irradiated

nanostructured Bi₂Fe₄O₉ clusters can be also photoexcited whereby the photogenerated electrons and holes are formed followed by charge migration to the surface of catalyst. Typically, the electrons will react with the adsorbed O₂ to form O₂^{•-} and further transform to autogenerated H₂O₂ and HO[•], while the holes are utilized to form autogenerated O₂ (Fujishima and Zhang 2006, Hu et al. 2014). The corresponding reactions are shown in Eqs (4.4)-(4.10).

4.4 Conclusions

This study has developed a delicate approach combining co-precipitation at a lower temperature in the aqueous system with hydrothermal treatment under mild conditions in methanol/water co-solvent system for synthesis of novel nanostructured Bi₂Fe₄O₉ clusters with controllable morphologies (i.e., cube-, cuboid-, plate-like). This technique has successfully hindered the fast crystal growth of the Bi₂Fe₄O₉. The nanostructured Bi₂Fe₄O₉ clusters consist of smaller crystals of 25 nm with grain sizes ranging from 80 to 600 nm in any dimensions. The aging time of hydrothermal treatment has a significant effect on both the resulting morphology and the crystalline phases of the nanostructured Bi₂Fe₄O₉ clusters. The pure mullite structure of the nanostructured Bi₂Fe₄O₉ cluster was successfully obtained. The resulted nanostructured Bi₂Fe₄O₉ clusters exhibit good crystallinity, uniform elemental distributions, high chemical stability, good dispersity and reusability. They have remarkable multiplex catalytic activities in the degradation of organic pollutants. Hence, there is a significant potential for the application of the nanostructured Bi₂Fe₄O₉ clusters in environmental pollution control as well as other fields.

Chapter 5 2D Composites — Low-temperature synthesis of graphene/Bi₂Fe₄O₉ NPs composites for synergistic adsorption-photocatalytic degradation of pollutant

5.1 Introduction

In Chapter 3, single-crystalline Bi₂Fe₄O₉ nanopads with exposing facet (001) prepared via a facile low-temperature co-precipitation method can effectively degrade BPA in water. In Chapter 4, nanostructured Bi₂Fe₄O₉ clusters with various morphologies synthesized by a delicate process can efficiently degrade MO in aqueous system. The multiplex catalytic activities of Bi₂Fe₄O₉ in the degradation of organic pollutants under simulated visible light at circumneutral pH were investigated. However, the Bi₂Fe₄O₉ had much lower photocatalytic activity compared to Fenton-like or photo-Fenton oxidation (Table 4.1 and Figure 3.11). To enhance photocatalytic performance of Bi₂Fe₄O₉, one effective strategy is to suppress the recombination of photogenerated e⁻/h⁺ pairs (as described in Chapter 2).

As mentioned in Chapter 2, previous studies have revealed that the composites comprising photocatalyst and carbon allotropes such as carbon nanotube (CNT) (Gao et al. 2009) and graphene oxide (GO) (Perera et al. 2012) can suppress the charge recombination as well as enhance adsorption capacity of pollutants on the composites. Both of them can effectively enhance photocatalytic performance of the pristine photocatalyst. As compared with CNT, graphene has a monolayer of sp² bonded carbon structure (Novoselov et al. 2004) with better electrical conductivity (Wu et al. 2009), larger specific surface area (higher adsorption capacity) (MacHado and Serp 2012, Stoller et al. 2008) and higher electronic carrier mobility (Bolotin et al. 2008). In general, GO can be exfoliated from natural graphites by the Hummers' method (Hummers and Offeman 1958) but it exhibits a poor electrical conductivity due to a lack of an extended π -conjugated orbital carbon (Park and Ruoff 2009). The electrical conductivity of GO can be efficiently improved through converting GO into reduced graphene oxide (rGO) (Gómez-Navarro et al. 2007). In recent years, there are only a few reports on the syntheses and applications of graphene/BFO composites in water treatment (An et al. 2013, Sun et al. 2013a). To the knowledge of the author, there is

no study on evaluation of low-temperature synthesized $\text{Bi}_2\text{Fe}_4\text{O}_9/\text{rGO}$ for removal of pollutants through solar photocatalysis.

In this study, a facile low-temperature co-precipitation method was used to prepare $\text{Bi}_2\text{Fe}_4\text{O}_9/\text{GO}$ composite (BFO249/GO) and $\text{Bi}_2\text{Fe}_4\text{O}_9/\text{rGO}$ composite (BFO249/rGO), respectively. A systematic characterization was carried out for the pristine materials (BFO249, GO and rGO) and their composites. The performance of BFO249, BFO249/GO and BFO249/rGO for BPA removal was investigated through evaluating their respective BPA adsorption and photocatalytic degradation. To further evaluate the practical application of BFO249/rGO, its photocatalytic activities at different wavebands (i.e., full solar spectrum, UV, and visible-light regions of solar spectrum) were investigated. Moreover, the influences of pH and inorganic anions on the photocatalytic efficiencies of BFO249/rGO under solar irradiation were investigated. The mechanism for BFO249/rGO-based photocatalysis is proposed.

5.2 Experimental

5.2.1 Chemicals

Natural graphite powder with 325 mesh (> 99.9%, Alfa Aesar), concentrated sulfuric acid (98%, Sigma-Aldrich), potassium permanganate (99%, Sigma-Aldrich), sodium nitrate (99%, Sigma-Aldrich), hydrochloric acid (37%, Sigma-Aldrich), and sodium borohydride (98%, Alfa Aesar). All the chemicals were of analytical grade and used without further purification. All other materials used in this study have been described in Chapter 3.

5.2.2 Materials synthesis

5.2.2.1 Synthesis of GO nanosheets

GO was synthesized by a modified Hummers' method (Hummers and Offeman 1958). Initially, a 250-mL beaker containing H_2SO_4 (50 mL, 98%) was kept inside an ice-water bath to maintain the temperature at $< 5^\circ\text{C}$. Then, graphite (1.0 g) and NaNO_3 (0.5 g) were added. After this mixture was stirred for 1 h ($< 5^\circ\text{C}$), KMnO_4 (3 g) was gradually added into the mixture (ensure $< 20^\circ\text{C}$). After that, the mixture was heated to

35°C and maintained for 2 h. The mixture would gradually turn into a gray-brown viscous slurry and then water (30 mL) was added slowly. Then the temperature was increased to 95°C and maintained for another 6 h. Thereafter, the mixture was cooled to room temperature and added with H₂O₂ (10 mL) slowly. The product was collected by filtration and washed thoroughly with water (100 mL) twice, HCl (30 mL, 5%) trice, water (50 mL) twice and absolute ethanol (30 mL) twice in order. Finally, the GO cake was dried using a vacuum freeze dryer at -44°C for further use.

5.2.2.2 Synthesis of Bi₂Fe₄O₉ nanoparticles

Bi₂Fe₄O₉ nanoparticles were synthesized by a co-precipitation method under a low temperature of 95°C. The synthesis procedure is as described in Chapter 3. Bi₂Fe₄O₉ powder (~1.112 g) could be obtained by drying in a vacuum freeze dryer (denoted as BFO249).

5.2.2.3 Synthesis of Bi₂Fe₄O₉/GO composites

Bi₂Fe₄O₉/GO composite was synthesized by a one-pot co-precipitation method under low temperature. Typically, the as-prepared GO (50 mg) was dispersed into H₂O (5 mL) with ultrasonication for 30 min. The precursor containing Bi/Fe sources was pre-prepared as mentioned in Chapter 3 (Section 3.2.2). In this study, half of the precursor was re-dispersed into NaOH (40 mL, 12 M) and the dispersion was then added into the GO solution followed by ultrasonication for 3 h. In the experiments, the corresponding mass ratio of GO to Bi₂Fe₄O₉ was 4.5 wt%. Thereafter, the mixture was transferred into a Teflon beaker and heated at 95°C in an oil bath. To produce composites, the aging time was set to 36 h. The final product (denoted as BFO249/GO4.5) was collected and washed following the same procedure as for BFO249.

5.2.2.4 Synthesis of Bi₂Fe₄O₉/rGO composites

The Bi₂Fe₄O₉/rGO composite was synthesized by a similar method as for BFO249/GO4.5 but with the use of a reducing agent to convert GO to rGO. GO (50 mg) was added into H₂O (5 mL) and ultrasonicated for 30 min to obtain a homogeneous dispersion. After that, NaBH₄ (50 mg) dissolved in H₂O (5 mL) was

added followed by ultrasonication for 2 h. The resulting rGO was collected by centrifugation followed by re-dispersion into water. The rGO was separated via filtration and further rinsed with water. The final rGO was re-dispersed into water with a total volume of 5 mL. Another half of the precursor was re-dispersed into NaOH (40 mL, 12 M) and the dispersion was then added into the rGO solution followed by ultrasonication for 3 h. The subsequent steps were similar to the synthesis of BFO249/GO4.5, and the final product was denoted as BFO249/rGO4.5.

5.2.3 Materials characterization

The material characterization techniques have been introduced in Chapter 3. Additionally, the point of zero charge (pH_{pzc}) was measured using Zetasizer (Malvern Nano-ZS). The elemental compositions were analyzed by analysis of the digestates of the materials with Perkin Elmer Series II 2400 CHNS/O elementary analyzer. The photoluminescence (PL) emission spectra were recorded by a Perkin Elmer LS55 fluorescence spectrophotometer. The thickness of material was quantified using atomic force microscopy (AFM) (Park Systems XE-100 equipped with Non-contact Cantilever NCHR 10M, the sample was prepared on mica substrate).

5.2.4 Photocatalytic degradation experiments

The photocatalytic degradation (PCD) of BPA was carried out using a solar simulator (150 W Xe arc lamp, Newport, USA) photoreactor with air bubbling. The light intensity measured at the water level is *ca.* 1000 W m^{-2} (SP 1065, Janco Impex). Dichroic mirrors were employed to control wavebands in specific ranges of 280-400 nm for UV region and 420-630 nm for visible-light region. The corresponding light intensities are *ca.* 52 and 409 W m^{-2} (measured with Accumax XRP-3000 radiometer and SP 1065 respectively). Typically, the catalyst (50 mg, corresponds to 0.5 g L^{-1}) was added into solution (100 mL) containing 10 mg L^{-1} of BPA, which is distinguished from the experiment mentioned in Chapter 3 (in which the catalyst loading is 1.5 g L^{-1} , and the BPA concentration is 15 mg L^{-1}). The analytical method in this study has been described as in Chapter 3. The total organic carbon (TOC) remaining in the solution was measured using a Shimadzu ASI-V TOC analyzer. The pH values at the beginning and the end of reaction were rather consistent at approximately pH 6.5. To investigate the effect of pH on the efficiency of BPA removal, the solution pH was adjusted using

0.25 M H₂SO₄ or 0.5 M NaOH. The concentration of SO₄²⁻ was estimated to be < 1 mM at pH 3. The influences of anions on PCD of BPA were studied by introducing various salts such as NaCl, NaNO₃, Na₂SO₄ and NaHCO₃, respectively, into the BPA solution. The concentrations of the various anions were controlled at 5 mM and they had no significant effects on the solution pH (remained at around circumneutral pH values). To evaluate the formation of different reactive oxygen species (ROS) during photocatalytic degradation of BPA, different scavengers of ROS, namely sodium oxalate (Na₂C₂O₄), benzoquinone (BQ), sodium azide (NaN₃), ascorbic acid (AsA) and dimethyl sulfoxide (DMSO), were added into the BPA solution. Various scavengers can selectively consume the different kinds of ROS during photocatalytic reaction, which leads to the inhibition of BPA degradation.

5.3 Results and discussion

5.3.1 GO and rGO

As shown in Figure 5.1a, the as-prepared GO exhibits a transparent 2D structure with wrinkles inside and curls along the edges due to the presence of lattice defects, and with a size of ~2 μm. Figure 5.2a shows that the thickness of GO sheets evaluated by Atomic Force Microscopy (AFM) is *ca.* 1.3 nm, which is slightly larger than that of the previous reports due to the presence of functional groups such as -O-, -COOH and -OH (Liu et al. 2010b). While the rGO sheet displays similar characteristics to that of GO sheet but its thickness is reduced to *ca.* 1.12 nm (Figure 5.2b), which could be due to the elimination of functional groups and reduction of epoxy groups (-O-). GO and rGO can be dispersed in water via appropriate ultrasonication. Their dispersions with certain solid contents (1 wt%) appear yellowish and black color (Figure 5.1b), respectively. The corresponding UV-vis spectra of the diluted dispersions of GO and rGO were analyzed with UV-vis spectrometer (UV-1800, Shimadzu). As shown in Figure 5.1c, GO has an absorption peak at 228 nm, attributed to π - π^* transition of the aromatic C-C ring and a weak absorption peak at 305 nm due to n- π^* transition of C=O bond. In contrast, only an intensive peak is observed for rGO with the red-shift from 228 to 264 nm, indicating that π -conjugated structure has been greatly extended through the deoxygenation and elimination of functional groups (Zhu et al. 2010).

Figure 5.1. TEM image of GO (a). 1 wt% dispersion of GO (left) and rGO (right) in water (b). UV-vis absorption spectra of GO and rGO dispersions (c).

Figure 5.2. AFM images of GO and rGO sheets and the corresponding two line scans.

5.3.2 Morphology and microstructure

Figure 5.3a and b exhibit that BFO249 has a uniform particle size distribution with a size of 5-7 nm. Figure 5.3b shows the HRTEM image of BFO249, in which the lattice spacings of individual BFO249 nanoparticles are 0.29, 0.27 and 0.24 nm, corresponding to the crystal planes of (220), (112) and (022), respectively. It indicates that the as-prepared BFO249 by low-temperature co-precipitation synthesis belongs to the mullite BFO (i.e., $\text{Bi}_2\text{Fe}_4\text{O}_9$) (Kostiner and Shoemaker 1971).

Figure 5.3. TEM and HRTEM images of BFO249 (a and b), BFO249/GO4.5 (c and d) and BFO249/rGO4.5 (e and f).

Figure 5.3c exhibits the microstructure of BFO249/GO. BFO249 nanoparticles were sparsely deposited on the 2D GO. It is obvious that BFO249 nanoparticles tend to accumulate along the edge of GO, which is similar to the previously reported TiO_2/GO composites (Zhang et al. 2009). This is possibly due to the steric hindrance that is induced by the surface functional groups of GO (this will be discussed later in this chapter). The HRTEM image (Figure 5.3d) shows that the deposited BFO249 nanoparticles have an average size of 5-6 nm and the corresponding clear lattice with a spacing of 0.24 nm, which can be assigned to the crystal plane of (022). The TEM image of BFO249/rGO4.5 (Figure 5.3e) exhibits that many BFO249 nanoparticles were well deposited on the rGO with a uniform size of 4-5 nm. Figure 5.3f shows the

clear crystallized nanoparticles of BFO249 with lattice spacings of 0.25, and 0.22 nm, which correspond to facets of (310), and (212). Overall, the TEM analyses provide strong evidences that BFO249/GO and BFO249/rGO were successfully synthesized. The deposited $\text{Bi}_2\text{Fe}_4\text{O}_9$ nanoparticles in BFO249/GO and BFO249/rGO have good crystallinity and their particle sizes are similar.

5.3.3 Structure and textural properties

Figure 5.4 shows XRD patterns of GO, BFO249, BFO249/GO4.5 and BFO249/rGO4.5. The diffraction peak for GO at 2θ of 10.8° (scan 1) can be attributed to the interlamellar water trapped between piled GO nanosheet stacks (Dikin et al. 2007), which are loose structure and can be easily destroyed by the intercalation of nanoparticles during synthesis of graphene-based composites (Liu et al. 2000). Hence, there is no observable characteristic diffraction peak of GO in the XRD pattern for the resulting composites (scans 3 and 4).

Figure 5.4. XRD patterns of GO (1), BFO249 (2), BFO249/GO4.5 (3) and BFO249/rGO4.5 (4).

As shown in Figure 5.4, the as-prepared three catalysts (i.e., BFO249, BFO249/GO4.5 and BFO249/rGO4.5) are mainly consisted of $\text{Bi}_2\text{Fe}_4\text{O}_9$ because all of them exhibit the characteristic diffraction peaks at 2θ of 14.8° , 28.2° , 28.9° , 29.8° , 30.9° , 33.7° , 47.1° and 56.7° , which are attributed to the different facets of the standard mullite BFO

along (001), (121), (211), (002), (220), (112), (141) and (332) (JCPDS PDF 04-009-6352) (Kostiner and Shoemaker 1971). The XRD analysis further confirms the high crystallinity of BFO249 nanoparticles and their effective intercalation into the GO and rGO stacks, which is in good agreement with the TEM observation. On the other hand, two additional diffraction peaks of $\text{Bi}_{25}\text{FeO}_{40}$ are present in the XRD pattern of BFO249 (scan 2), which correspond to facets of (310) and (321) (JCPDS PDF 01-073-9538) (Infante and Carrasco 1986). The $\text{Bi}_{25}\text{FeO}_{40}$ phase will disappear while preparing the graphene-supported $\text{Bi}_2\text{Fe}_4\text{O}_9$ composites (scans 3 and 4).

Table 5.1 shows that the atomic composition of GO is 46.1% C, 0.82% H, 51.27% O, and 1.81% S by weight, suggesting that a large quantity of oxygen epoxide groups exist on the GO surface (Liu et al. 2000). The functional groups, including epoxy and other functional groups, were identified later using FT-IR analysis. BFO249 consists of 47.15% Bi, 27.59% Fe, 23.87% O, 0.54% C, and 0.85% H by weight. The carbon source is probably due to the ethanol residue remained in the post-treatment process. As compared with BFO249 (containing 0.54% C), the percentages of C in BFO249/GO4.5 and BFO249/rGO4.5 increased to 1.67% and 1.78%, respectively. The increase in the percentages of C is ascribed to the GO or rGO in the composites.

Table 5.1. Physicochemical properties of GO and various catalysts

	Element composition (wt%)							PS ^c (nm)	SSA ^e (m ² g ⁻¹)	Eg ^f (eV)	<i>d</i> -spacing ^d (nm)	Adsorption isotherm		
	Bi ^a	Fe ^a	C ^b	H ^b	N ^b	S ^b	O ^b					<i>S</i> _{max} (mg g ⁻¹)	<i>K</i> _{ads} (L mg ⁻¹)	<i>R</i> ²
GO	0	0	46.1	0.82	0	1.81	51.27	-	N.D.*	-	-	-	-	-
BFO249	47.15	27.59	0.54	0.85	0	0	23.87	5-7	142.5	2.3	0.243, 0.266, 0.286	0.74 ± 0.02	0.16 ± 0.04	0.934
BFO249/GO4.5	47.14	26.99	1.67	0.71	0	0	23.49	5-6	-	-	0.240	1.72 ± 0.08	0.19 ± 0.04	0.963
BFO249/rGO4.5	47.02	27.19	1.78	0.98	0	0	23.03	4-5	-	-	0.216, 0.221, 0.250	3.95 ± 0.28	0.20 ± 0.02	0.844
P25	-	-	-	-	-	-	-	-	58.1	3.2	-	-	-	-

*S*_{max}: Maximum adsorption capacity.

*K*_{ads}: Langmuir adsorption constant.

^a Metal elements were analyzed by ICP-OES.

^b Non-metal elements were analyzed by CHNS/O Analyzer.

^{c, d} Particle size and crystal lattice were measured through HRTEM.

^e Specific surface area was determined by the BET equation.

^f Band gap energy was derived using Kubelka-Munk function.

* N.D.: Not detected.

5.3.4 Surface properties

The various surface functional groups of GO are clearly displayed in Figure 5.5 (spectrum 4), including C-O stretching vibration at 1050 cm^{-1} , phenolic C-OH stretching at 1224 cm^{-1} , carboxyl C-OH stretching at 1387 cm^{-1} and C=O stretching vibration of carboxyl at 1724 cm^{-1} , which are attributed to the typical functional groups of GO (e.g., -O-, -COOH, and -OH) (Cao et al. 2010a, Titelman et al. 2005, Xu et al. 2008).

Figure 5.5. FT-IR transmittance spectra of BFO249 (1), BFO249/GO4.5 (2), BFO249/rGO4.5 (3), and GO (4).

The peak at 1618 cm^{-1} can be assigned to the C=C skeletal vibration of unoxidized graphitic domains and/or the H-O-H bending band of the adsorbed H_2O (Liu et al. 2010b, Xu et al. 2008). Obviously, some characteristic peaks of GO are present in the FT-IR spectrum of BFO249/rGO4.5 with position shift and intensity alteration (Figure 5.5, spectrum 3), including carboxyl C-OH stretching from 1387 to 1342 cm^{-1} , C=C skeletal vibration from 1618 to 1565 cm^{-1} and C=O stretching vibration of carboxyl from 1724 to 1629 cm^{-1} , which are possibly caused by the chemical bonding between $\text{Bi}_2\text{Fe}_4\text{O}_9$ and rGO, such as Fe-O-C and/or Bi-O-C (Li et al. 2014, Sakthivel and Kisch 2003, Sun et al. 2014, Zhang et al. 2009). In contrast, only one characteristic peak of GO for C=C skeletal vibration is present in the FT-IR spectrum of BFO249/GO4.5 with position shift from 1618 to 1567 cm^{-1} and intensity diminution (Figure 5.5,

spectrum 2). Figure 5.5 (spectrum 1) exhibits characteristic peaks for BFO249 at 448 cm^{-1} (Fe-O stretching vibrations of the FeO_6 octahedra), 494 and 524 cm^{-1} (O-Fe-O bending vibrations of the FeO_4 tetrahedra), 634 cm^{-1} (a broad peak simultaneously assigned to Fe-O stretching vibrations of the FeO_4 tetrahedra, Fe-O-Fe bending stretching with Fe on the both FeO_4 tetrahedral sites, and Bi-O vibration in the BiO_6 octahedra), and 811 cm^{-1} (Fe-O stretching vibrations of the FeO_4 tetrahedra). The FT-IR results of BFO249 is similar to the described in Chapter 3 (Section 3.3.5) After individually combining with GO and rGO, although the peak's positions of BFO249 are present in the FT-IR spectra of BFO249/GO4.5 and BFO249/rGO4.5 that have no significant change, the corresponding intensities have changed considerably, especially for BFO249/rGO4.5 (Figure 5.5, spectrum 3). It further confirms that there is a possibility of formation of chemical bonding between $\text{Bi}_2\text{Fe}_4\text{O}_9$ and rGO (Sakthivel and Kisch 2003).

5.3.5 Optical properties

Figure 5.6a shows the UV-vis diffuse reflectance spectra (DRS) of Evonik P25, BFO249, BFO249/GO4.5, BFO249/rGO4.5 and GO, as well as the Kubelka-Munk transformed reflectance spectrum of BFO249 (inset). P25 displays a steep absorption in the UV region at $\lambda < 400$ nm, while BFO249 with a bandgap of *ca.* 2.3 eV (Figure 5.6a, inset) shows a broad absorption in the visible-light range. It indicates that BFO249 has the potential for being used as a visible light-responsive photocatalyst. On the other hand, GO exhibits a very broad absorption in the wavelength ranging from 250 to 850 nm (Figure 5.6a, spectrum 5), which can contribute to the more effective light absorption of BFO249/rGO4.5 and BFO249/GO4.5 than that of BFO249 (Ren et al. 2007, Zhang et al. 2009). As shown in the figure, the order of visible light absorption ability follows $\text{BFO249/rGO4.5} > \text{BFO249/GO4.5} > \text{BFO249}$. PL spectroscopy can be used to investigate the effect of GO and rGO on the anti-recombination of e^-/h^+ pairs (An et al. 2013, Yu et al. 2003). Figure 5.6b exhibits PL spectra of BFO249, BFO249/GO4.5 and BFO249/rGO4.5 with a maximum emission at $\lambda = 556$ nm under an excited wavelength of 372 nm. BFO249/GO4.5 displays a strong PL emission intensity which is similar to that of BFO249, whereas the BFO249/rGO4.5 exhibits a significantly lower PL emission intensity, indicating

that rGO is more effective than GO in suppressing e^-/h^+ recombination because rGO can efficiently transport e^- compared to non-conductive GO.

Figure 5.6. (a) UV-vis absorption spectra of P25 (1), BFO249 (2), BFO249/GO4.5 (3), BFO249/rGO4.5 (4) and GO (5), and Kubelka-Munk transformed reflectance spectra of BFO249 (inset). (b) PL spectra (excitation at 372 nm) of BFO249 (1), BFO249/GO4.5 (2) and BFO249/rGO4.5 (3).

5.3.6 Adsorption characteristics of various photocatalysts

The adsorption of a pollutant on a photocatalyst is an important prerequisite for a synergistic adsorption-photocatalytic degradation process. Figure 5.7a shows the adsorption isotherms of BFO249, BFO249/GO4.5 and BFO249/rGO4.5 for BPA, while their maximum adsorption capacities ($S_{\max}$) and Langmuir adsorption constants (K_{ads}) are shown in Table 5.1. BFO249, BFO249/GO4.5 and BFO249/rGO4.5 exhibit $S_{\max}$ of 0.74, 1.72 and 3.95 mg g^{-1} , respectively. It is obvious that graphene-supported $\text{Bi}_2\text{Fe}_4\text{O}_9$ show higher $S_{\max}$ especially for BFO249/rGO4.5, which could be due to enhancement of surface area and formation of π - π stacking interaction between the skeletal structure of graphene in composites and hydrophobic BPA molecules. In addition, the adsorption can be increased with the increase of rGO wt% in the composites, almost proportionally (Figure 5.7b). Theoretically, graphene has a surface area of $\sim 2600 \text{ m}^2 \text{ g}^{-1}$ (Stoller et al. 2008), which can significantly contributes to the increased density of the active sites of BFO249/GO4.5 and BFO249/rGO4.5. On the other hand, benzene ring in BPA has the ability to induce π - π stacking interaction with the skeletal structure of graphene (Perera et al. 2012). However, it seems that π - π stacking interaction is limited for BFO249/GO4.5 because of excessive functional groups of GO (as discussed in Section 5.3.4), which causes BFO249/GO4.5 to show a

lower adsorption of BPA than that of BFO249/rGO4.5. On the other hand, Figure 5.7a (inset) shows that 1 h in dark is sufficient to achieve adsorption-desorption equilibrium between BPA and the catalysts, which would be adopted as adsorption equalization time before commencement of photocatalysis experiments.

Figure 5.7. Adsorption isotherms and time-dependent adsorption (inset) of BPA for BFO249, BFO249/GO4.5 and BFO249/rGO4.5 (a). Adsorption isotherms for BPA of BFO249, BFO249/rGO4.5 and BFO249/rGO9.0 (b).

5.3.7 Photocatalytic degradation and proposed mechanism

5.3.7.1 Comparison of photocatalytic performance of various catalysts

Figure 5.8a shows the photocatalytic performances of different catalysts in BPA removal through visible-light photocatalysis. In the absence of the catalysts, the degradation of BPA through photolysis can be negligible (< 0.4% over 3 h). However, the degradation of BPA can be enhanced significantly in the presence of the catalysts. Their photocatalytic activities are in the order of BFO249/rGO4.5 > BFO249/GO4.5 > BFO249. The corresponding degradation efficiencies of BPA and TOC in 3 h (Figure 5.8a, inset) are 62%/47%, 44%/29% and 33%/19% respectively. The BPA removal by BFO249/rGO4.5 can reach up to 74% through its enhanced adsorption capacity and synergistic adsorption-photocatalytic degradation process (Figure 5.8a). Obviously, the graphene-supported BFO249 catalysts especially Bi₂Fe₄O₉/rGO composite exhibits significantly higher photocatalytic activities than that of the pristine BFO249. However, the excess loading of rGO can inhibit photocatalytic activity of BFO249 because the excessive rGO could cause attenuation of light penetration throughout the

photoreactor (Figure 5.8b). The photocatalytic activity of BFO249/rGO4.5 and BFO249/GO4.5 show *ca.* 2.0 and 1.3 times higher than that of BFO249, respectively.

Figure 5.8. (a) Photocatalytic performance of different catalysts in BPA removal through visible-light photocatalysis and the corresponding removal efficiencies of BPA and TOC at 3 h (inset). (b) Photocatalytic performance of BFO249, BFO249/rGO4.5 and BFO249/rGO9.0 in BPA removal through visible-light photocatalysis.

The higher photocatalytic activity of BFO249/rGO4.5 compared with BFO249/GO4.5 could be ascribed to the synergistic adsorption-photocatalytic degradation process, which includes suppression of recombination of photogenerated e^-/h^+ pairs and

enhanced adsorption of hydrophobic BPA by π - π stacking interaction. The photogenerated e^- can be transferred from the conduction band of $\text{Bi}_2\text{Fe}_4\text{O}_9$ to the rGO followed by transfer along the extended π -conjugated aromatic domain and electron storage on the surface of rGO (Lightcap et al. 2010). GO is inferior to rGO in the e^-/h^+ separation and BPA adsorption because of its excessive functional groups and poor electron conductivity. The discrepancy between rGO and GO is also reflected by their varying PL spectra (Figure 5.6b) and UV-vis absorption spectra (Figure 5.1c). To a lesser extent, the increased photocatalytic activities of BFO249/rGO4.5 and BFO249/GO4.5 compared to BFO249 could be attributed to the increased specific surface area and density of adsorption sites for BPA.

Figure 5.9. Visible photocatalytic performance of BFO249/rGO4.5 in BPA removal with the presence of different scavengers of ROS at 3 h (a). Visible photocatalytic degradation of BPA via BFO249/rGO4.5 in the presence of different scavengers of ROS (b).

Electron spin resonance (ESR) is a spectroscopic technique used for tracking the generated reactive oxygen species (ROS) directly (He et al. 2014), while employing scavenger is an indirect method to evaluate the kinds of ROS during the photocatalytic process (Wang and Lim 2011, Zou et al. 2013). A variety of scavengers, such as $\text{Na}_2\text{C}_2\text{O}_4$, BQ, NaN_3 , AsA and DMSO could be used to determine h^+ , $\text{O}_2^{\bullet-}$, $^1\text{O}_2$, H_2O_2 and $\text{HO}^\bullet$, respectively (Abellán et al. 2009, Gekko et al. 2012, Granados-Oliveros et al. 2011, Li et al. 2011a, Savory et al. 2011, Styliadi et al. 2004). BPA degradation efficiency at $t=3$ h and the corresponding degradation at different time intervals in the presence of different radical scavengers are presented in Figure 5.9a and b, respectively. As shown in the figures, there are different degrees of inhibitory effect on BPA degradation with the different radical scavengers indicating the presence of the corresponding ROS (i.e., $\text{O}_2^{\bullet-}$, $^1\text{O}_2$, H_2O_2 and $\text{HO}^\bullet$) in BFO249/rGO4.5-based photocatalytic process. Remarkable inhibitions of BPA degradation occurred with the addition of BQ, oxalate or NaN_3 , while for AsA and DMSO only marginal effects were observed. This indicates that the $\text{O}_2^{\bullet-}$ can be scavenged by BQ is the predominant oxidative species. The $\text{O}_2^{\bullet-}$ is produced by the reduction of diatomic O_2 molecules which can be introduced into the photoreactor through aeration or autogenic production via oxidation of H_2O by h^+ . The contribution of h^+ in $\text{O}_2^{\bullet-}$ generation is supported by the observation of the moderate reduction in the percent BPA removal when h^+ scavenger ($\text{Na}_2\text{C}_2\text{O}_4$) was added.

Herein, a possible mechanism to illustrate the photocatalysis induced by BFO249/rGO4.5 with $\text{Bi}_2\text{Fe}_4\text{O}_9$ bandgap of 2.3 eV is proposed (Figure 5.10). Under visible light irradiation, the photoexcited $\text{Bi}_2\text{Fe}_4\text{O}_9$ could generate e^-/h^+ pair. The valence band hole (VBH) and conduction band electron (CBE) of $\text{Bi}_2\text{Fe}_4\text{O}_9$ are located at 1.3 V and -1.0 V vs NHE, respectively (Sun et al. 2009). The VBH of $\text{Bi}_2\text{Fe}_4\text{O}_9$ is too weak to oxidize H_2O to $\text{HO}^\bullet$ at pH ~6.5 ($E^\circ(\text{HO}^\bullet/\text{H}_2\text{O}) = 2.27$ V vs NHE at pH 7) but can oxidize H_2O into O_2 ($E^\circ(\text{O}_2/\text{H}_2\text{O}) = 0.83$ V vs NHE, pH 7). The autogenerated (and introduced) O_2 can be reduced by CBE to form $\text{O}_2^{\bullet-}$ as well as other reactive oxygen species (ROSs), as illustrated in Eqs (5.1) to (5.5), with the corresponding redox potentials vs NHE at pH 7 of $E^\circ(\text{O}_2/\text{O}_2^{\bullet-}) = -0.28$ V, $E^\circ(\text{O}_2/\text{HO}_2^\bullet) = -0.037$ V, $E^\circ(\text{HO}_2^\bullet/\text{H}_2\text{O}_2) = 0.94$ V, and $E^\circ(\text{H}_2\text{O}_2/\text{H}_2\text{O}) = 1.35$ V (Bielski et al. 1985, Fujishima and Zhang 2006, Wardman 1989).

Figure 5.10. Schematic illustration of proposed photocatalytic mechanism of BFO249/rGO4.5.

This ROS contributes to BPA removal in the entire scheme of photocatalysis (Figure 5.10). Their production upon photoexcitation of $\text{Bi}_2\text{Fe}_4\text{O}_9$ is accelerated as a result of e^- transfer to rGO which promotes efficient e^-/h^+ separation. The separated e^- could migrate along the surface of rGO depending on the extended π -conjugated aromatic domain and then could be stored temporarily in rGO. Subsequently, the e^- on the surface of both $\text{Bi}_2\text{Fe}_4\text{O}_9$ and rGO could be trapped by the adsorbed O_2 to form $\text{O}_2^{\bullet-}$. Besides $\text{O}_2^{\bullet-}$, $\text{HO}_2^\bullet$, H_2O_2 and $\text{HO}^\bullet$, singlet oxygen ($^1\text{O}_2$) could be also produced by the photoexcited BFO249/rGO4.5 which transfers the photonic energy from solar light to excite the triplet oxygen ($^3\text{O}_2$) and to $^1\text{O}_2$, as illustrated by Eq. (5.6) with $E^\circ(^1\text{O}_2/\text{O}_2^{\bullet-}) = 0.65 \text{ V vs NHE at pH 7}$ (Wardman 1989). This mechanism is analogous to $^1\text{O}_2$ generation by photosensitizers (Ishii 2012). The $^1\text{O}_2$ has a higher energy and can react with complex molecules such as DNA, proteins and lipids (Ishibashi et al. 2000) and has a possibility to degrade BPA as well (Wang and Lim 2011).

5.3.7.2 Photocatalytic degradation kinetics

BPA photocatalytic degradation process in aqueous BFO249/rGO4.5 suspension is similar to the conventional heterogeneous photocatalytic reactions which involves

several steps (as mentioned in Section 2.1 in Chapter 2). In this study, BPA molecules would diffuse into the surface of composites to occupy active sites where ROS is generated. Consequently, through interacting with ROS, BPA is degraded. Thereafter, the products would desorb from the interface of composites and diffuse into the bulk fluid phase. Typically, the kinetics of above-mentioned process follows Langmuir-Hinshelwood model (Eqs. (5.7)-(5.8)) (Herrmann 2005):

$$r = k\theta = k\left(\frac{KC}{1+KC}\right) \quad (5.7)$$

$$r = -\frac{dC}{dt} = -\frac{kKC}{1+KC} \quad (5.8)$$

where r is the reaction rate, θ is the substrate coverage, k is the intrinsic reaction rate constant, K is the Langmuir adsorption equilibrium constant, C is the BPA concentration and t is the reaction time. As the initial concentration for BPA is 0.044 mM (i.e., $KC \ll 1$), the Langmuir-Hinshelwood model can be simplified into a pseudo-first-order kinetics model (Eqs. (5.9)-(5.10)).

$$r = -\frac{dC}{dt} = -kKC \quad (5.9)$$

$$\ln\left(\frac{C}{C_0}\right) = -kKt = -k_{app}t \quad (5.10)$$

where k_{app} is the apparent degradation rate constant and C_0 is the initial concentration of BPA. The values of k_{app} for various photocatalytic conditions are summarized in Table 5.2.

Table 5.2. Kinetic constants and PCD efficiencies using BFO249/rGO4.5 at various photocatalytic conditions

Light source	pH	Catalyst load (g L ⁻¹)	BPA (mg L ⁻¹)	Anion (5 mM)	k_{app} ($\times 10^{-3}$ min ⁻¹)	R^2	PCD at 3 h (%)	TOC at 3 h (%)
Visible light	6.5 $\pm$ 0.1	0.5	10	-	6.1	0.955	62	47
UV	6.5 $\pm$ 0.1	0.5	10	-	8.6	0.951	73	63
Solar light	6.5 $\pm$ 0.1	0.5	10	-	9.2	0.951	76	66
Solar light	3.0 $\pm$ 0.1	0.5	10	-	8.8	0.969	75	-
Solar light	5.0 $\pm$ 0.1	0.5	10	-	10.1	0.955	79	-
Solar light	9.0 $\pm$ 0.1	0.5	10	-	9.3	0.942	75	-
Solar light	6.6 $\pm$ 0.1	0.5	10	Cl ⁻	8.2	0.942	71	-
Solar light	6.6 $\pm$ 0.1	0.5	10	NO ₃ ⁻	7.8	0.949	70	-
Solar light	6.6 $\pm$ 0.1	0.5	10	SO ₄ ²⁻	8.5	0.942	72	-
Solar light	6.8 $\pm$ 0.1	0.5	10	HCO ₃ ⁻	6.3	0.928	60	-

5.3.7.3 Effect of different wavebands of solar irradiation

The efficiencies of BFO249/rGO4.5 in BPA removal and TOC reduction under different wavebands of solar irradiation were investigated. As shown in Figure 5.11,

the PCD efficiencies at different wavebands are in the order of full solar spectrum > UV region of solar spectrum (280-400 nm) > visible-light region of solar spectrum (420-630 nm). The corresponding removal efficiencies of BPA and TOC for the three different wavebands after 3 h are 76%/66%, 73%/63% and 62%/47%, respectively. Their corresponding k_{app} values are compared in Table 5.2. The finding indicates that BFO249/rGO4.5 can effectively utilize the UV and visible-light wavebands of solar irradiation for photocatalysis.

Figure 5.11. Effect of different wavebands under solar irradiation on photocatalytic degradation of BPA and the corresponding removal of BPA and TOC at 3 h (inset).

Figure 5.12. Effect of different pH value on photocatalytic degradation of BPA and the corresponding adsorption status after 1 h (inset).

5.3.7.4 Effect of pH

There is no significant effect of pH on the PCD efficiencies of BPA through BFO249/rGO4.5-based photocatalysis under full solar spectrum (Figure 5.12), and the corresponding k_{app} at different pH values are shown in Table 5.2. There is a moderate influence of pH on the adsorption behavior of BPA on BFO249/rGO4.5 (Figure 5.12, inset), which exhibits a trend of pH 3 > pH 5 > pH 6.5 > pH 9. BPA can display three forms of molecules, namely, undissociated molecules (BPA), BPA monoanion (BPA^-) and BPA dianion (BPA^{2-}), with pK_{a1} and pK_{a2} values of 9.6 and 10.2 respectively (Kosky et al. 1991). However, the fractions of BPA^- and BPA^{2-} can be negligible at acidic and circumneutral pH range. Besides, BPA has two negative oxygen atoms at the hydroxyl groups because they carry four lone pairs of electrons (Lin et al. 2009). Therefore, adsorption of BPA to BFO249/rGO4.5 is relatively lower at pH 6.5 because the composite catalyst shows a slightly net negative charge (its $pH_{pzc} = \sim 6.2$ measured by zeta potential). With the decrease of pH from 6.5 to 3, BPA adsorption can be moderately enhanced (Figure 5.12, inset) because the catalyst develops a net positive charge at $pH < pH_{pzc}$. At a high pH such as pH 9 ($> pH_{pzc}$), BPA adsorption decreases because of net negative charge of catalyst and formation of bisphenolate anions (BPA^- & BPA^{2-}). However, a high pH favors formation of $O_2^{\cdot-}$ (over $HO_2^{\cdot}$) and 1O_2 (Eqs. (5.2) and (5.6)). There is no significant effect of pH on the degradation of BPA. Based on experimental findings, the favorable pH for BPA degradation by BFO249/rGO4.5 is around pH 5.

5.3.7.5 Effect of anions

Since some common inorganic anions such as sulfate, chloride, nitrate, and bicarbonate are omnipresent in the natural aqueous systems and wastewater effluents, it is imperative to investigate their influence on the PCD of the target pollutant. As shown in Figure 5.13, the anions at 5 mM exhibit different degrees of inhibitory effects on the PCD of BPA with BFO249/rGO4.5. Their inhibitory effects follow the order of bicarbonate > nitrate $\approx$ chloride $\approx$ sulfate. The corresponding PCD efficiencies at 3 h are 60, 70, 71 and 72% respectively. Since the pH values are constant at ~ 6.6 for all the suspensions and pH has insignificant influence on PCD of BPA (Table 5.2), the most plausible explanation for the varying PCD results is that the

anions exhibit different propensity to scavenge $\text{HO}^\bullet$ and transform into ionic radicals of less reactive than $\text{HO}^\bullet$, as illustrated in Eq. (5.11) (Rincón and Pulgarin 2004).

In addition, the anions will compete with BPA to occupy active sites on the surface of BFO249/rGO4.5, and even form negative charge layers to repel BPA molecules. Herein, the adsorption abilities of BPA to BFO249/rGO4.5 in the presence of different anions were investigated. As shown in Figure 5.13 (inset), it is evident that the adsorption removal of BPA in the presence of the corresponding anions (5 mM) is less than that occurred in the solution without the anions. It has been reported that the interactions between catalysts and some of anions (e.g., nitrate, chlorine and sulfate) through *van der Waals'* force are reversible except for bicarbonate (Hu et al. 2004) (which causes the highest inhibition of BPA degradation). The $-\text{OH}$ group of bicarbonate might interact with the functional groups on the surface of BFO249/rGO4.5 through formation of hydrogen bonding. Since hydrogen bonding is stronger than that of *van der Waals*, it results in irreversible bicarbonate adsorption and thus decreases the available adsorption site for BPA.

Figure 5.13. Effect of different common anions on photocatalytic degradation of BPA and the corresponding adsorption status after 1 h (inset).

5.4 Conclusions

In this study, a facile low-temperature co-precipitation method has been successfully developed to prepare BFO249/GO4.5 and BFO249/rGO4.5. Both of them show 2D

composite structures, higher crystallinities for the deposited $\text{Bi}_2\text{Fe}_4\text{O}_9$ nanoparticles, and possible formation of chemical bonds between $\text{Bi}_2\text{Fe}_4\text{O}_9$ and supports (GO or rGO). As compared with the pristine $\text{Bi}_2\text{Fe}_4\text{O}_9$, both of them, especially BFO249/rGO4.5, exhibit improved removal of BPA (74% in 4 h) under visible irradiation through a synergistic adsorption-photocatalytic degradation process. BFO249/rGO4.5 shows a significantly higher PCD efficiency for removal of BPA and TOC under visible-light region of solar spectrum because rGO can enhance photocatalytic activity of $\text{Bi}_2\text{Fe}_4\text{O}_9$ through transferring and storing conduction band e^- , and adsorbing hydrophobic BPA. BFO249/rGO4.5 can exhibit photocatalytic activity at the different wavebands of the solar spectrum. It shows a better PCD efficiency of BPA in a weak acidic solution. The predominant ROS for the BPA removal was identified to be the $\text{O}_2^{\bullet-}$. Among the omnipresent aqueous anions, bicarbonate shows the larger inhibition on BPA removal with BFO249/rGO4.5 while sulfate, chloride and nitrate do not cause much interference effect. This study signifies that the $\text{Bi}_2\text{Fe}_4\text{O}_9/\text{rGO}$ can be used for photocatalytic degradation of organic pollutants in real water under sunlight and indoor visible light.

Chapter 6 Multiphase Composites — Cuboid-like $\text{Bi}_2\text{Fe}_4\text{O}_9/\text{Ag}$ with graphene wrapping tribrid composites for degradation of pollutant

6.1 Introduction

The results presented in Chapter 5 reveal that $\text{Bi}_2\text{Fe}_4\text{O}_9/\text{rGO}$ composites can be used for photocatalytic degradation of organic pollutants under sunlight and indoor visible light. However the removal rate of pollutants is not fast enough (e.g., 74% BPA in 4 h in the presence of 0.5 g L^{-1} catalysts). In Chapter 4, BFO as a multi-functional catalyst has remarkable multiplex catalytic activities in the degradation of organic pollutants, which is attributed to the following advantages: It can be used to degrade organic pollutants through (1) photo-Fenton oxidation under visible-light irradiation, (2) solar photocatalysis, and (3) Fenton-like oxidation with interconversion of $\text{Fe}^{3+}/\text{Fe}^{2+}$ in dark. In this study, the author strives for further enhancement of the photo-Fenton oxidation of $\text{Bi}_2\text{Fe}_4\text{O}_9$ in degradation of organic pollutants along with higher efficiency and a lower catalyst loading.

Noble metal nanoparticles (NPs), e.g., Ag, Au, Pt, exhibit unique properties including surface plasmon resonance (SPR) and excellent electron conductivities, which have been used to enhance the photocatalytic activity of the pristine semiconductors (Awazu et al. 2008, Jiang et al. 2014, Sun et al. 2013b, Zhang et al. 2011a). Extensive efforts for the fabrication of noble metal-decorated photocatalyst have been reported. For example, AgNPs (20-50 nm) decorated ZnO microrods synthesized by a two-step method gave a solar photocatalytic degradation rate of methylene blue (MB) ~ 5.6 times faster than that of ZnO (Deng et al. 2012). AuNPs (~ 5 nm) decorated CeO_2 nanotubes which were fabricated by pulsed laser ablation in liquid showed notably high catalytic activity for degradation of nitrophenol (Zhang et al. 2013a). TiO_2 nanotubes which were decorated with PtNPs of 4-5 nm in diameter exhibited a highly efficient production of H_2 under UV or visible light illumination (Basahel et al. 2014). The enhanced photocatalysis could be attributed to the enhanced light harvesting due to the plasmonic properties of the noble metal NPs and the enhanced charge separation efficiency by their electrical conduction property. However, the efficiency of a

photocatalyst is determined not only by the charge separation of photogenerated electron/hole pairs but also by that of recombination effect.

As described in Chapter 5, graphene or reduced graphene oxide (rGO) can effectively enhance photocatalytic activity of the semiconductors via suppression of photogenerated electron/hole recombination (Hu et al. 2015a, Perera et al. 2012). It has a large surface area of $\sim 2600 \text{ m}^2 \text{ g}^{-1}$ with excellent properties such as physical adsorption, electrical conductivity, electronic carrier mobility and electron storage (Bolotin et al. 2008, Stoller et al. 2008, Wu et al. 2009). Additionally, the Ag-decorated TiO_2 possesses a better photocatalytic activity on the degradation of organic compounds than that of Pt-decorated TiO_2 (Moonsiri et al. 2004). Therefore, it is hypothesized that a tribrid nanoarchitecture of Ag-decorated $\text{Bi}_2\text{Fe}_4\text{O}_9$ with graphene wrapping may significantly enhance the performance of $\text{Bi}_2\text{Fe}_4\text{O}_9$ for the removal of organic pollutants under visible-light irradiation.

The purpose of this study is to develop a tribrid nanocomposites of BFO and to effectively enhance the performance of the pristine $\text{Bi}_2\text{Fe}_4\text{O}_9$ in organic pollutants removal. Ag-decorated BFO (BFO/Ag1) and Ag-decorated BFO with rGO wrapping (BFO/Ag1/rGO) were fabricated via a multi-step synthesis. The characteristics of and the differences between the as-prepared samples were investigated through different characterization techniques. Their performances in water treatment were evaluated through visible-light photo-Fenton oxidation and visible-light photocatalysis in which methylene blue (MB) was employed as the model pollutant. The mechanism of organic pollutants removal using the multi-functional BFO/Ag1/rGO ternary hybrid nanoarchitecture in water treatment is proposed.

6.2 Experimental

6.2.1 Chemical and Materials

The materials used in this study have been described in previous chapters. Additionally, sodium dihydrogen phosphate monohydrate ($\geq 98\%$, Merck), (3-Aminopropyl) trimethoxysilane (ATPES, $\geq 98\%$, Sigma-Aldrich), glutaraldehyde (GA, 25%, Sigma-Aldrich), silver nitrate (99%, Sigma-Aldrich), ammonia solution (25%, Merck), methanol (LC grade, Merck), and methylene blue (95%, Sigma-Aldrich) were used in

this study. All the chemicals were of analytical grade and used without further purification.

6.2.2 Synthesis of GO and cuboid-like $\text{Bi}_2\text{Fe}_4\text{O}_9$ (BFO)

GO was as-synthesized by the modified Hummers' method and the detailed procedures could be found in Chapter 5. The nanostructured $\text{Bi}_2\text{Fe}_4\text{O}_9$ clusters with a cuboid-like shape (denoted as BFO in this study) were prepared using a delicate synthesis process through combining co-precipitation at a lower temperature in water system with hydrothermal treatment in methanol/water co-solvent system. The citric acid was used as an additive during the synthesis of BFO. The detailed procedures were described in Chapter 4.

6.2.3 Synthesis of Ag-decorated BFO

Ag-decorated BFO was prepared by a multi-step synthesis, as illustrated in Figure 6.1. The first step is the fabrication of amino functionalized BFO. BFO (100 mg) dispersed in 170 mL of ethanol was added with 5 mL of ATPES aqueous solution (2%, v/v) with continuous stirring at 30°C for 2 h. The product obtained was collected and washed with ethanol. The following step was fabrication of aldehyde functionalized BFO where the as-obtained amino functionalized BFO was dispersed into 20 mL of phosphate buffer solution (0.02 M) followed by addition of 25 mL of glutaraldehyde (GA) aqueous solution (25%) with stirring at 30°C for 2 h. The product was centrifuged and washed with ethanol/water (50%, v/v). For fabrication of Ag-decorated BFO, the obtained aldehyde-terminated BFO was re-dispersed in 30 mL of ethanol. To AgNO_3 (10 mg) dissolved in 50 mL of water was added a certain amount of ammonia (4%) which induces the conversion of Ag^+ to $[\text{Ag}(\text{NH}_3)_2]^+$ (Figure 6.1). It was mixed with the as-prepared BFO solution under stirring at room temperature for 10 min. The mixture was transferred to a water bath and heated at 80°C. After 40 min, Ag nanoparticles (AgNPs) were successfully decorated on the surface of BFO (Figure 6.1). The product was collected and washed with ethanol/water and absolute ethanol. The final product was dried in a vacuum oven at 65°C overnight followed by calcination at 250°C for 1 h under N_2 atmosphere. The Ag-decorated BFO was denoted as BFO/Ag1. For comparison, 30 and 50 mg of AgNO_3 were used to fabricate additional Ag-decorated BFO samples (denoted as BFO/Ag3 and BFO/Ag5).

6.2.4 Synthesis of Ag-decorated BFO with rGO wrapping

GO (5 mg) and water (20 mL) were added into a blue cap bottle. The mixture was sonicated for 60 min to obtain clear dispersion and was added with NaBH_4 (5 mg) as a reducing agent to induce conversion of GO into rGO (as shown in Figure 5.1) with ultrasonication for 60 min. After that, a certain amount of ammonia (4%) was added to stabilize the negatively charged rGO in water phase. Ag-decorated BFO (BFO/Ag1, 100 mg) dispersed in ethanol (20 mL) was then added into the blue cap bottle. The mixture was stirred continuously for 24 h followed by evaporation in a water bath with constant stirring at 75°C . Thereafter, the concentrated suspension was cooled down naturally to room temperature. The product was collected and washed with ethanol. The final product was then dried in a vacuum oven at 65°C overnight followed by calcination at 250°C for 1 h under N_2 atmosphere. The obtained Ag-decorated BFO with rGO wrapping as shown in Figure 6.1 was denoted as BFO/Ag1/rGO.

Figure 6.1. Schematic illustration of evolution from pure $\text{Bi}_2\text{Fe}_4\text{O}_9$ to Ag-decorated $\text{Bi}_2\text{Fe}_4\text{O}_9$ (via surface modification procedures) and further to Ag-decorated $\text{Bi}_2\text{Fe}_4\text{O}_9$ with rGO wrapping.

6.2.5 Characterization

The material characterization techniques have been introduced in previous chapters. Additionally, the materials were further characterized using UV-vis diffuse reflectance spectroscopy (DRS, UV-2600, SHIMADZU), and thermogravimetric analysis (TGA, PerkinElmer, TGA-4000). The as-prepared samples (i.e., BFO, BFO/Ag1 and

BFO/Ag1/rGO) were evaluated for their performances in photo-Fenton oxidation and photocatalysis under visible-light irradiation ($420 < \lambda < 630$ nm) using methylene blue (MB) as the model pollutant. Typically, the pH of the reaction system was consistent at circumneutral value (~ 6.5) and the desired amount of the catalyst (0.12 g L^{-1}) was added into 50 mL of solution containing 5 mg L^{-1} of MB followed by continuous stirring for 1 h in dark to achieve adsorption-desorption equilibrium. Thereafter, for the photo-Fenton oxidation, the suspension was added with 1 mmol of H_2O_2 (20 mM). For the visible-light photocatalysis, the reactions were carried out in the absence of H_2O_2 but with air bubbling.

6.3 Results and discussion

6.3.1 Characteristics

Figures 6.2 and 6.3 show the SEM and TEM images of the as-prepared nanostructured $\text{Bi}_2\text{Fe}_4\text{O}_9$ clusters (BFO), Ag-decorated BFO (BFO/Ag1) and Ag-decorated BFO with rGO wrapping (BFO/Ag1/rGO). Energy dispersive X-ray (EDX) elemental distribution mappings of Bi, Fe, Ag and O within BFO/Ag1 are shown in Figure 6.2b(1-4), while suspensions in ethanol/water co-solvent of BFO, BFO/Ag1 and BFO/Ag1/rGO are shown in Figure 6.3d.

Figure 6.2. SEM images of (a) pure $\text{Bi}_2\text{Fe}_4\text{O}_9$ (BFO), (b) Ag-decorated $\text{Bi}_2\text{Fe}_4\text{O}_9$ (BFO/Ag1), and (c) Ag-decorated $\text{Bi}_2\text{Fe}_4\text{O}_9$ with rGO wrapping (BFO/Ag1/rGO), and the corresponding EDX elemental distribution mappings of Bi (b1), Fe (b2), Ag (b3), and O (b4) within BFO/Ag1.

Figure 6.2a shows that cuboid-like $\text{Bi}_2\text{Fe}_4\text{O}_9$ has the side length of ~ 230 nm and height of ~ 600 nm consisting of subunits, which was further investigated via transmission

electron microscopy (TEM). As shown in Figure 6.3a, it further confirmed the as-prepared $\text{Bi}_2\text{Fe}_4\text{O}_9$ with cuboid-like morphology. The TEM image also displays that there is a strong contrast between dark and lighter regions within the as-prepared $\text{Bi}_2\text{Fe}_4\text{O}_9$, implying that the cuboid-like $\text{Bi}_2\text{Fe}_4\text{O}_9$ are composed of smaller units (plate-like crystals with size of ~ 25 nm). The selected area electron diffraction (SAED) patterns (inset of Figure 6.3) reveal that the as-prepared $\text{Bi}_2\text{Fe}_4\text{O}_9$ are poly-crystalline, indicating the nanostructured $\text{Bi}_2\text{Fe}_4\text{O}_9$ with a cuboid-like morphology is present as a cluster. Figures 6.2b and 6.3b show the SEM and TEM images of the sample after decoration with AgNPs, in which AgNPs with an average diameter of 9 nm were homogeneously deposited on the surface of BFO. It has been confirmed by the EDX elemental mapping of BFO/Ag1 (Figure 6.2b(3)). In addition, the elemental distributions of Bi, Fe and O within the as-prepared BFO/Ag1 are very uniform.

Figure 6.3. (a) TEM image and the corresponding SAED patterns (inset) of BFO. (b) TEM image of BFO/Ag1. (c) TEM image of BFO/Ag1/rGO. (d) Suspensions in an ethanol/water cosolvent of BFO, BFO/Ag1, and BFO/Ag1/rGO.

The as-synthesized GO exhibit a transparent 2D structure with wrinkles inside and curls, which has a size of ~ 2.7 μm and a thickness of ~ 1.3 nm. The partially reduced

GO (rGO) can be well-dispersed in water with light black color. Due to the extensive π -conjugated structure of rGO, UV-vis spectrum of the diluted dispersion of rGO displays a characteristic absorption peak at 264 nm. The synthesized rGO sheet, as an excellent support and stabilizer, is expected to promote the charge transfer and anti-recombination of electron/hole pairs, and the physical adsorption of organic pollutants. More detailed information on GO/rGO has been described in Chapter 5. Herein, it was used to fabricate BFO/Ag1/rGO via evaporation process in ethanol/water co-solvent system. In Figure 6.2c, the surface of BFO/Ag1 is shown to be wrapped by rGO. The structure of BFO/Ag1/rGO was further characterized by TEM. Figure 6.3c shows a large rGO sheet wrapping on a BFO/Ag1 as well as entanglement with others and a small amount of AgNPs were sparsely deposited on the rGO sheet. Hence, Ag-decorated BFO with rGO wrapping will be beneficial for the function of photocatalysis (Tian et al. 2012). Hence, the results of SEM and TEM characterization provide reasonable evidences that three samples (i.e., BFO, BFO/Ag1, BFO/Ag1/rGO) were successfully prepared. For BFO/Ag1/rGO, rGO might act as “matchmaker” to chemically bond with BFO/Ag1, which will be discussed in detail later. On the other hand, Figure 6.3d displays a clear progression in color change with progression in synthesis. BFO in ethanol/water co-solvent (50%, v/v) exhibit deep-yellow color, indicating it has the capability of visible light absorption. When AgNPs were decorated onto the surface of BFO, the suspension became a brownish color. It further became a light black color after combining with rGO.

The color change possibly reflects that the as-prepared samples have different light absorption in the visible light region. As shown in Figure 6.4a, BFO displays two absorption peaks at ~ 440 and ~ 690 nm and the corresponding optical bandgap is about 2.1 eV (Figure 6.4a, inset). It indicates that BFO have good light harvesting properties under visible-light irradiation and could be used as a visible-light-driven photocatalyst. Ag-decorated BFO (BFO/Ag1) exhibits higher light harvesting with a broad absorption in the visible-light range, which can be attributed to the plasmonic property of AgNPs (Jiang et al. 2014). The light harvesting capability of Ag-decorated BFO can be tailored by controlling the amount of Ag ions added (Figure 6.4b). BFO/Ag1/rGO exhibits the best light absorption ability among the three as-prepared samples, which can be ascribed to the synergistic effect from BFO core, AgNPs and rGO tribrid.

Figure 6.4. (a) UV-vis absorption spectra of BFO, BFO/Ag1 and BFO/Ag1/rGO, and Kubelka-Munk transformed reflectance spectra of BFO (inset). (b) UV-vis absorption spectra of BFO, BFO/Ag1, BFO/Ag3 and BFO/Ag5.

To study the recombination states of electron/hole pairs within the as-prepared samples, the respective photoluminescence (PL) spectra were measured under an excitation wavelength of 372 nm. As shown in Figure 6.5, PL spectra of BFO, BFO/Ag1 and BFO/Ag1/rGO have a maximum emission at $\lambda = 556$ nm. As compared with BFO, BFO/Ag1 shows only a slight decrease in PL emission intensity, whereas BFO/Ag1/rGO displays a significantly lower PL emission intensity. It indicates that rGO with both electron transfer and storage can effectively suppress the recombination of electron/hole pairs during photoexcitation. In contrast, AgNPs can enhance charge separation by serving as an electron reservoir but it also act as a recombination center (Zhang et al. 2011a). Nonetheless, AgNPs effectively extend the migration path of charges with minor loss of electrons/holes, which possibly contributes to the slight decrease in PL emission intensity of BFO/Ag1.

Figure 6.5. Photoluminescence spectra (excitation at 372 nm) of BFO, BFO/Ag1 and BFO/Ag1/rGO.

Figure 6.6. (a) XRD patterns of BFO, BFO/Ag1 and BFO/Ag1/rGO. (b) XRD patterns of BFO/Ag1, BFO/Ag3 and BFO/Ag5 and the corresponding suspension in ethanol/water co-solvent.

The crystalline phases of the as-prepared samples were analyzed by X-ray powder diffraction (XRD). As shown in Figure 6.6a, the XRD pattern of BFO shows all the characteristic diffraction peaks, which can match well with the standard pattern of $\text{Bi}_2\text{Fe}_4\text{O}_9$ (JCPDS PDF 04-009-6352) (Kostiner and Shoemaker 1971). The high intensities of diffraction peaks indicate that the as-prepared BFO has good crystallinity. The peak broadening of the XRD pattern of BFO suggests that it is possibly composed of small nanocrystalline grains, as it is consistent with the TEM results (Figure 6.3a). The peaks of $\text{Bi}_2\text{Fe}_4\text{O}_9$ become noticeably weaker with the incursion of AgNPs and/or rGO, which might contribute to the variation of mass fraction. The characteristic peak of AgNPs cannot be observed in the pattern of BFO/Ag1 because of its lower mass fraction. With the increase in the amount of AgNPs addition, the corresponding

characteristic reflection peak (111) could be detected at $2\theta = 38.2^\circ$ (Figure 6.6b), which is consistent with the literature values (JCPDS PDF 04-0783). On the other hand, the diffraction peak for the as-prepared GO powder can be detected at $2\theta = 10.8^\circ$ (see Figure 5.4 in Chapter 5) which contributes to the interlamellar water trapped between piles GO nanosheet stacks (Dikin et al. 2007), while no characteristic peak of GO can be found in the sample of BFO/Ag1/rGO (Figure 6.6a). The results imply that the partially reduced GO dispersion has been successfully combined with BFO/Ag1.

Figure 6.7. (a) TGA curves of BFO, BFO/Ag1, BFO/Ag1/rGO and GO. (b) TGA curves of BFO/Ag1/rGO.

Thermogravimetric analysis (TGA) is used to examine BFO/Ag1/rGO. As shown in Figure 6.7a, the weight loss profile of GO under dry air atmosphere also exhibits three clear steps (Jiang et al. 2011). The TGA curve shows weight loss from 30 to 105°C because of the physic-sorbed moisture or residual organic solvents on the surface of GO. At the second step from 105 to 600°C, the mass loss is probably due to the decomposition of oxygen-containing groups associated with tiny carbon oxidations leaving the main carbon skeleton of GO (Liu et al. 2000, Szabó et al. 2006). At last, the skeleton of GO composed of aromatic rings is completely decomposed at 730°C. As shown in Figure 6.7b, the profile of the TGA curve of BFO/Ag1/rGO is similar to that of GO with a certain shift. It might contribute to the conversion from GO to rGO and/or the interaction between rGO and BFO/Ag1 within the as-prepared BFO/Ag1/rGO, while it implies a successful composition between rGO and BFO/Ag1 during the synthesis process. Besides, the weight loss of BFO/Ag1/rGO at 105 and 800°C is ~1.1 and ~8.1% (Figure 6.7a, inset). As compared with that of BFO/Ag1, the experimental rGO loading is 4.6% by weight which agrees well with the theoretical

mass fraction of GO (5 mg : 105 mg = 0.048). The weight losses at 800°C are ~5.4 and ~2.7% in BFO and BFO/Ag1 respectively, which can be attributed to the physic-sorbed moisture and residual organics in the as-prepared samples.

Figure 6.8. XPS survey spectra of GO, BFO, BFO/Ag1 and BFO/Ag1/rGO, and the corresponding high-resolution XPS spectra of Ag 3d (a), C 1s (b), Bi 4f (c) and Fe 2p (d).

X-ray photoelectron spectroscopy (XPS) was used to investigate the chemical compositions and chemical binding states within the as-prepared samples. **Figure 6.8** shows the XPS survey spectra of GO, BFO, BFO/Ag1 and BFO/Ag1/rGO, and the corresponding high-resolution XPS spectra of Ag 3d, C 1s, Bi 4f and Fe 2p (Figure 6.8(a-d)). The survey spectra of BFO contain Fe 2p, Bi 4p, O 1s, Bi 4d, C 1s and Bi 4f without impurities. It is indicative of the chemical compositions of Bi, Fe and O within BFO. The additional C 1s peak probably comes from the residual carbon in the organic compound or adsorbed carbon dioxide. When BFO was decorated with AgNPs, the

XPS signals for the elements of BFO slightly weaken while the characteristic peaks of Ag 3p and Ag 3d were successfully detected within BFO/Ag1, indicating that the AgNPs exist in the hybrid structure and are successfully decorated on the BFO. After decoration of BFO/Ag1 with rGO, the corresponding XPS signals are still detectable but became relatively weaker as a result. This further confirmed the successful fabrication of tribrid nanoarchitecture of BFO/Ag1/rGO.

Figure 6.8a shows the high-resolution spectra of AgNPs in the BFO/Ag1 and BFO/Ag1/rGO, individually. For the BFO/Ag1 sample, AgNPs exhibit Ag 3d_{3/2} and Ag 3d_{5/2} satellite peaks at binding energies of 374.3 and 368.3 eV, which is in good agreement with the metallic nature of silver (Prieto et al. 2012, Sumesh et al. 2011). The satellite peaks of AgNPs in the BFO/Ag1/rGO shifted slightly to the higher binding energies of 374.4 and 368.5 eV, probably because of transfer of electrons from AgNPs to rGO (Deng et al. 2012). As shown in Figure 6.8b, GO powder displays two satellite peaks at binding energies of 286.8 and 284.6 eV, which is assigned to C-O and C-C bonds and is consistent with the previous report (Liu et al. 2010a). The corresponding XPS deconvolution analysis using Thermo Advantage V5.945 is shown in Figure 6.9a. The binding energy of C-C bond for BFO, BFO/Ag1 and BFO/Ag1/rGO are 284.74, 284.55 and 284.4 eV, respectively. BFO/Ag1/rGO displays a weak C 1s XPS peak at 285.79 eV and this extra peak with a slight shift can be attributed to rGO (Figure 6.9b).

Figure 6.9. XPS deconvolution analysis of C1s for GO (a) and BFO/Ag1/rGO (b).

Figure 6.8c presents the high resolution XPS spectra of Bi 4f for BFO, BFO/Ag1 and BFO/Ag1/rGO. The satellite peaks of Bi 4f_{5/2} and Bi 4f_{7/2} for the BFO sample with binding energies at 163.8 and 158.5 eV which are attributed to the spin-orbit splitting of the Bi 4f components and in good agreement with the Bi³⁺ species. There are no significant changes in binding energies of Bi 4f after BFO decorated with AgNPs.

However, once rGO is introduced to fabricate the BFO/Ag1/rGO sample, the satellite peaks of Bi 4f_{5/2} and Bi 4f_{7/2} shift to higher binding energies at 164.4 and 159.0 eV.

Figure 6.10. XPS deconvolution analysis of Fe2p for BFO (a), BFO/Ag1 (b) and BFO/Ag1/rGO (c).

The high resolution XPS spectra of Fe 2p for the as-prepared samples are shown in Figure 6.8d (For the XPS deconvolution analyses, see Figure 6.10(a-c)). Fe of the BFO sample displays Fe 2p_{1/2} and Fe 2p_{3/2} peaks at 725.44 and 711.43 eV, individually. It corresponds to the binding energy of Fe³⁺ species. There are no obvious reduced states of Fe such as Fe²⁺ and Fe⁰ (Figure 6.10a). For BFO/Ag1 and BFO/Ag1/rGO samples, an additional peak of Fe(II) 2p_{3/2} with a binding energy of ~719.8 eV was detected (see Figure 6.10b and c), possibly because of the interaction between AgNPs and BFO. Similarly, the Fe 2p peaks, especially for Fe 2p_{3/2}, shift to higher binding energies at 725.8 and 712.2 eV. These evidences are indicative of the incorporation of Bi and Fe into rGO with chemical bonding (e.g., Bi-O-C and Fe-O-C bonds) (An et al. 2013).

6.3.2 Application Performance, Stability and Reusability

Figure 6.11a shows the removal performance of MB as a function of time with the as-prepared samples (BFO, BFO/Ag1 and BFO/Ag1/rGO) through physical adsorption in dark followed by visible-light illumination in the presence of H₂O₂. In the absence of the catalysts, the removal efficiency of MB is ~10% in 3 h due to the oxidation by

H₂O₂. In contrast, a rapid removal of MB was observed in the presence of the catalysts with the order of BFO/Ag1/rGO > BFO/Ag1 > BFO, indicating that Bi₂Fe₄O₉ can effectively catalyse visible-light photo-Fenton oxidation and its performance for MB removal in water treatment can be effectively enhanced with co-association of AgNPs and rGO.

Figure 6.11. (a) MB removal performance of BFO, BFO/Ag1 and BFO/Ag1/rGO via combining physical adsorption and visible-light photo-Fenton oxidation. (b) Color fading of MB during visible-light photo-Fenton oxidation in the presence of BFO/Ag1/rGO. (c) MB removal performance of rGO, Ag1/rGO and BFO/rGO via combining physical adsorption and visible-light photo-Fenton oxidation.

As a comparison based on the physical adsorption, it is obvious that the physical adsorptions for the as-prepared samples (i.e., BFO and BFO/Ag1) can be neglected (only about 2-3%) while it can reach up to 50% for BFO/Ag1/rGO even with a lower catalyst loading of 0.12 g L⁻¹, which is contributed by rGO because of its large surface area and high adsorption site density. MB could be removed upto more than 99% within 60 min through BFO/Ag1-driven visible-light photo-Fenton oxidation, whereas

the removal performance of BFO is $\sim 74\%$ in 120 min. This implies that AgNPs with electron conduction and SPR are beneficial for the process of photo-Fenton oxidation driven by $\text{Bi}_2\text{Fe}_4\text{O}_9$, which will be discussed in detail in the following section. The MB removal efficiency in visible-light photo-Fenton oxidation could be further accelerated by using BFO/Ag1/rGO. As shown in the figure, most of MB can be removed in 30 min. The corresponding color fading process of MB solution is shown in Figure 6.11b. It indicates that the simultaneous association of AgNPs and rGO can synergistically promote the performance of $\text{Bi}_2\text{Fe}_4\text{O}_9$ rather than use of AgNPs only. For comparison, a range of comparable materials such as rGO, Ag1/rGO and BFO/rGO were also synthesized and evaluated for MB removal. The results (Figure 6.11c) show that they are not as effective as BFO/Ag1 and BFO/Ag1/rGO in MB degradation. According to the mass fraction, the powder load is 5.7 mg L^{-1} , 6.5 mg L^{-1} and 0.12 g L^{-1} for rGO, Ag1/rGO and BFO/rGO, respectively. Due to the formation of AgNPs via reduction of the adsorbed Ag^+ , the intergrain space between BFO and AgNPs can be neglected compared with that of the synthesis process for the BFO/Ag1 and rGO. Hence, the electrons formed within $\text{Bi}_2\text{Fe}_4\text{O}_9$ become more easily transported from $\text{Bi}_2\text{Fe}_4\text{O}_9$ to AgNPs through the heterojunction and then transfer to rGO. For this reason, the loaded rGO also plays another important role to suppress AgNPs acting as a recombination center of electron/holes pairs. This phenomenon has been demonstrated by the resulted PL spectra (Figure 6.5). For the as-prepared samples, visible-light photocatalysis was carried out to further investigate the above conclusions.

Figure 6.12a shows MB removal performance of BFO, BFO/Ag1 and BFO/Ag1/rGO via the mechanism of physical adsorption and visible-light photocatalysis. Similarly, the MB removal efficiencies for the as-prepared samples via the physical adsorption are consistent. The photolysis degradation efficiency of MB is $\sim 3\%$ in 4 h under visible-light irradiation. In the presence of catalysts but without H_2O_2 , the degradation processes become slower. It is obvious that the degradation reaction still carries on for the BFO and BFO/Ag1 along with slow rates while for the BFO/Ag1/rGO with a significant efficiency. It further reveals the collaborative relationship between AgNPs and rGO. AgNPs can mainly function as electrical conduction rather than anti-recombination that can be further verified by the slightly enhanced photocatalytic degradation of MB (Figure 6.12a, inset).

Figure 6.12. (a) MB removal performance of BFO, BFO/Ag1 and BFO/Ag1/rGO via combining physical adsorption and visible-light photocatalysis. (b) Efficiency of reused BFO/Ag1/rGO in MB removal through visible-light photo-Fenton oxidation and visible-light photocatalysis.

Chemical stability of a catalyst is important for its practical application. The corresponding investigations for BFO/Ag1/rGO were carried out through visible-light photo-Fenton oxidation and visible-light photocatalysis and the results show that it exhibits good reusability potential (Figure 6.12b). The reaction solutions were also analyzed with inductively coupled plasma-optical emission spectrometer (ICP-OES, Perkin Elmer Optima 2000DV) during the corresponding processes. The results display that the concentrations of the ion species (i.e., Bi^{3+} , $\text{Fe}^{3+}/\text{Fe}^{2+}$, Ag^+) are quite low ($< 0.1 \text{ mg L}^{-1}$). The above results indicate that the as-prepared BFO/Ag1/rGO has a good chemical stability and reusability.

6.3.3 Proposed Mechanism

Figure 6.13 illustrates plausible mechanisms of organic pollutants removal by the nano-designed tribrid nanoarchitecture of BFO/Ag1/rGO in water treatment at pH ~6.5. As mentioned in Chapter 2 (Section 2.1), heterogeneous catalytic oxidation processes involve five steps including mass transfer of pollutants from the bulk solution to the catalyst surface and redox process, etc (Herrmann 2005, Herrmann and Pichat 1982). The purpose of this study is to design AgNPs and rGO co-decorated BFO enhancing the removal efficiency of pollutants through optimization of mass transfer of pollutants and redox performance. As shown in the figure (lower panel), MB dissolved in water has more efficient mass transfer to the rGO-wrapped catalyst, which has been confirmed by the adsorption performance of BFO/Ag1/rGO (Figures 6.11a and 6.12a). Under illumination of visible light, the reactive oxygen species (ROSs) can be formed on the surface of catalysts and used to degrade the adsorbed MB. A plausible formation process of ROSs (e.g., $\text{HO}^\bullet$, $\text{O}_2^{\bullet-}$) is proposed and discussed below.

Figure 6.13. Schematic illustration of the mechanism of organic pollutants removal using the multi-functional BFO/Ag1/rGO ternary hybrid nanoarchitecture in water treatment.

Initially, the $\text{Bi}_2\text{Fe}_4\text{O}_9(\text{Fe}^{2+})$ state (shown as Fe(II) in Figure 6.13) exists within BFO due to the interaction between AgNPs and BFO as can be inferred from XPS results (Figures 6.8d and 6.10). The electrons can be formed through the conversion from $\text{Bi}_2\text{Fe}_4\text{O}_9(\text{Fe}^{2+})$ to $\text{Bi}_2\text{Fe}_4\text{O}_9(\text{Fe}^{3+})$ state (shown as Fe(III) in Figure 6.13) and photocatalysis within BFO under visible-light illumination. Due to the electron conduction path provided by AgNPs, the electrons will transfer to AgNPs and further to rGO along with both the formation of ROSs and consumption of H_2O_2 on the surface of AgNPs and rGO (Figure 6.13, upper panel). The reaction pathways can be described by Eqs (6.1) and (6.2) (Chong et al. 2010). The interconversion from $\text{Bi}_2\text{Fe}_4\text{O}_9(\text{Fe}^{3+})$ to $\text{Bi}_2\text{Fe}_4\text{O}_9(\text{Fe}^{2+})$ state can progress through photo-Fenton oxidation under visible-light irradiation (i.e., Eq (6.3)) with the formation of $\text{HO}^\bullet$ (Koppenol et al. 1978, Pignatello 1992b, Pignatello et al. 1999). Due to the surface plasmon resonance of AgNPs, the generated electron might be utilized to reduce $\text{Bi}_2\text{Fe}_4\text{O}_9(\text{Fe}^{3+})$ to $\text{Bi}_2\text{Fe}_4\text{O}_9(\text{Fe}^{2+})$ state within BFO as well (i.e., Eq (6.4)).

6.4 Conclusions

In summary, the author has successfully prepared AgNPs decorated and AgNPs/rGO co-decorated $\text{Bi}_2\text{Fe}_4\text{O}_9$ based on the as-synthesized nanostructured $\text{Bi}_2\text{Fe}_4\text{O}_9$ clusters by using multi-step method. The AgNPs with a mean size of 9 nm in diameter have been deposited uniformly on the surface of $\text{Bi}_2\text{Fe}_4\text{O}_9$. The as-prepared single-layer rGO has been successfully introduced to wrap over the Ag-decorated $\text{Bi}_2\text{Fe}_4\text{O}_9$. The AgNPs and rGO can effectively enhance the optical performance of $\text{Bi}_2\text{Fe}_4\text{O}_9$ for visible light absorption. In water treatment, AgNPs effectively enhance the performance of $\text{Bi}_2\text{Fe}_4\text{O}_9$ probably due to its excellent conductivity and surface plasmon resonance. These two properties of AgNPs are beneficial for the interconversion between $\text{Bi}_2\text{Fe}_4\text{O}_9(\text{Fe}^{3+})$ and $\text{Bi}_2\text{Fe}_4\text{O}_9(\text{Fe}^{2+})$ states within $\text{Bi}_2\text{Fe}_4\text{O}_9$ during visible-light photo-Fenton oxidation, and can accelerate the formation of ROSs. AgNPs function in the similar ways as that occurring in visible-light photocatalysis. However, there is only a minor increase in MB degradation via using $\text{Bi}_2\text{Fe}_4\text{O}_9/\text{Ag}$ as

compared to $\text{Bi}_2\text{Fe}_4\text{O}_9$. It is because AgNPs conduct electrons but cannot effectively suppress e^-/h^+ recombination. The findings demonstrate that rGO can further enhance the performance of Ag-decorated $\text{Bi}_2\text{Fe}_4\text{O}_9$ through promoting mass transfer of pollutants and anti-recombination of e^-/h^+ pairs. Through investigation of the synthesis of $\text{Bi}_2\text{Fe}_4\text{O}_9$ -based ternary hybrid nanoarchitecture (i.e., BFO/Ag1/rGO) and its performance in water treatment, the results indicated that the delicate design of nanoarchitecture can realize the enhanced performance of $\text{Bi}_2\text{Fe}_4\text{O}_9$. The significant findings of this study is that BFO/Ag1/rGO has a superior capability in water treatment.

Chapter 7 Magnetism Optimization — Magnetically recoverable Bi/Fe-based hierarchical nanostructures via self-assembly for water decontamination

7.1 Introduction

For practical application of heterogeneous catalysis in water decontamination using BFO, the BFO nanoparticles or nanocomposites have to be retained or recovered in the continuous flow-through (e.g. completely mixed or plug flow) treatment systems which are the prevalent flow modes in water and wastewater treatment facilities. There are three main technologies to retain and recover the dispersed nanocatalyst applied in water decontamination, namely (i) sedimentation, (ii) membrane separation and (iii) magnetic separation. Sedimentation may be the easiest to implement but it is difficult to effectively recover the dispersed nanocatalysts due to their low settling velocity. Membrane separation is very effective to retain the nanocatalyst from the treated water but the nanocatalysts could foul the membrane through pore blocking, straining, or cake layer formation. Magnetic recovery is an emerging separation technology for water treatment using magnetic materials. It has potential to be the most cost-effective separation technology for recovering the magnetic nanocatalysts from the treated water.

The different types of $\text{Bi}_2\text{Fe}_4\text{O}_9$ nanostructured/nanocomposite materials described in Chapters 3 to 6 have magnetic property because $\text{Bi}_2\text{Fe}_4\text{O}_9$ is essentially a paramagnetic material. However, they have weak paramagnetic properties at room temperature, e.g., a saturation magnetism (M_s) of only $\sim 1 \text{ emu g}^{-1}$ for the $\text{Bi}_2\text{Fe}_4\text{O}_9$ described in Chapter 3. Indeed, the magnetic property of the pristine BFO is generally too weak (M_s of $0.1\text{--}3 \text{ emu g}^{-1}$ at room temperature) for practical application (Hu et al. 2014, Park et al. 2007, Sun et al. 2013c, Tan et al. 2012, Wang et al. 2013c). Therefore, a strategy to enhance the magnetic properties of BFO is desirable to realize its magnetic separation for reuse during water decontamination.

The magnetic property of pristine BFO is ascribed to its slightly distorted crystal structure (Friedrich et al. 2010, Ravindran et al. 2006). In order to enhance its magnetic property, doping or substitution of metal cations (M^{n+} , where $n = 2, 3, \text{ or } 4$)

into the octahedral and/or tetrahedral crystal structure of the pristine BFO is one of the effective approaches, which could induce further distortion/asymmetry of crystal structure of the pristine material. Through doping, the M^{n+} dopants with different ionic radii and physiochemical properties will replace some of Bi^{3+} or Fe^{3+} located at the center of BiO_6 or FeO_6 octahedra and/or FeO_4 tetrahedra (Cantoni et al. 2014, Das and Mandal 2012, Jayakumar et al. 2010, Kan et al. 2010, Pradhan et al. 2010, Qian et al. 2010, Srikrishna Ramya and Mahadevan 2014, Verma et al. 2015, Xi et al. 2014, Yang et al. 2010). However, doping usually involves toxic metal ions and high-temperature processing. There are alternative approaches to promote the magnetic property of a material. For examples, interconversion of Fe^{3+} to Fe^{2+} state (e.g., in BFO) can enhance the distortion of the pristine BFO crystal structure (Mao et al. 2014, Safi and Shokrollahi 2012), which is possibly ascribed to the different ionic radii of Fe^{3+} and Fe^{2+} (65 pm and 77 pm, respectively). Magnetic properties of materials can be tuned through changing their morphologies (Li et al. 2011b, Wang et al. 2010a, Zhu and Deng 2015). Previous researchers have also reported the phenomena of morphology-dependent magnetic properties of materials such as Fe_2O_3 and $\text{Ni}/\text{Ni}(\text{OH})_2$ (Wang et al. 2010a, Zhu and Deng 2015). For interconversion of Fe^{3+} to Fe^{2+} state and tuning morphology of a magnetic material, it is worth considering the solvent-assisted synthesis method. The solvent-assisted synthesis has several advantages such as (1) it allows a good control of the crystal growth without the use of templates or other organic additives; (2) the final product has a clean surface without chemical residuals; and (3) the solvent can function as the reducing agent (Clavel et al. 2007).

This study attempted to make an investigation on reduction of Fe^{3+} into Fe^{2+} state in the as-prepared $\text{Bi}_2\text{Fe}_4\text{O}_9$ clusters (P-BFO) using a facile solvothermal treatment, in which the organic solvent such as methanol functioned as a reducing agent. In order to gain insight into the transformation mechanism of P-BFO into the final product (BFO-M), the effects of synthesis parameters such as reaction volume, temperature and time on the formation of BFO-M were investigated. BFO-M would be used to remove different types of organic pollutants (i.e., dyes, pharmaceuticals, pesticides) via photo-Fenton oxidation and heavy metal ions (e.g., $\text{Pb}(\text{II})$, $\text{Cd}(\text{II})$, $\text{As}(\text{V})$, $\text{Cr}(\text{III})$, $\text{Cu}(\text{II})$, $\text{Mn}(\text{II})$, $\text{Ba}(\text{II})$ and $\text{Co}(\text{II})$) via adsorption. A proposed application scheme of BFO-M in water treatment is shown in Figure 7.1.

Figure 7.1. A proposed application scheme of BFO-M in water treatment. BFO-M functions both as adsorbent and catalyst, as well as can be recovered by magnetic separation. A representative example is shown at the top right-hand corner in which MO dye is used as the pollutant model.

7.2 Experimental

7.2.1 Chemicals and materials

The materials used in this study have been described in Chapter 4. Additionally, ethylene glycol ($\geq 95\%$, aMReSCO[®]) was used in this study. All the chemicals were used as received without further purification.

7.2.2 Preparation of materials

BFO-M was fabricated from a $\text{Bi}_2\text{Fe}_4\text{O}_9$ precursor using a solvothermal treatment in methanol system. The precursor, i.e., the as-prepared $\text{Bi}_2\text{Fe}_4\text{O}_9$ clusters (P-BFO), was prepared using a delicate synthesis process (the detailed procedure has been shown in Chapter 4). The as-prepared P-BFO was stored in absolute ethanol with a certain solid content. Then, 50 mg dry weight of P-BFO (after solvent removal) was dispersed into 10 ml of methanol using sonication. After several minutes of sonication, the dispersion was subsequently transferred into a 50-mL Teflon-lined stainless steel autoclave. The reaction was carried out at 200°C for 3 d in an electric oven. After reaction, the autoclave was cooled down naturally to room temperature. The product was collected and washed thoroughly with water followed by absolute ethanol. At last, the final

product was dried in a vacuum oven at 65°C overnight. For comparison, other products were also prepared using other reaction systems such as water, ethanol or ethylene glycol (EG). They are denoted as BFO-A, BFO-E and BFO-G, respectively. For the methanol system, the effect of the reaction conditions on the formation of resultant BFO-M was also investigated using different reaction volumes (2, 5, and 7.5 mL), temperatures (90, 150, and 220°C), and times (1 and 6 d).

7.2.3 Material Characterization

The material characterization techniques have been introduced in previous chapters. Additionally, the material was further characterized using X-ray photoelectron spectroscopy (XPS) (Phoibos 100 Spectrometer equipped with a monochromatic Mg X-ray source, SPECS, Germany) and Fourier transform-infrared spectroscopy (FT-IR) (PerkinElmer Frontier).

7.2.4 Performance evaluation

7.2.4.1 Removal of organic pollutants

BFO-M were evaluated for its catalytic performance in photo-Fenton oxidation under visible-light irradiation ($420 < \lambda < 630$ nm) using different types of organic compounds as the model pollutants. They are methyl orange (MO) dye, 5-fluorouracil (5-FU) pharmaceutical and isoproturon (IPU) pesticide. The detailed experimental procedures have been described in Chapter 6. In particular, an aliquot sample was drawn out from the reaction vessel and solid catalyst was separated with magnet. For MO, the supernatant solutions were analyzed for UV-vis absorption by UV-vis spectrometer. For 5-FU and IPU, they were analyzed using HPLC equipped with Hypersil GOLD C18 column under the following conditions of 10:90 acetonitrile to water ratio, 1 mL min⁻¹ flow rate and a UV detector at $\lambda_{\text{max}} = 265$ nm, and 70:30 acetonitrile to water ratio, 0.75 mL min⁻¹ flow rate and a UV detector at $\lambda_{\text{max}} = 230$ nm, respectively. For comparison, pad-like single crystalline Bi₂Fe₄O₉ (SP) and plate-like nanostructured Bi₂Fe₄O₉ cluster (NSP) were also investigated in the same experiment when MO was used as a representative organic pollutant. SP and NSP were as-prepared products in Chapter 3 and Chapter 4, respectively. A brief description of these materials is given in Table 7.1.

Table 7.1. A summary of various performances for the as-prepared materials using different synthesis methods with different morphologies/structures

No.	Acronyms	Morphologies/ Structures	^a S_{BET} ($\text{m}^2 \text{g}^{-1}$)	^b Physical adsorption removal	^c Total removal	Synthesis method
1	PS	Pad-like single crystals of $\text{Bi}_2\text{Fe}_4\text{O}_9$	5.8	0.5%	~67%	A co-precipitation method at a significantly lower temperature of 95°C
2	NSP	Plate-like nanostructured clusters of $\text{Bi}_2\text{Fe}_4\text{O}_9$	8.6	1.4%	~71%	A delicate synthesis process through combination of co-precipitation at a lower temperature in water system with hydrothermal treatment in methanol/water co-solvent system
3	BFO-M	Coral-like hierarchical structure with nanoflakes and nanowires fabricated from $\text{Bi}_2\text{Fe}_4\text{O}_9$ precursor	13.8	46.6%	~95%	A delicate synthesis process through combination of co-precipitation at a lower temperature in water system with hydrothermal treatment in methanol/water co-solvent system, and further solvothermal treatment

^a Specific surface area (SSA) by BET.

^b Physical adsorption processes 1 h in dark atmosphere with 5ppm MO and 0.12 g L⁻¹ material loading.

^c Photo-Fenton oxidation undergoes 105 min under visible light irradiation (420 < λ < 630 nm) with addition of 20 mM H₂O₂.

7.2.4.2 Adsorption of heavy metal ion

The solutions containing different concentrations of Pb(II) (20, 50, 100, 200, 300 and 500 mg L⁻¹) were prepared using PbCl₂. The pH of the reaction system was ~5. To obtain the adsorption isotherm, BFO-M was added to these solution at 0.5 g L⁻¹. The dispersions were then placed in SK-3100 Shaker. After 1 h, the solid and solution were separated. The solutions were determined for Pb concentration using inductively coupled plasma-optical emission spectroscopy (ICP-OES) (PerkinElmer Optima 8300). A competitive adsorption experiment was also conducted to compare adsorption of various heavy metal ions by BFO-M in a solution containing a mixture of Pb(II), Cd(II), As(V), Cr(III), Cu(II), Mn(II), Ba(II) and Co(II), each at 100 mg L⁻¹, prepared using PbCl₂, CdCl₂·H₂O, Na₂HAsO₄·7H₂O, CrCl₃·6H₂O, Cu(NO₃)₂·H₂O, Mn(NO₃)₂, BaCl₂·H₂O and Co(NO₃)₂·6H₂O. For this experiment, the pH of the reaction system was adjusted to ~7 using 0.5M NaOH solution.

Figure 7.2. FESEM images of as-prepared (a) BFO-A, (b) BFO-M, (c) BFO-E, and (d) BFO-G.

7.3 Results and discussion

7.3.1 Characteristics of P-BFO after post-treatment

Figure 7.2 shows the FESEM images of the as-prepared BFO-A, BFO-M, BFO-E and BFO-G materials (more FESEM images are shown in Figure 7.3 under a lower

magnification). As compared with the precursor P-BFO (cuboid-like nanostructured $\text{Bi}_2\text{Fe}_4\text{O}_9$ clusters shown in Figure 4.5c and d in Chapter 4), the morphologies for BFO-A and BFO-G are consistent with P-BFO (Figure 7.2a and d respectively), whereas the morphologies of BFO-M (Figure 7.2b) and BFO-E (Figure 7.2c) are different. P-BFO, after undergoing solvothermal treatment in methanol or ethanol system, was converted to coral-like and square sheet-like morphologies, respectively. It is worth noting that when a material has a hierarchically three-dimensional (3D) morphology, it is possible to show unique properties (Dujardin and Mann 2002, Mo et al. 2005, Park et al. 2004, Zhong et al. 2006).

Figure 7.3. FESEM images of as-prepared (a) BFO-A, (b) BFO-M, (c) BFO-E and (d) BFO-G under a lower magnification.

XRD patterns of the as-prepared BFO-A, BFO-M, BFO-E, BFO-G and P-BFO are shown in Figure 7.4a. The XRD patterns for the as-prepared BFO-A and BFO-G are similar with that of the precursor P-BFO. There is no significant effect of reaction system in water or EG on the characteristic peak positions of the resultant BFO. All the characteristic diffraction peaks match well with the standard diffraction pattern of $\text{Bi}_2\text{Fe}_4\text{O}_9$ phase (JCPDS PDF 04-009-6352) (Kostiner and Shoemaker 1971).

Additionally, for the fabricated BFO-E in ethanol system, there is a minor effect of reaction system in ethanol on the XRD pattern. The intensities of the characteristic diffraction peaks become weaker and there is a slight shift of the peak positions.

Figure 7.4. (a) XRD patterns of as-prepared BFO-A, BFO-M, BFO-E, BFO-G and P-BFO. (b) Local magnification of (201), (202), (212), (411), (331), (412), and (332) reflections.

On the other hand, the methanol system induces a significant effect on the XRD pattern of BFO-M. The intensities and positions of the characteristic diffraction peaks become different from the others (Figure 7.4a). The corresponding peaks attributed to planes (201), (202), (212), (411), (331), (412) and (332) are shown in Figure 7.4b. For BFO-M, the peak positions have been shifted and the corresponding intensities become stronger, which possibly resulted from microstrain in the BFO-M with bending morphology (Figure 7.2b) (Guo and Li 2004, Patel et al. 2012, Tang et al. 2014). Also, it implies that the qualitative change in morphology possibly caused a

change in the crystal structure of material. Some of impurity phases might have formed in the final product, such as discrete metal oxide phases (i.e., Bi_2O_3 , hematite Fe_2O_3 or magnetite Fe_3O_4) (Catti et al. 1995, Gattow and Schutze 1964, Okudera et al. 1996) and other BFO phases (i.e., BiFeO_3 or $\text{Bi}_{25}\text{FeO}_{40}$) (Infante and Carrasco 1986, Ravindran et al. 2006). Most probably, BFO-M is a multicomponent composite, including $\text{Bi}_2\text{Fe}_4\text{O}_9$ (54.90%), Fe_2O_3 (41.84%), BiFeO_3 (2.14%), and $\text{Bi}_{25}\text{FeO}_{40}$ (1.12%), estimated by Rietveld analysis (TOPAS V4.1).

Figure 7.5. (a) M-H hysteresis loops of as-prepared BFO-A, BFO-M, BFO-E and BFO-G. (b-e) The corresponding zoom-in loops and the observed magnetic separation performance (inset).

Figure 7.5 shows that the saturation magnetization (M_s) values for the as-prepared BFO-A, BFO-M, BFO-E and BFO-G are 0.375, 30.7, 3.53 and 0.445 emu g⁻¹, respectively. The corresponding coercivity (H_c) are 40, 248, 472 and 204 Oe, respectively. It indicates that the magnetic property of the pristine Bi₂Fe₄O₉ could be significantly enhanced after undergoing solvothermal treatment compared with hydrothermal treatment. Specifically, there is a highly effective enhancement of the magnetic property for BFO-M fabricated in methanol system (Figure 7.5a). The M_s can reach up to 30.7 emu g⁻¹ which is far higher than those of the BFO reported previously (Hu et al. 2014, Park et al. 2007, Sun et al. 2013c, Tan et al. 2012, Wang et al. 2013c). As shown in Figure 7.5c, BFO-M is properly classified as a superparamagnetic material on the basis of its hysteresis characteristics (i.e., high M_s and negligible remanent magnetization (M_r)), suggesting that it remains one magnetic domain within BFO-M at the nanoscale (more discussion on the size of BFO-M will be shown later). The BFO-M can be easily separated with an external magnetic field (Figure 7.5c, inset) as compared with the other resultant products (Figure 7.5b, d and e, insets), suggesting its potential for recovery through magnetic separation in practical application. Herein, the enhanced magnetic property of BFO-M may be related to its hierarchical 3D morphology (Li et al. 2011b, Wang et al. 2010a, Zhu and Deng 2015).

7.3.2 Characterization of BFO-M and formation mechanism

Figure 7.6 shows that the variation in reaction volumes of methanol could induce significant change on the hierarchical morphology of the obtained final products. With reaction volume of 2 mL methanol, the final product formed flower-like hierarchical structure (Figure 7.6a). It is ascribed to the self-assembly of the generated nanosheets and the incomplete dissolution of P-BFO (Figures 7.6a). This evolution occurred more extensively when the reaction volume was adjusted to 5 mL (Figure 7.6b). Square nanosheets with length of 500 nm and thickness of 12 nm were formed (Figure 7.6b, inset) along with incompletely dissolved cuboid-like P-BFO (Figure 7.6b, inset). As shown in Figure 7.6c and d, the FESEM images reveal the more well-developed hierarchical morphology with further increase of reaction volumes. The final product consists of ultrathin nanoflakes derived from the completely dissolved P-BFO when the reaction volume is 10 mL (Figure 7.6d).

Figure 7.6. FESEM images of products obtained via solvothermal treatment in (a) 2 mL, (b) 5 mL, (c) 7.5 mL, (d) 10 mL methanol (P-BFO was used at a fixed amount of 50 mg). (Note: the P-BFO loading is 50 mg; the reaction temperature is 200°C; the reaction time is 3 d.)

Besides the volume of methanol, the reaction temperature is one of the critical parameters which could promote the crystal dissolution process of the P-BFO precursor. The P-BFO morphology of cuboid-like shape was maintained when the solvothermal treatment was carried out at a temperature $\leq 150^{\circ}\text{C}$. When the temperature was increased to 200°C , the morphology was converted to a coral-like shape (Figure 7.7). On the other hand, when the reaction time was further increased to 6 d, the morphology was changed to sphere-like shapes with no noticeable coral-like shapes (Figure 7.8). As compared with the previously reported BFO which were generally sheet-, plate-, cube-, cuboid- or rod-like shapes (Hu et al. 2014, Hu et al. 2015c, Joshi et al. 2008, Liu et al. 2014, Sun et al. 2009, Zhang et al. 2007), the findings of the present study indicate that the shape of cuboid-like $\text{Bi}_2\text{Fe}_4\text{O}_9$ (P-BFO) can be transformed into hierarchical morphologies via a facile solvothermal treatment in methanol system. The evolution on its hierarchical morphology can be controlled via tuning reaction parameters such as volume of methanol, temperature and reaction time.

Figure 7.7. FESEM images of products obtained via methanol solvothermal treatment at reaction temperature of (a) 90°C, (b) 150°C, (c) 200°C, (d) 220°C. (Note: the P-BFO loading is 50 mg; the volume of methanol is 10 mL; the reaction time is 3 d.)

Figure 7.8. FESEM images of products obtained via methanol solvothermal treatment at reaction time of (a) 1 d, (b) 3 d, (c) 6 d. (Note: the P-BFO loading is 50 mg; the volume of methanol is 10 mL; the reaction temperature is 200°C.)

AFM was conducted to quantify the thickness of the nanoflakes in BFO-M material. The thickness of the nanoflake in BFO-M is only ~4.7 nm (Figure 7.9). Wire-like shapes in BFO-M can be also observed in the thickness of ~5.2 nm (the green curve in Figure 7.9a). The results imply that BFO-M with coral-like morphology is possibly self-assembled by nanoflakes and nanowires. The corresponding 3D AFM image is shown in Figure 7.9b. It is obvious that the nanoflake has relatively flat surface. Figure 7.9c shows a 2D AFM image of nanowire in higher magnification, in which the image displays a strong mass-thickness contrast observed as the dark and light spots within the nanowires, indicating that it has hierarchical feature. It could be verified via its 3D AFM image (inset).

Figure 7.9. AFM images of as-prepared BFO-M. (a) 2D AFM image with two line scans, (b) 3D AFM image, (c) 2D AFM image of local magnification and the corresponding 3D AFM image.

Figure 7.10. (a) TEM image of as-prepared BFO-M. (b,c) local magnification of TEM images show nanoflake structure of BFO-M and (d) the corresponding HRTEM image, (e, f) local magnification of TEM images show nanowire structure of BFO-M, and (g) the corresponding HRTEM image.

Figure 7.10a shows that BFO-M material displays the coexistence of 2D nanoflakes and 1D nanowires. The nanoflakes randomly agglomerate with each other as shown in the TEM images (Figure 7.10b and c). The high-resolution TEM (HRTEM) image shows clear lattice fringes with d -spacing of 0.27 nm (Figure 7.10d), which might correspond to mullite bismuth ferrite (112) crystal plane base on JCPDS PDF 04-009-6352. The nanowires with an average diameter of ~6 nm agglomerated randomly (Figure 7.10e and g). Figure 7.10g (inset) shows the clear lattice fringes of the nanowire with d -spacing of 0.32 nm. The observed contrast between dark and light

spots with random distribution in the nanowire (Figure 7.10g) further verifies the hierarchical growth of nanowires, which is consistent with AFM (Figure 7.9c).

Figure 7.11. Schematic illustration of synthesizing BFO-M (red dash line square) using P-BFO (black dash line square) through solvothermal treatment processes (green dash line square). Here, (1)-(2) formation of Bi/Fe-based nanoparticles through crystal dissolution of P-BFO into methanol; (2)-(3) formation of Bi/Fe-based 1D nanowires and 2D nanoflakes via self-assembly process of Bi/Fe-based nanoparticles.

According to the investigation mentioned above, the formation of BFO-M material could be ascribed to a spontaneously self-assembled growth/agglomeration mechanism. A schematic illustration of the proposed mechanism is shown in Figure 7.11. Some of weak interactions may have various effects on the self-assembly, such as crystal-face attractions, hydrogen bonds, *van der Waals* forces, π - π interactions, and/or electrostatic attractions (Service 2005, Zhong et al. 2006). The figure (top row) shows the change in morphology evolving from P-BFO (cuboid-like nanostructured cluster) to BFO-M (coral-like hierarchical morphology with composition of nanoflakes and nanowires) via a solvothermal treatment in methanol system. The solvothermal treatment process possibly consists of two stages as shown in Figure 7.11 (bottom row), namely (1) formation of Bi/Fe-based nanoparticles through dissolution of P-BFO into methanol under a condition of high temperature and pressure, and (2) formation of Bi/Fe-based 1D nanowires and 2D nanoflakes *via* self-assembly of the nanoparticles.

7.3.3 Physiochemical properties

BFO-M was further investigated for FT-IR spectroscopy, nitrogen adsorption-desorption, UV-vis spectroscopy characteristics and XPS. In the FT-IR transmittance spectrum (Figure 7.12a), although the spectra of P-BFO and BFO-M show some of difference with position shift and intensity alteration, the main peaks are still displayed clearly. The peaks at ~ 3420 and ~ 1634 cm^{-1} are assigned to $-\text{OH}$ stretching vibration and H-O-H bending stretching of the adsorbed H_2O , respectively (Liu et al. 2010b, Xu et al. 2008). C=C vibration at ~ 1560 cm^{-1} and carboxyl C-OH stretching at ~ 1383 cm^{-1} could be observed, which are possibly caused by the residual organic compounds in both BFO-M and P-BFO. The spectrum of P-BFO shows the characteristic peaks in the region of 400-1100 cm^{-1} . The characteristic peaks at ~ 1049 , ~ 808 , and ~ 641 cm^{-1} are assigned to Fe-O stretching vibration of the FeO_4 tetrahedral unit. Moreover, the peaks at ~ 586 and ~ 478 cm^{-1} are attributed to Bi-O stretching vibration of the BiO_6 octahedra and Fe-O stretching vibrations of the FeO_6 octahedra, respectively (Aroyo et al. 2006, Murshed et al. 2013, Voll et al. 2006). For BFO-M, the characteristic peaks occurred some of changes with intensity alteration and slight shift. In particular, a broad peak marked at ~ 576 cm^{-1} is possibly combined by Fe-O stretching vibration of the FeO_4 tetrahedra at 641 cm^{-1} and Bi-O stretching vibration of the BiO_6 octahedra at 586 cm^{-1} . The nitrogen adsorption/desorption measurement shows that it is a type III isotherm for BFO-M with a hysteresis loop in the relative pressure (Figure 7.12b). As shown in the figure, the surface area of P-BFO has been significantly improved after converting it into BFO-M. The corresponding BET surface area for BFO-M is $13.8 \text{ m}^2 \text{ g}^{-1}$, which is also larger than that of our previously prepared Bi/Fe-based materials (i.e., Table 7.1). On the other hand, BFO-M exhibits photo-absorption in the visible light region (400 to 750 nm) and the short-wavelength near-infrared (SW-NIR) region (800 to 1100 nm) with an extension towards longer wavelengths (Figure 7.12c). In contrast, P-BFO shows relatively weaker photo-absorption in the visible light region and insignificantly response in IR region.

Figure 7.12. (a) FI-IR transmittance spectrum in the $4000\text{--}400 \text{ cm}^{-1}$, (b) Nitrogen adsorption-desorption isotherms, (c) UV-vis and short-wavelength near-infrared absorption spectrum of P-BFO and BFO-M.

XPS survey spectrum is shown in Figure 7.13a which displays the characteristic peaks of Fe 2p, O 1s and Bi 4f. The results indicate BFO-M material has chemical compositions of Bi, Fe and O. The elemental composition at the sample surface and the corresponding atomic percentages are shown in Figure 7.13a (inset). Figures 7.13b and c present the high-resolution XPS spectra of Bi 4f and Fe 2p in BFO-M, respectively. The satellite peaks of Bi 4f_{5/2} and Bi 4f_{7/2} have the binding energies of 164.3 and 159.0 eV respectively, which are attributed to the spin-orbit splitting of the Bi 4f components and in good agreement with the Bi³⁺ species (Hu et al. 2015b, Hu et al. 2015c). The characteristic peaks of Fe 2p, i.e., Fe 2p_{1/2} and Fe 2p_{3/2}, are present in Figure 7.13c at 725.4 and 710.2 eV respectively, which correspond to Fe³⁺ species. There is no observed reduced state of Fe (e.g., Fe²⁺) in the as-prepared BFO-M. Apparently, the supermagnetic property of BFO-M does not seem to be induced by the reduction of Fe³⁺ to Fe²⁺ state. According to the results shown above (i.e., the order of

magnetic properties is $\text{BFO-M} > \text{BFO-E} > \text{BFO-G} \approx \text{BFO-A}$, which is proportional to the variation degree of the change of morphology), the enhanced magnetism could be ascribed to the revulsion (or changes in anisotropy) in material morphology and/or structure. This finding is consistent with the phenomena that magnetic properties of materials are dependent on their morphologies (Clavel et al. 2007, Li et al. 2011b, Wang et al. 2010a, Zhu and Deng 2015).

Figure 7.13. (a) XPS survey spectrum of as-prepared BFO-M (the inset shows a quantification table with chemical compositions at the sample surface and their atomic concentrations). (b-c) Satellite peaks of Bi 4f 5/2, Bi 4f 7/2, Fe 2p 1/2 and Fe 2p 3/2 for BFO-M.

7.3.4 Evaluation of BFO-M performance in water decontamination

7.3.4.1 Adsorption and catalytic degradation of organic pollutants

The BFO materials can be used as heterogeneous photo-Fenton catalysts in degradation of organic pollutants. Figure 7.14a shows a comparison of the as-prepared BFO-M, PS and NSP with respect to visible light photo-Fenton oxidation of MO dye.

Figure 7.14. (a) Application performance of BFO-M, NSP and PS on MO removal using visible light photo-Fenton oxidation. (b) Application performance of BFO-M on removal of MO, 5-FU and IPU using visible light photo-Fenton oxidation.

In the absence of the BFO, MO removal is only ~2% in 120 min which is ascribed to the oxidation by H_2O_2 . In the presence of the as-prepared BFO-M, PS, or NSP, a rapid removal of MO was observed. Apparently, it indicates that the as-prepared materials can effectively catalyze visible light photo-Fenton oxidation of recalcitrant pollutants and have a great potential to utilize solar energy directly. The removal of MO for BFO-M can reach up to 95% in 105 min, partly assisted by its remarkable adsorption capability (Figure 7.14a). At adsorption-desorption equilibrium in the dark, the removal of MO is 47% and then further increases when illuminated by simulated solar

light. In comparison, PS and NSP which show insignificant adsorption of MO can only remove 67 and 71% of MO, respectively, in 105 min (Table 7.1). Besides dyes, the BFO-M can be used to degrade the other types of organic pollutants (physiochemical properties are shown in Table 7.2). The degradation efficiencies for 5-FU (a pharmaceutical) and IPU (a pesticide) are > 98% within 105 min and 90 min, respectively, via visible light photo-Fenton oxidation in the presence of BFO-M (Figure 7.14b). Obviously, the adsorption capability of BFO-M is significantly higher for MO than 5-FU and IPU. Herein, MO with a charged functional group interacts with BFO-M *via* electrostatic interaction, whereas the interaction between 5-FU (or IPU) and BFO-M possibly via dipole-dipole interaction which is much weaker (Table 7.2). In addition, the BFO-M also shows a good reusability potential (Figure 7.15a)

Table 7.2. Physiochemical properties of investigated pollutants

Pollutant	Type	Chemical structure	Chemical formula	Molar mass (g mol ⁻¹)	Solubility in water (mg L ⁻¹)	LD ₅₀ (mg kg ⁻¹ , rat, oral)
Methyl orange (MO)	Dye		C ₁₄ H ₁₄ N ₃ NaO ₃ S	327.33	5000	60
5-fluorouracil (5-FU)	Pharmaceutical		C ₄ H ₃ FN ₂ O ₂	130.08	12000	230
Isoproturon (IPU)	Pesticide		C ₁₂ H ₁₈ N ₂ O	206.29	72	1830

Figure 7.15. Efficiency of reused BFO-M on removal of IPU using visible light photo-Fenton oxidation (a), and Pb(II) at the condition of 50 mg L⁻¹ initial metal concentration, 0.5 g L⁻¹ BFO-M (b).

7.3.4.2 Removal of heavy metal ions

Figure 7.16a shows the results of Pb(II) adsorption by BFO-M and the well-fitted Langmuir adsorption model:

$$q_e = q_m b C_e / (1 + b C_e) \quad (1)$$

where, q_e (mg g^{-1}) is the amount of Pb(II) adsorbed at equilibrium, q_m (mg g^{-1}) is the maximal adsorption capacity, b (L mg^{-1}) is the Langmuir equilibrium constant, and C_e (mg L^{-1}) is the equilibrium Pb(II) concentration. The maximal adsorption capacity of BFO-M for Pb(II) is 214.5 mg g^{-1} , which is much higher than the recently reported urchin-like α -FeOOH hollow spheres (80 mg g^{-1}) (Wang et al. 2012), multiwalled carbon nanotubes (50 mg g^{-1}) (Yu et al. 2011), graphene nanosheets (35 mg g^{-1}) (Huang et al. 2011), carbon particles (27 mg g^{-1}) (Momčilović et al. 2011), goethite (α -FeOOH) nanoparticles (18 mg g^{-1}) (Villalobos and Pérez-Gallegos 2008), ceria hollow nanospheres (9.2 mg g^{-1}) (Cao et al. 2010b), and hematite hollow spindles (5.3 mg g^{-1}) (Zeng et al. 2007). In addition, the BFO-M also shows a good reusability potential (Figure 7.15b). The removal ability of P-BFO for Pb(II) was also investigated (Figure 7.17). The corresponding maximal adsorption capacity is only 19 mg g^{-1} . The better performances for BFO-M could be attributed to its high surface area and hierarchical nanostructure, as well as its surface property such as functional groups (Figure 7.12a).

Figure 7.16. (a) Langmuir isotherm of Pb(II) for BFO-M adsorption and the corresponding percentage removal of Pb(II). (b) Adsorption performance of BFO-M for different metal ions at the condition of 100 mg L^{-1} initial metal concentration, 0.5 g L^{-1} BFO-M and $\text{pH} \sim 7.0$.

Figure 4.16b shows the results of competitive adsorption of various heavy metals by BFO-M at circumneutral condition. At 100 mg L^{-1} of each metal loading, Pb(II), Cr(III), Cu(II) and As(V) are the most favorably adsorbed, achieving almost 100% removal by BFO-M. These metals have possibility to exhibit chemical interactions

(e.g., surface complexation) with iron oxides (Stumm 1992). BFO-M, an iron-oxide adsorbent with coral-like morphology and relatively higher surface area, is an effective adsorbent for these heavy metals. The least adsorption of Ba(II) could be attributed to the fact that Ba(II), as a Group II metal, interacts with metal oxide adsorbent mainly through electrostatic interaction which is limited by the adsorbent loading used and and degree of hydrolysis of heavy metal ions in this experiment.

Figure 7.17. Adsorption of P-BFO on Pb(II) at different concentrations of Pb(II) (20, 50, 100, 200, 300 and 500 mg L⁻¹) and the corresponding percentage removal of Pb(II).

7.4 Conclusions

A supermagnetic Bi/Fe-based nanomaterial with coral-like hierarchical morphology has been fabricated using a facile solvothermal treatment in methanol system. Although it seems that the interconversion between Fe³⁺ and Fe²⁺ state does not work during the solvothermal treatment with reducing agents, the findings indicate that the promoted magnetic property is possibly ascribed to the qualitative change in morphology from the cuboid-like P-BFO to the coral-like hierarchical BFO-M. The formation of BFO-M material with 1D nanowires and 2D ultrathin nanoflakes can be ascribed to a spontaneously self-assembled growth/agglomeration mechanism while the evolution on its hierarchical morphology can be controlled effectively via tuning reaction parameters. BFO-M has outstanding catalytic capability in the presence of visible light and H₂O₂ as well as physical adsorption. The used BFO-M could be recovered through simple magnetic separation and reused after rinsing with clean water. The findings have demonstrated that BFO-M can be used to remove different types of heavy metal ions (i.e., Pb(II), Cr(III), Cu(III), As(V), Cd(II), etc.) and organic pollutants (e.g., dyes, pharmaceuticals and pesticides) in water treatment. This product has a great promise as the next-generation multifunctional material for environmental decontamination as well as other applications.

Chapter 8 Conclusions and recommendations

8.1 Conclusions

In this study, $\text{Bi}_2\text{Fe}_4\text{O}_9$ and $\text{Bi}_2\text{Fe}_4\text{O}_9$ -based nanomaterials were fabricated via facile or delicate techniques. The facile approaches were low-temperature co-precipitation method, calcination method, and solvothermal treatment, respectively. The delicate synthesis methods involved combination of co-precipitation in water system with hydrothermal treatment in co-solvent system and multi-step method with surface functionalization, respectively. The as-prepared nanomaterials could be in the forms of nanoparticle, single crystal, cluster, hierarchical nanostructure, 2D composites, or 3D multi-phase composites. The multifunctionalized nanomaterials exhibited multiplex heterogeneous catalyses at circumneutral pH, including photocatalysis, photo-Fenton oxidation and Fenton-like oxidation (in dark), for effective degradation of different types of organic pollutants (e.g., BPA, MO, MB, 5-FU and IPU) under visible light of the simulated solar spectrum. The resulted nanomaterial (i.e., BFO-M) also could be used to remove different types of heavy metal ions, such as Pb(II) , Cr(III) , Cu(III) , As(V) , Cd(II) , Co(II) , Mn(II) and Ba(II) , via physical adsorption and can be recovered via magnetic separation.

Both the catalytic activities of $\text{Bi}_2\text{Fe}_4\text{O}_9$ for degradation of organic pollutants and its magnetic property can be enhanced (or influenced) via control of crystal facet, nanostructurization or morphology, and fabrication of nanoarchitected composites. The $\text{Bi}_2\text{Fe}_4\text{O}_9$ nanopad with exposing facet (001) showed a higher photocatalytic degradation efficiency of BPA than that of $\text{Bi}_2\text{Fe}_4\text{O}_9$ nanoparticle under visible-light irradiation. For visible light photo-Fenton oxidation, the catalytic activity of $\text{Bi}_2\text{Fe}_4\text{O}_9$ was significantly influenced by its morphology in the order of NSP- $\text{Bi}_2\text{Fe}_4\text{O}_9$ (plate-like) > NSCC- $\text{Bi}_2\text{Fe}_4\text{O}_9$ (cuboid-like) > NSC- $\text{Bi}_2\text{Fe}_4\text{O}_9$ (cube-like). The nanostructured $\text{Bi}_2\text{Fe}_4\text{O}_9$ cluster (i.e., NSC- $\text{Bi}_2\text{Fe}_4\text{O}_9$) for Fenton-like oxidation exhibited a better catalytic performance for degradation of MO than those of other $\text{Bi}_2\text{Fe}_4\text{O}_9$. The BFO249/rGO4.5 composite showed 5.5 times higher affinity for BPA adsorption and 2 times higher for BPA removal by synergistic adsorption-photocatalytic degradation under visible-light irradiation than that of $\text{Bi}_2\text{Fe}_4\text{O}_9$ nanoparticle, respectively. The multi-phase composites (i.e., BFO/Ag1/rGO)

showed more than 97% MB removal within 30 min through visible light photo-Fenton oxidation by virtue of synergistic actions among $\text{Bi}_2\text{Fe}_4\text{O}_9$, AgNP and rGO, whereas the removal performance of BFO is 74% in 120 min. On the other hand, BFO-M with coral-like hierarchical morphology, which could be easily recovered via a magnet, exhibited a much stronger paramagnetism compared to $\text{Bi}_2\text{Fe}_4\text{O}_9$ with cuboid-like shape.

The fabrication of $\text{Bi}_2\text{Fe}_4\text{O}_9$ was significantly influenced by reaction conditions, such as molar ratio of Bi/Fe, reaction time, reaction temperature, concentration of reactants, heat treatment, additive, and co-solvent system. The effect of weak interactions during synthesis may be considered in terms of crystal-face attractions, hydrogen bonds, *van der Waals* forces, π - π interactions, and electrostatic attractions. The mechanisms of the formation of nanomaterials, including grain growth, crystallographic orientation, recrystallization, self-assembly, polycrystalline array, and multicomponent composite are proposed.

The mechanism of formation of ROSs through $\text{Bi}_2\text{Fe}_4\text{O}_9$ -driven catalyses is defined as hybrid advanced oxidation processes (HAOPs). HAOPs consist of visible-light photocatalysis, Fenton-like oxidation, and photo-Fenton oxidation which occur simultaneously. At circumneutral pH, the formation of radical species were investigated. For $\text{Bi}_2\text{Fe}_4\text{O}_9$ -driven photocatalysis, the possible ROSs generated are $\text{O}_2^{\bullet-}$, $^1\text{O}_2$, H_2O_2 and $\text{HO}^{\bullet}$ which were revealed via employing appropriate radical scavengers. The predominant ROS for the removal of organic pollutants was identified to be the $\text{O}_2^{\bullet-}$. In the presence of visible light and auxiliary H_2O_2 , the predominant ROS could be $\text{HO}^{\bullet}$ which was produced through $\text{Bi}_2\text{Fe}_4\text{O}_9$ -driven photo-Fenton oxidation. The mechanisms of the enhanced removal of organic pollutants by the $\text{Bi}_2\text{Fe}_4\text{O}_9$ -based composites were demonstrated as well. The inhibitive processes, i.e., mass transfer limitation and recombination of e^-/h^+ pairs, could be addressed effectively using BFO/rGO4.5 and BFO/Ag1/rGO as composite catalysts, because rGO can transfer and store e^- and meanwhile adsorb organic pollutants effectively. In BFO/Ag1/rGO, the interconversion between $\text{Bi}_2\text{Fe}_4\text{O}_9(\text{Fe}^{3+})$ and $\text{Bi}_2\text{Fe}_4\text{O}_9(\text{Fe}^{2+})$ states could be enhanced via the SPR of the attached AgNPs, which could effectively accelerate the photo-Fenton oxidation of $\text{Bi}_2\text{Fe}_4\text{O}_9$. For $\text{Bi}_2\text{Fe}_4\text{O}_9$ (-based) nanomaterial, the catalytic degradation rate of organic pollutants in water depends on factors, such as wavebands

of solar irradiation, pH value, anion species, and type of organic pollutants. BFO249/rGO4.5 showed a better photocatalytic degradation efficiency of BPA in a weak acidic solution. Among the omnipresent anions, bicarbonate showed the larger inhibition on the catalytic degradation of BPA by BFO249/rGO4.5. For the pollutants with different functional groups, the adsorption capability of BFO-M on pollutants showed the difference in the order of MO > 5-FU > IPU.

8.2 Recommendations

To realize practical application of BFO for water and wastewater treatment, several recommendations for the future study are proposed below.

The synthesis approaches for preparation of BFO and BFO-based nanomaterials need to be further developed. The fabricated BFO (or BFO-based) nanomaterial should possess both high catalytic activities and strong magnetism, rather than only possess either of these characteristics. The fabricated BFO could be effectively applied for photocatalytic wastewater treatment process integrated with a magnetic separation system. The developed synthesis process should be eco-friendly, up-scalable, and economical.

The mechanism of HAOPs for the formation of ROSs needs to be further investigated. To gain in-depth insights, both the catalytic kinetics for degradation of organic pollutants in aqueous system and the formation of the types of ROSs in BFO-driven photo-Fenton and Fenton-like oxidation can be investigated via detecting the ROSs formed on the surface of catalysts. The characterization technique can be electron spin resonance (ESR) spectroscopy. The transient decay, charge transfer kinetics, or recombination of either e^- or h^+ is worth studying using transient absorption spectroscopy (TAS), electrochemical impedance spectroscopy (EIS), surface photovoltage (SPV) spectroscopy etc.

The determination of the reaction pathways and identification of intermediates or final products for degradation of organic pollutant in HAOPs are suggested in the future study. The advanced characterization equipments, ion chromatograph (IC), liquid chromatograph-mass spectrometer (LC-MS/MS) and nuclear magnetic resonance (NMR) spectroscopy, are recommended. In order to assess the potential impacts on the

environment and human health, the toxicity of the intermediates and the final products needs to be evaluated too. The performance of the fabricated BFO nanomaterials needs to be evaluated under illumination of real sunlight in real wastewater system, i.e., the permeate water from membrane filtration or membrane bioreactor.

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Appendix

Appendix I: Crystal structure information of mullite $\text{Bi}_2\text{Fe}_4\text{O}_9$ structure

data_262861-ICSD

#?013 by Fachinformationszentrum Karlsruhe, and the U.S. Secretary of
#Commerce on behalf of the United States. All rights reserved.

_database_code_ICSD	262861
_audit_creation_date	2012/08/01
_chemical_name_systematic	'Dibismuth Tetrairon Nonaoxide'
_chemical_formula_structural	'Bi2 Fe4 O9'
_chemical_formula_sum	'Bi2 Fe4 O9'
_publ_section_title	

;

Mixed crystal formation and structural studies in the mullite-type
system $\text{Bi}_2\text{Fe}_4\text{O}_9$ - $\text{Bi}_2\text{Mn}_4\text{O}_{10}$

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Kann, Z.R.;Auletta, J.T.;Hearn, E.W.;Weber, S.U.;Becker,
K.D.;Schneider, H.;Lufaso, M.W.

;

_cell_length_a	7.97765(6)
_cell_length_b	8.44565(6)
_cell_length_c	6.00662(4)
_cell_angle_alpha	90.
_cell_angle_beta	90.
_cell_angle_gamma	90.
_cell_volume	404.7
_cell_formula_units_Z	2
_symmetry_space_group_name_H-M	'P b a m'
_symmetry_Int_Tables_number	55
_refine_ls_R_factor_all	0.103

loop_

_symmetry_equiv_pos_site_id	
_symmetry_equiv_pos_as_xyz	
1	'x+1/2, -y+1/2, z'
2	'-x+1/2, y+1/2, z'
3	'x, y, -z'

```

4      '-x, -y, -z'
5      '-x+1/2, y+1/2, -z'
6      'x+1/2, -y+1/2, -z'
7      '-x, -y, z'
8      'x, y, z'
loop_
_atom_type_symbol
_atom_type_oxidation_number
Bi3+    3
Fe3+    3
O2-     -2
loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_symmetry_multiplicity
_atom_site_Wyckoff_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_occupancy
_atom_site_attached_hydrogens
_atom_site_B_iso_or_equiv
Bi1 Bi3+ 4 g 0.17740(17) 0.17531(18) 0 1. 0 0.17(3)
Fe1 Fe3+ 4 f 0.5 0 0.2611(8) 1. 0 0.16(12)
Fe2 Fe3+ 4 h 0.3550(6) 0.3385(7) 0.5 1. 0 0.18(11)
O1 O2- 2 b 0 0 0.5 1. 0 0.63(25)
O2 O2- 8 i 0.3703(15) 0.2040(16) 0.2549(19) 1. 0 0.63(25)
O3 O2- 4 h 0.1347(24) 0.4008(22) 0.5 1. 0 0.63(25)
O4 O2- 4 g 0.1478(25) 0.4282(23) 0 1. 0 0.63(25)
#End of data_262861-ICSD

```

Appendix II: Equation derivation of an overall reaction of photo-Fenton oxidation

Photo-Fenton oxidation has been reported that it can be excited under UV radiation, visible light irradiation or solar light illumination (Gogate and Pandit 2004, Pignatello et al. 1999, Pignatello 1992), which depends on the kind of Fe^{3+} /ligand complexes with the different ligands (Pignatello et al. 1999, Graf et al. 1984, Benkelberg and Warneck 1995, Allmand and Webb 1929a, Allmand and Webb 1929b). The ligand-to-metal charge transfer (LMCT) as a theoretical basis is widely used to explain the process of photo-Fenton oxidation. Without organic ligands in the pure photo-Fenton system, the mainly existing Fe^{3+} complexes are FeOH^{2+} and $\text{Fe}(\text{O}_2\text{H})^{2+}$. Herein, assuming under ideal conditions (e.g., pH 2.8), the discussion shown below

focuses on the possibility of an overall reaction of photo-Fenton oxidations. Surely, all of derivative processes are based on the previously accepted reports.

When the wavelength locates at a range of 280-420 nm, the photo-Fenton oxidation can be induced by aquocomplexes (FeOH^{2+}) (Benkelberg and Warneck 1995, Faust and Hoigne 1990). An overall reaction of the photo-Fenton oxidation can be expressed as Eq.(A1) in the presence of H_2O_2 , $\text{Fe}^{3+}/\text{Fe}^{2+}$, and light irradiation. It is derived from Eqs. (A2), (A3) and (A4). The pathways of formula derivations are shown below. The derivation is deduced progressively based on the known conditions, such as the initial scheme of Fenton reaction, the hydrolysis reaction of Fe^{3+} , and the original scheme of photo-Fenton oxidation.

Initial scheme of Fenton reaction (Rigg et al. 1954):

Hydrolysis reaction (Benkelberg and Warneck 1995):

Original scheme of photo-Fenton oxidation of aquocomplexes (Gogate and Pandit 2004, Benkelberg and Warneck 1995, Faust and Hoigne 1990):

Formula derivation:

Combining Eqs. (A3) and (A4) give

Eq. (A5) can be rewritten as

Combining Eqs. (A2) and (A6) give

Where $\text{H}^+ + \text{OH}^- = \text{H}_2\text{O}$, thus giving the overall reaction of photo-Fenton oxidation as Eq. (A1).

When the $\text{Fe}(\text{O}_2\text{H})^{2+}$ complexes absorb visible light ($\lambda \leq 650 \text{ nm}$), the $\text{HO}_2^\bullet$ will be formed through another photo-Fenton oxidation (Eq. (A8)) followed by partial conversion to $\text{HO}^\bullet$ via the Eq. (A9) (Pignatello et al. 1999, Koppenol et al. 1978). Through combining and re-arranging Eqs. (A8), (A9) and (A10), an initial overall

reaction of photo-Fenton oxidation in the presence of H_2O_2 , $\text{Fe}^{3+}/\text{Fe}^{2+}$ and visible-light irradiation also can be expressed by Eq. (A11),

Original scheme of photo-Fenton oxidation of Fe^{3+} /hydrogen peroxide complexes (Pignatello et al. 1999):

Conversation between $\text{HO}^\bullet$ and $\text{HO}_2^\bullet$ (Koppenol et al. 1978):

Formation of Fe^{3+} /hydrogen peroxide complexes (Lewis et al. 1963):

Overall reaction of photo-Fenton oxidation under visible-light irradiation

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Appendix II: Crystal grain size estimated by Scherrer equation (A12) (Debye and Scherrer 1917)

$$D = \frac{K \cdot \lambda}{\beta \cdot \cos \theta} \quad (A12)$$

Where D = crystallite size (nm), K = Scherrer's constant (0.9), λ = wavelength of X-ray radiation (nm), β = full width half maxima (FWHM), the unit is radian, θ = X-ray diffraction angle.

Reference:

Debye, P. and Scherrer, P. (1917), "Interference on inordinate orientated particles in X-ray light. III", Physikalische Zeitschrift, Vol. 18, No. pp. 291-301.

Appendix III: Optical bandgap of semiconductor (E_g) extracted via drawing the plot of $(\alpha h\nu)^{1/n}$ vs E_g

$$(\alpha h\nu)^{1/n} = B(h\nu - E_g) \quad (A13)$$

$$\alpha = \frac{(1-R)^2}{2R} \quad (A14)$$

$$R = 10^{-A} \quad (A15)$$

Where α = optical absorption coefficient, h = Planck's constant, ν = light frequency, n = constant relating to a mode of transition, B = proportional constant, E_g = bandgap, R = reflection coefficient, A = optical absorption.