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**Design and Modification of Spinel Type Ferrites ( $MFe_2O_4$ ,  
 $M = Zn \text{ \& \ } Ca$ ) with Highly Efficient Photocatalytic  
Performance**

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## Abstract

Organic pollutant in wastewater has become a severe environmental and safety problem. The semiconductor-based photocatalytic degradation is emerging as a high-efficiency and environmentally friendly approach because it only uses photocatalyst and solar energy. For the better utilization of visible light accounting for about 47.7% of solar energy, spinel type ferrites ( $\text{ZnFe}_2\text{O}_4$  and  $\text{CaFe}_2\text{O}_4$ ) with narrow bandgap (approximately 1.9 eV) are becoming emerging efficient photocatalysts. However, the serious photogenerated charges recombination limits the photocatalytic performance. To solve this problem, some modifications including forming heterojunction, fuel ratio adjustment, and shape modification have been carried out in this thesis.

In chapter 1, an overview of photocatalysis including photocatalytic dye degradation, water splitting, and  $\text{CO}_2$  reduction was introduced first. Then a review on spinel type ferrite photocatalysts including common structure, and synthesis method was summarized. In the end, various modification methods of photocatalysts for enhanced photocatalytic properties were introduced.

In chapter 2,  $\text{ZnFe}_2\text{O}_4/\text{SnO}_2$  (ZFO/ $\text{SnO}_2$ ) composites were fabricated via a facile solution combustion synthesis (SCS) method for methylene blue (MB) degradation. The crystallite and morphology characterizations revealed that ZFO/ $\text{SnO}_2$  composites have relatively small crystallite and particle size compared to pure ZFO. The introduction of  $\text{SnO}_2$  remarkably improved the photocatalytic performance of pure ZFO catalyst. Specifically, ZFO- $\text{SnO}_2$  (10%) exhibited the highest photocatalytic degradation rate constant of  $0.01970 \text{ min}^{-1}$  in the composites, approximately 3.08 and 2.64 times higher than that of single ZFO ( $0.00640 \text{ min}^{-1}$ ) and  $\text{SnO}_2$  ( $0.00747 \text{ min}^{-1}$ ), respectively. The band alignment analysis showed that the improvement of photocatalytic activity was due to the

improved charges separation efficiency in the ZFO/SnO<sub>2</sub> composite. ZFO-SnO<sub>2</sub> (10%) with H<sub>2</sub>O<sub>2</sub> showed the highest photo-Fenton degradation rate constant of 0.05301 min<sup>-1</sup> and could remove 95.2% of MB within 60 min under irradiation.

In chapter 3, CaFe<sub>2</sub>O<sub>4</sub> (CFO) was fabricated by solution combustion synthesis (SCS) method using different fuels (urea and glucose) and fuel ratios (0.5, 1.0, and 1.5). CFO-Glucose shows a smaller crystallite size than CFO-Urea sample. CFO-1.0 presents the smallest crystallite size among various fuel ratios products. CFO-1.0 photocatalyst presents the best photocatalytic MB degradation with a kinetic constant of 0.00372 min<sup>-1</sup> compared to CFO-Urea (0.00123 min<sup>-1</sup>), CFO-0.5 (0.00176 min<sup>-1</sup>), and CFO-2.0 (0.00249 min<sup>-1</sup>). Based on the PL and XPS characterizations, the efficient photocatalytic performance of CFO-1.0 is attributed to the efficient charge separation and suitable photocatalyst surface state.

In chapter 4, CaFe<sub>2</sub>O<sub>4</sub> nanorods (CFO NRs) and aggregated particles (CFO APs) were fabricated with and without the help of molten salt-assisted shape modification, respectively. CFO APs present inferior photocatalytic performance due to the plenty of grain boundaries which hinder photogenerated charges transfer and act as charge recombination sites. Molten salt-assisted modification can easily change the shape of CFO NRs and significantly suppresses the formation of grain boundaries, facilitating photogenerated charges separation and transfer for highly efficient photocatalytic degradation of methylene blue (MB). Surface state investigation indicates a decreased amount of unsuitable oxygen vacancies and defects in CFO NRs, which is beneficial in alleviating the recombination of photogenerated charges in CFO NRs. The CFO NRs show a ten-time increased kinetic constant of MB degradation from 0.0013 to 0.013 min<sup>-1</sup> by virtue of the alleviative charge recombination.

In chapter 5, an overall conclusion of this dissertation was presented. Overall, this thesis performed a systematic research on the design and modification of spinel type ferrites with highly efficient photocatalytic performance. This work also shows forming semiconductor heterojunction structure with suitable band position is an efficient way to enhance the photocatalytic performance of photocatalysts. The fuel ratio of SCS has a great effect on the final product composition and photocatalytic performance. Meanwhile, molten salt-assisted shape modification of photocatalyst is also an efficient way to improve their photocatalytic properties.



## **Chapter 1 Introduction**

## 1.1. Photocatalysis

With the increase of population and the development of industry, energy shortage and environmental pollution have become increasingly serious problems [1, 2]. Clean energy production by a sustainable approach is important for the future energy structure. Organic pollutant degradation by a novel method is also important for the sustainable development of cloth industry.

Since Fujishima and Honda first produced  $H_2$  from  $TiO_2$  photoelectrode through photoelectrochemical (PEC) water splitting in 1972 [3], the research on semiconductor-based photocatalytic reaction has attracted increasing attention. Specifically, the number of paper publications with the topic of photocatalytic obtained from Web of Science database has increased dramatically as shown in Figure 1.1. Solar energy as an inexhaustible clean energy can be used as an effective solution to energy and environmental problems. Compared with other methods, solar driven photocatalysis has plenty of advantages including cost-effective, environmentally friendly, without other energy source, highly effective, and high reusability. Photocatalytic reaction has been introduced to many fields including pollutants removal [4, 5], water splitting [6, 7],  $CO_2$  reduction[8, 9], and selective organic synthesis [10, 11] and so on.

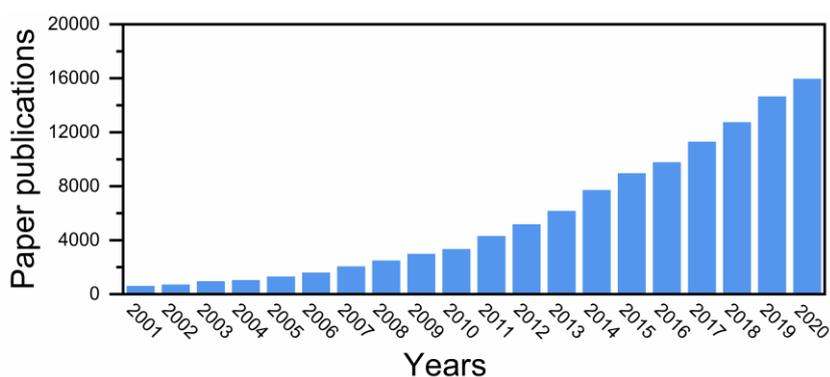


Figure 1.1 Paper publications with the topic of photocatalytic

Generally, photocatalysis occurs in the following three steps as shown in Figure 1.2: (1) absorption of photons with energy larger than that of band gap ( $E_g$ ) to produce electron and hole pairs, (2) photoinduced charge pairs separation and transportation to the reactive sites on the surface, and (3) surface oxidation-reduction reaction by the photoinduced holes and electrons [12]. Therefore, there are the following principles when developing high-efficiency photocatalysts. Semiconductors with narrow bandgaps are more conducive to utilize more solar energy. Effective charges separation is also important to enhance photocatalytic performance.

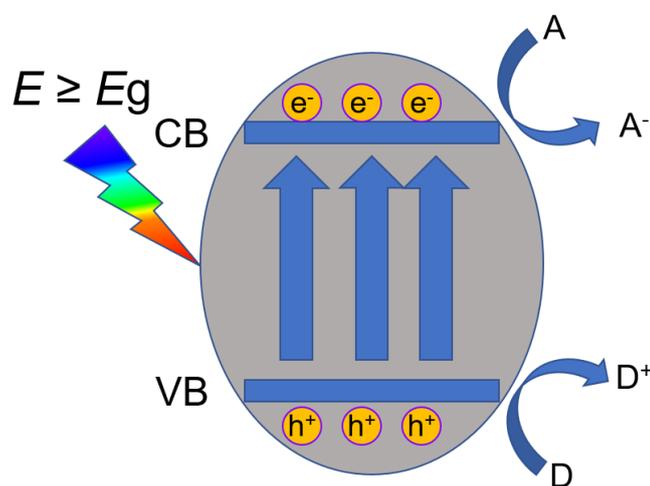


Figure 1.2 The generation, separation, and reaction of electron-hole pairs in a semiconductor.

### 1.1.1. Photocatalytic pollutant degradation

Due to the extensive use of organic dyes in the textile industry, a large amount of colored wastewater has become a serious problem, threatening environmental safety and human health [13, 14]. Chemical structures of common dyes are shown in Figure 1.3.

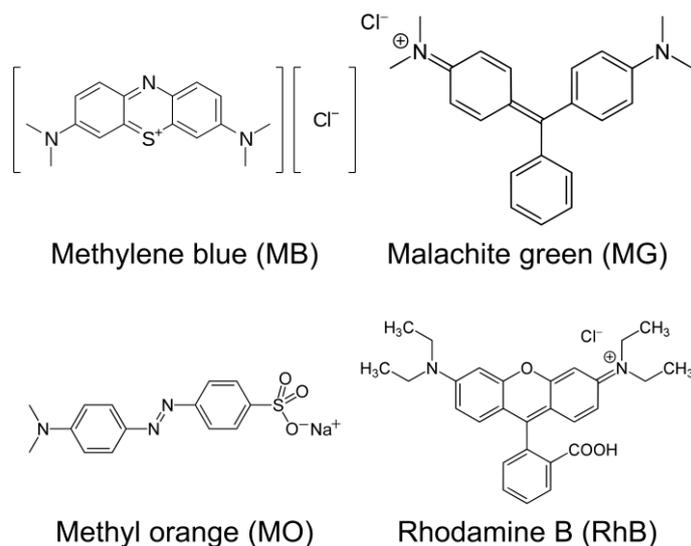
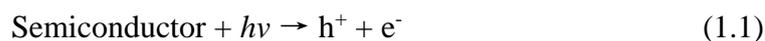


Figure 1.3 Common dyes chemical structure

Compared with many other methods to degrade organic pollutants, including biomass method, advanced oxidation method, and activated carbon, using photocatalysts to degrade organic dyes through photocatalytic method is a green and efficient method because it only uses environmentally stable photocatalyst and solar energy [15, 16].

Typically, when the semiconductor photocatalyst is under irradiation with the energy higher than the bandgap, a photogenerated electron ( $e^-$ ) will be excited from the valence band to conduction band, and there will be forming a photogenerated hole ( $h^+$ ) in the valence band (equation (1.1)). After separation and diffusion, parts of photogenerated  $e^-$  and  $h^+$  will transfer to the surface of semiconductor to take part in specific reaction. The photogenerated  $e^-$  at conduction band can be easily captured by dissolved oxygen in the solution to produce reactive superoxide free radical ( $\cdot O_2^-$ ) through equation (1.2) [17]. Parts of will further react with hydrogen ion to form active free hydroxyl radical ( $\cdot OH$ ) and hydroxyl ion ( $H^+$ ) as shown in equation (1.3). Meanwhile,  $h^+$  on the surface of photocatalyst will react with water to form  $\cdot OH$  and  $H^+$  according to equation (1.4). These active radicals can degrade the organic pollutant in the solution by photocatalytic reaction (equation (1.5)) [18].



### 1.1.2. Photocatalytic water splitting

Photocatalytic water splitting is a promising way to produce hydrogen from water under irradiation. A simple photocatalytic water splitting process with the help of co-catalysts can be illustrated in Figure 1.4 [19]. Common photocatalytic water splitting reaction can be presented as the following equations:

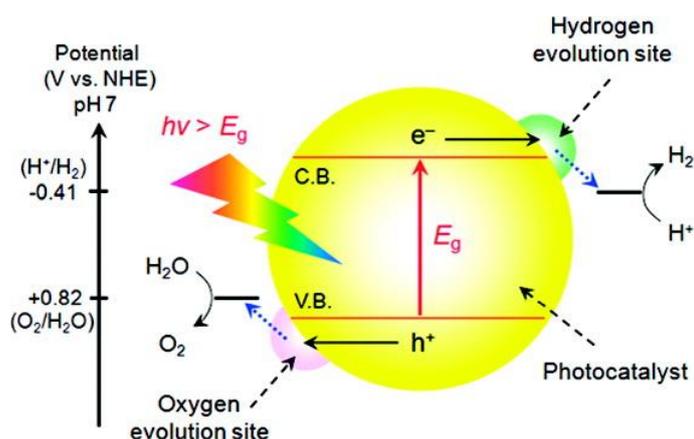
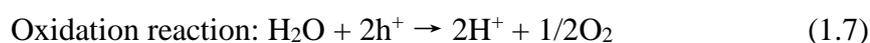
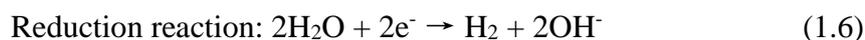
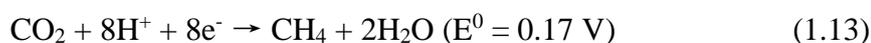
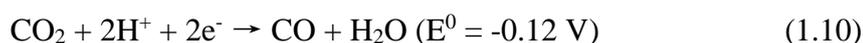


Figure 1.4 Schematic energy diagrams of photocatalytic water splitting [19]

### 1.1.3. Photocatalytic CO<sub>2</sub> reduction

The photocatalytic CO<sub>2</sub> reduction into valuable hydrocarbon fuels is a promising path to solve the increasing carbon dioxide emissions and energy shortage crisis. Due to the

diversity of reduction products, the photocatalytic CO<sub>2</sub> reduction still faces huge challenges. The standard potentials of CO<sub>2</sub> reduction to different products are summarized as below (vs. normal hydrogen electrode, NHE), pH = 0: [20]



## 1.2. Spinel type ferrite photocatalysts

Titanium oxide, as the most widely studied photocatalyst, exhibits excellent photocatalytic performance in many fields [21-24]. Nevertheless, TiO<sub>2</sub> with wide bandgap (3.2 eV) only shows high photocatalytic efficiency under ultraviolet (UV) light irradiation [25]. As shown in Figure 1.5, UV light irradiation only accounts for 4.6% of the solar spectrum, but visible light irradiation accounts for 47.7% of the solar spectrum [26]. Therefore, it is necessary to develop visible-light-active and property stable semiconductor photocatalysts with narrow bandgap to take full advantage of solar irradiation. Spinel type ferrites are suitable photocatalysts with wide photocatalytic applications due to their narrow optical bandgap (<2.2 eV), low cost, and superior durability [27]. They are effective photocatalysts for organic pollutant degradation [28, 29] and water splitting [30]. However, their inferior charge separation efficiency, low electrical conductivity, and limited synthesis methods limit the further development of spinel type ferrites photocatalysts. Therefore, it is necessary to review the spinel type ferrites photocatalysts and find other modification methods.

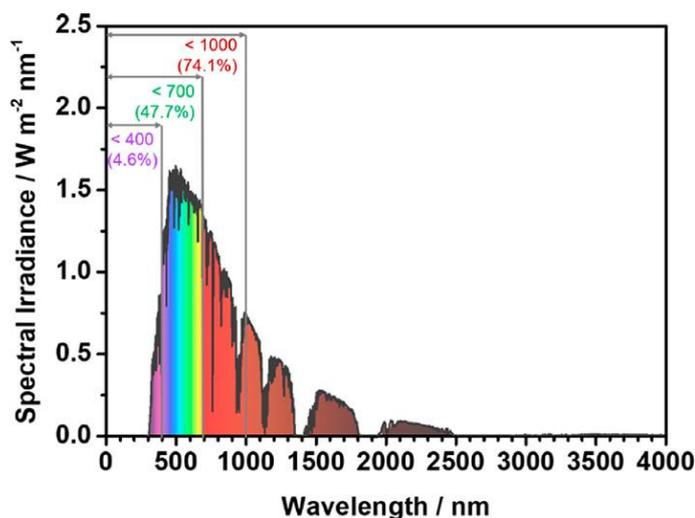


Figure 1.5 AM 1.5 G solar spectrum based on the ASTM G173-03 reference spectrum [26].

### 1.2.1. The structure of spinel type ferrites

Spinel type ferrites have a general formula  $M_xFe_{3-x}O_4$ , where M refers to the divalent metal ( $M = Ni, Co, Zn, Ca, Mg, Mn$ , and so on). They always show magnetic properties, which are significantly important for the recycle after photocatalytic application process. They are always used as photocatalysts for the photocatalytic degradation of organic pollutants [31, 32]. The common crystal structures of spinel type ferrites are shown in Figure 1.6. The structure of spinel ferrites is derived from the mineral spinel,  $MgAl_2O_4$ , by replacing the trivalent Al ion with Fe and Mg ion by other divalent metal ions. In normal spinel structure (Figure 1.6(a)), all M ions are in the tetrahedral sites, and all Fe ions are in the octahedral sites. Samples with normal spinel structure include  $ZnFe_2O_4$ ,  $CdFe_2O_4$ , and so on. When few parts of Fe ions occupy the tetrahedral sites, the structure is called as inverse spinel structure as shown in Figure 1.6(b). Some other spinel ferrites, such as  $CaFe_2O_4$  [33],  $MgFe_2O_4$  [34], and  $BaFe_2O_4$  [35], present orthorhombic structure as shown in Figure 1.6(c). Spinel ferrites photocatalysts always show super photo and chemical stability in aqueous systems [36]. Spinel ferrite like  $ZnFe_2O_4$  is very stable in alkaline

solution system. Spinel ferrite like  $\text{CaFe}_2\text{O}_4$  is very stable in acidic solution system.

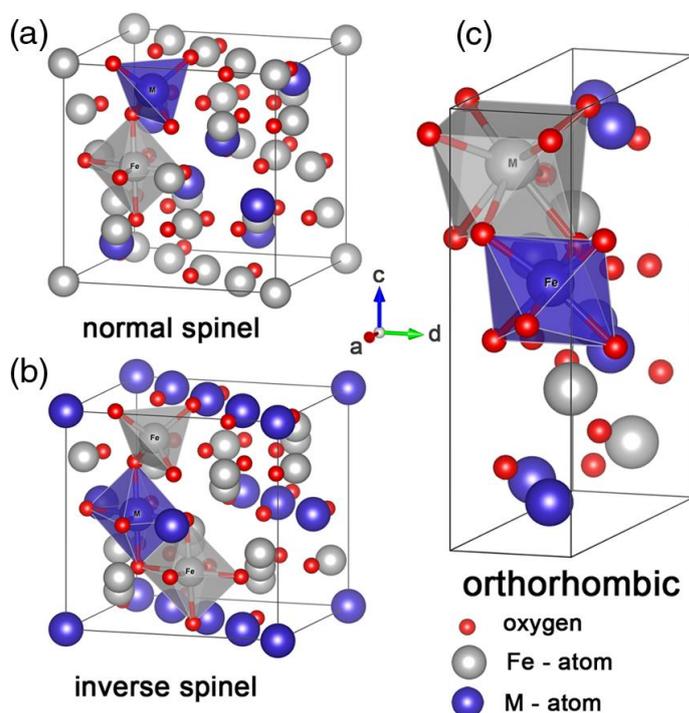


Figure 1.6 Crystal structures of spinel ferrites: (a) normal spinel, (b) inverse spinel, and (c) orthorhombic each demonstrating the three crystallographic sites [37].

Most of spinel ferrites are narrow bandgap semiconductors. Their band positions are shown in Figure 1.7.

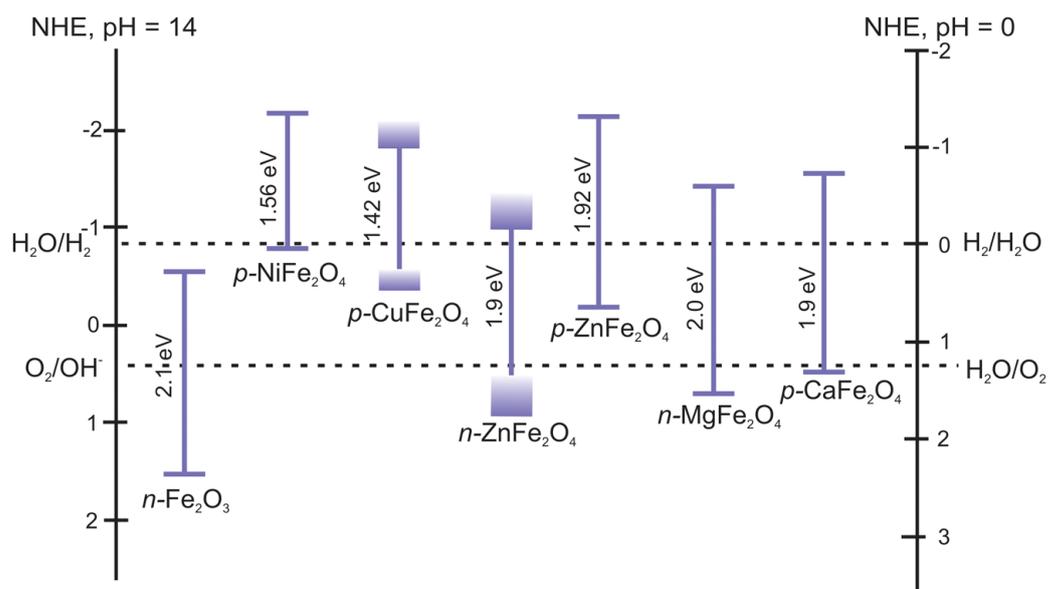
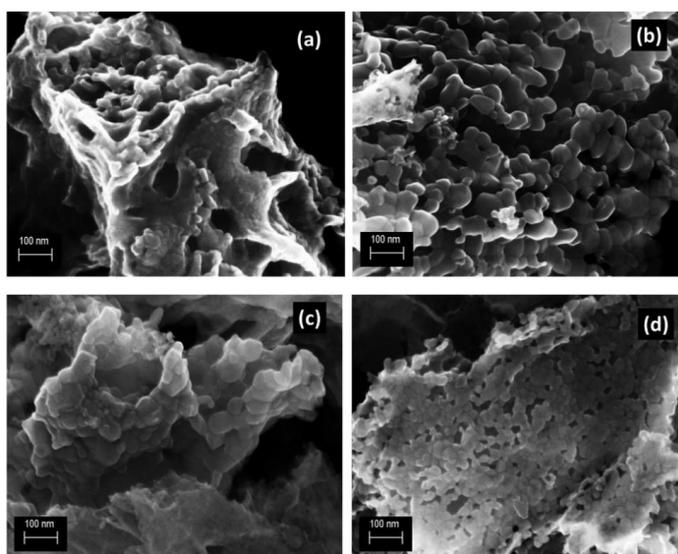


Figure 1.7 Band positions of spinel ferrites [37].

### 1.2.2. Synthesis methods

A number of different synthesis methods including solution combustion synthesis, thermal methods, and co-precipitation are used to fabricate spinel ferrite catalysts.

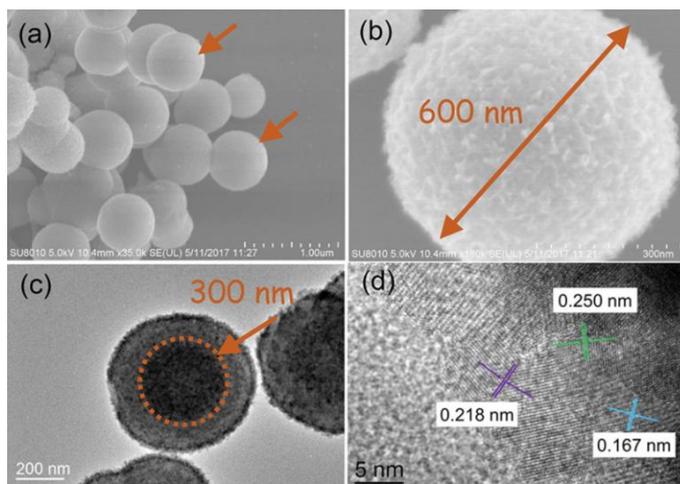
Solution combustion synthesis (SCS) is a facile method to produce spinel ferrite product using metal nitrates and fuels (such as urea, glycine, glucose, and citric acid). Some experimental factors such as fuel ratio, fuel kind, and calcination temperature have great effect on the final product [38, 39]. SCS method usually has energy saving, high efficiency, and high output characteristics. However, the products obtained by SCS method usually present aggregated morphology by multiple nanoparticles [40].



Equation 1.14 FESEM images of (a)  $\text{CoFe}_2\text{O}_4$ , (b)  $\text{Co}_{0.5}\text{Mn}_{0.5}\text{Fe}_2\text{O}_4$ , (c)  $\text{Co}_{0.5}\text{Ni}_{0.5}\text{Fe}_2\text{O}_4$ , and (d)  $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$  [40]

The thermal synthesis methods for ferrites photocatalysts include hydrothermal, solvothermal, seed-hydrothermal, mechano-thermal, and microwave. In each method, an iron salt is often used, usually  $\text{Fe}(\text{NO}_3)_3$  or  $\text{FeCl}_3$ , and another metal salt is used, such as  $\text{M}(\text{NO}_3)_2$ ,  $\text{MSO}_4$ , or  $\text{MCl}_2$ . These salts are usually first dissolved in water or other solvents, and the pH is adjusted to an appropriate range according to different metal salt precursors. Then the mixed solution is placed in the reactor, usually at a temperature lower than 200

°C and heated for 12-24 h. Finally, after cooling to room temperature, it is centrifuged and dried in a drying oven at approximately 85 °C overnight. The products obtained by thermal synthesis method usually show specific nano morphology. A yolk-shell  $\text{ZnFe}_2\text{O}_4$  in was fabricated by solvothermal synthesis method using  $\text{Zn}(\text{NO}_3)_2$ ,  $\text{Fe}(\text{NO}_3)_3$ , and dopamine as raw materials [41].



Equation 1.15 SEM images (a, b), TEM images (c), high resolution TEM image (d) of CN- $\text{ZnFe}_2\text{O}_4$  [41]

Co-precipitation method to prepare ferrites are similar to thermal methods. Fe(III) and metal salts are dissolved in water along with a surfactant, oleic acid, under stirring and gentle heating. The pH of the solution is adjusted to 7-10 to fabricate precipitation products usually with small size. The synthesized precipitation product is centrifuged and washed with water and then dried at 80-100 °C. Further, the as-synthesized product can be heated at different temperature and different heating rates to form product with different morphologies. [42, 43].

### 1.3. Modification of photocatalysts for enhanced performance

Common photoinduced formation of an electron-hole pair in a semiconductor with possible decay paths as shown in Figure 1.8 [44]. Generally, to overcome these decay paths, some modification methods have been introduced in photocatalysts for enhanced

performance, such as forming heterojunction, co-catalysts, doping, plasma, photodeposition, and flux modification.

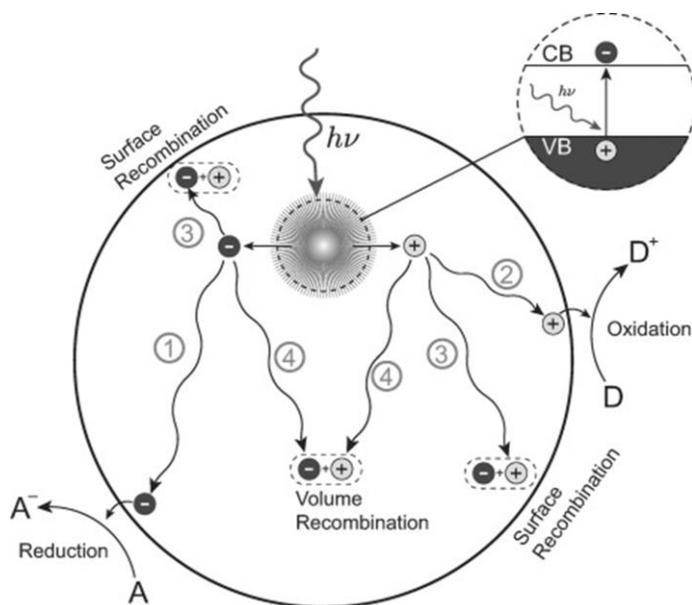


Figure 1.8 Schematic illustration of the basic mechanism of a semiconductor photocatalytic process. A = electron acceptor, D = electron donor. Pathways 1 and 2: donation of the carrier to the acceptor reactants on the surface, which results in the desired redox reactions. Pathway 3: carriers recombination occurs on the surface of a semiconductor. Pathway 4: carriers recombination occurs in the bulk of the semiconductor [44].

### 1.3.1. Heterojunction

The formation of heterojunction can cause band bending and internal electric field to promote effective separation of charges in space so that more photo-generated charges participate in the photocatalytic reaction. Generally, the types of semiconductor heterojunctions can be divided into four types, such as Schottky junction, Type I, Type II and Type III heterojunctions as shown in Figure 1.9. Among these heterojunctions, only Schottky junction and Type II can effectively improve the photo-generated charge separation rate and prolong the photo-generated charge lifetime.

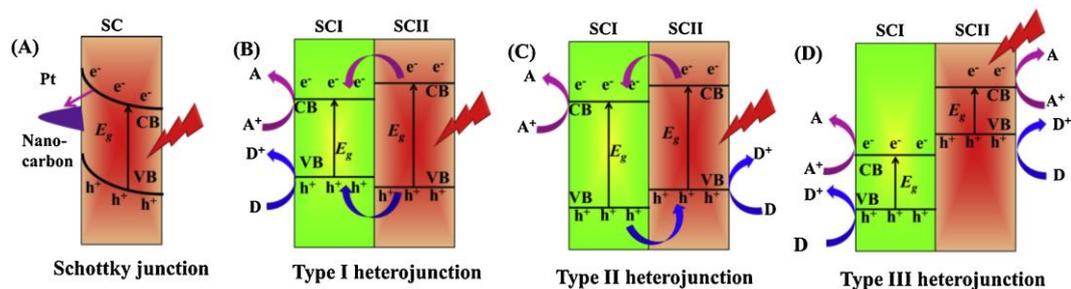


Figure 1.9 Spatial charge-separation mechanisms for four different types of semiconductor heterojunctions: (A) Schottky junction, (B) Type I, (C) Type II, and (D) Type III heterojunctions [45].

Up to now, the combination of spinel ferrites-based semiconductors, such as NiFe<sub>2</sub>O<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub> [46], CdS/NiFe<sub>2</sub>O<sub>4</sub> [47], PdO/SrFe<sub>2</sub>O<sub>4</sub> [48], CaFe<sub>2</sub>O<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub> [49], ZnO/ZnFe<sub>2</sub>O<sub>4</sub> [50], and CoFe<sub>2</sub>O<sub>4</sub>-g-C<sub>3</sub>N<sub>4</sub> [51], have been constructed for enhanced photocatalytic performance.

### 1.3.2. Doping

Generally, doping of exotic elements can enhance the visible light harvesting ability because of the formation of localized or delocalized electronic states. Additionally, the introduction of multiple impurities leads to disorder effects and thus form tail states (Urbach tails) in the electronic structure [52]. Jannat reported the nickel doped zinc ferrite (ZnFe<sub>2-x</sub>Ni<sub>x</sub>O<sub>4</sub>) nano-composites were synthesized using a facile auto-combustion method using glycine as fuel for efficient methylene blue degradation [53].

## 1.4. Objectives and dissertation organization

In this dissertation, some modification methods have been applied to enhance the photocatalytic performance of ZFO and CFO semiconductor photocatalysts. **Chapter 1** gives basic introduction about photocatalysis, spinel type ferrite photocatalysts, and common modification methods for enhanced photocatalytic performance. **Chapter 2** introduces SnO<sub>2</sub> semiconductor to form a ZFO/SnO<sub>2</sub> heterojunction for enhanced photocatalytic MB degradation. **Chapter 3** shows the effect of fuel kinds and fuel ratios on

photocatalytic activity of CFO. **Chapter 4** introduces a molten salt-assisted shape modification method to enhance the photocatalytic performance of CFO NRs. **Chapter 5** gives some conclusions about this thesis and some future prospects.

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**Chapter 2 Facile Synthesis of ZnFe<sub>2</sub>O<sub>4</sub>/SnO<sub>2</sub> Composites for  
Efficient Photocatalytic Degradation of Methylene Blue**

## 2.0. Brief summary

In this chapter, ZnFe<sub>2</sub>O<sub>4</sub>/SnO<sub>2</sub> (ZFO/SnO<sub>2</sub>) composites were fabricated via a facile solution combustion synthesis (SCS) method for methylene blue (MB) degradation. The crystallite and morphology characterizations revealed that ZFO/SnO<sub>2</sub> composites have relatively small crystallite and particle size compared to pure ZFO. The introduction of SnO<sub>2</sub> remarkably improved the photocatalytic performance of pure ZFO catalyst. Specifically, ZFO-SnO<sub>2</sub> (10%) exhibited the highest photocatalytic degradation rate constant of 0.01970 min<sup>-1</sup> in the composites, approximately 3.08 and 2.64 times higher than that of single ZFO (0.00640 min<sup>-1</sup>) and SnO<sub>2</sub> (0.00747 min<sup>-1</sup>), respectively. The band alignment analysis showed that the improvement of photocatalytic activity was due to the improved charges separation efficiency in the ZFO/SnO<sub>2</sub> composite. ZFO-SnO<sub>2</sub> (10%) with H<sub>2</sub>O<sub>2</sub> showed the highest photo-Fenton degradation rate constant of 0.05301 min<sup>-1</sup> and could remove 95.2% of MB within 60 min under irradiation.

## 2.1. Introduction

In the last few decades, organic dye aqueous solution pollution treatment has been receiving great attention due to the increasing industry wastewater in leather, textile, and food industries [1, 2]. Conventional methods such as physical adsorption [3], biodegradation [4, 5], membrane separation [6], Fenton reaction [7], and photocatalytic degradation [8, 9] have been developed as promising technologies for organic dyes degradation. Among them, Fenton reaction and semiconductor photocatalytic degradation can be operated under mild conditions. H<sub>2</sub>O<sub>2</sub> in the Fenton reaction can be activated to produce ·OH species with high reactivity and ferrous ion (Fe<sup>2+</sup>) can be oxidized to ferric ion (Fe<sup>3+</sup>) [10]. However, the sluggish recycling from Fe<sup>3+</sup> to Fe<sup>2+</sup> often limits the Fenton reaction process of catalysts [11]. Generally, the photocatalytic degradation of organic dye

pollutants includes three main reaction processes: transition of electron and forming of hole, separation of charge carrier pairs and diffusion to the semiconductor/solution interface, and degradation of dye molecules with reactive radicals on the surface [9]. However, the photocatalytic degradation performance of semiconductor was limited by some intrinsic properties of catalysts, such as narrow absorption range, lower charges separation efficiency and fast charges recombination in the bulk, consumption of charges on the surface [12]. As mentioned above, single Fenton reaction or photocatalytic process for dye degradation cannot meet the needs of practical application. The Fenton reaction process can be promoted by light irradiation due to the increasing of  $\cdot\text{OH}$  and  $\text{Fe}^{2+}$  from the reaction of  $\text{Fe}^{3+}$  and  $\text{OH}^-$ , which is called the photo-Fenton reaction [13]. Meanwhile, photogenerated electron will be captured by  $\text{H}_2\text{O}_2$  in the photo-Fenton reaction, improving separation efficiency of charge carriers. Thus, these synergistic effects will lead to enhanced dye degradation efficiency in the photocatalyst/ $\text{H}_2\text{O}_2$  system under irradiation.

Recently, spinel ferrites ( $\text{MFe}_2\text{O}_4$ ) have drawn increasing attention by virtue of their suitable bandgap and remarkable durability under irradiation for solar fuel energy conversion and solar-induced environmental remediation [14, 15]. Among them,  $\text{ZnFe}_2\text{O}_4$  (ZFO) is a promising n-type semiconductor catalyst for dye photocatalytic degradation due to its suitable bandgap (approximately 1.9 eV), superior durability, and natural abundance [16]. Unfortunately, fast charge recombination often limited its practical application [17]. Forming semiconductor composites with suitable band levels is a reliable and promising strategy due to its enhanced photogenerated charge separation efficiency. Recently, a lot of work has been investigated on ZFO/semiconductor composites, such as ZFO/ $\text{ZnO}$  [18], ZFO/ $\text{Fe}_2\text{O}_3$  [19], ZFO/ $\text{TiO}_2$  [20], ZFO/ $\text{C}_3\text{N}_4$  [21], ZFO/ $\text{La}_2\text{O}_2\text{CO}_3$  [22], and ZFO/ $\text{SnFe}_2\text{O}_4$  [23]. Recently, a hollow microtubes  $\text{SnO}_2$  has been fabricated by electrospinning with a

highly photocatalytic property for dyes degradation [24]. Some studies show that SnO<sub>2</sub> as a superior electron acceptor semiconductor [25] can form a composite with other semiconductors to achieve high photocatalytic activity like CdS/SnO<sub>2</sub> [26], ZnO/SnO<sub>2</sub> [27], TiO<sub>2</sub>/SnO<sub>2</sub> [28]. However, there are few researchers studied the photocatalytic activity of ZFO/SnO<sub>2</sub> composites.

In this chapter, ZFO/SnO<sub>2</sub> composites were fabricated through a solution combustion synthesis (SCS) method. The photocatalytic degradation performance of catalysts was investigated through degradation of methylene blue (MB) aqueous solution under irradiation. The photo-Fenton degradation of MB was also studied under H<sub>2</sub>O<sub>2</sub> condition. The optimization amount of SnO<sub>2</sub> in ZFO/SnO<sub>2</sub> composites was also investigated for MB photocatalytic degradation. The charge separation and transfer over ZFO/SnO<sub>2</sub> composite and possible MB degradation mechanism were proposed.

## **2.2. Experimental**

### *2.2.1. Materials*

Commercially available iron nitrate enneahydrate (Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, 99.0%), zinc nitrate hexahydrate (Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 99.0%), urea (CO(NH<sub>2</sub>)<sub>2</sub>, 99.0%), tin chloride pentahydrate (SnCl<sub>4</sub>·5H<sub>2</sub>O, 98.0%), and ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>, 99.0%) were directly used without further purification.

### *2.2.2. Synthesis of ZFO/SnO<sub>2</sub> composites*

Pre-experiments were performed to show the effect of SCS precursor on final product composition. Solution precursor and gel precursor samples are prepared according to Figure 2.1. Stoichiometric number of reagents according to Equations (2.1) were dissolved with deionized water (30 mL) and stirred for 30 min to form transparent solution precursor. Then put it directly into the furnace, heat it up to 500 °C from room temperature, keep it

for 10 minutes, and cool it down to room temperature in the furnace. After carefully grinding, it is heated at 1000 °C for 2 h. The final product is named as S500ZFO. Unlike the process of preparing solution precursor samples, gel precursor samples synthesis process also needs additional gel forming process before heating to 500 °C. Then perform the same process and the final produce is named as G500ZFO.

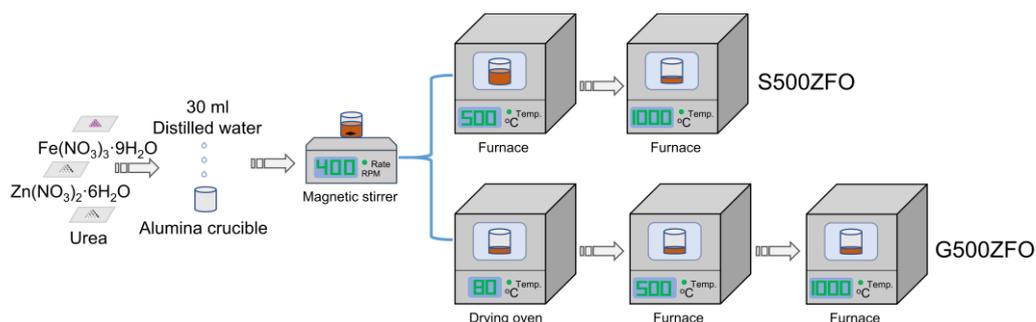


Figure 2.1 Schematic illustration of the  $\text{ZnFe}_2\text{O}_4$  powders preparation procedure.

To further understand the SCS process of ZFO using different precursors. A lab-made temperature monitoring apparatus were made, as shown in Figure 2.2. The equipment is consisted of a heater, a stainless-steel bin with a long vertical stainless-steel mesh chimney and a thermocouple coupled with monitor.

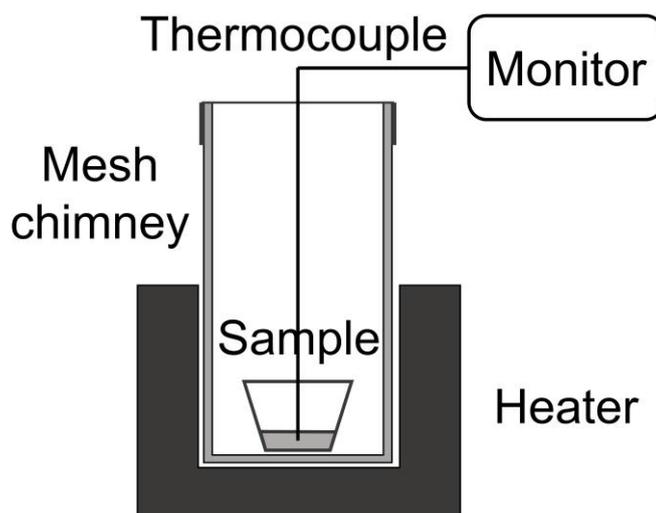


Figure 2.2 Temperature test equipment

Photocatalysts used in this study were fabricated by a SCS method using urea as fuel

according to the following reactions.



For synthesis of single ZFO or SnO<sub>2</sub>, stoichiometric number of reagents according to Equations (2.1) and (2.2) were dissolved with deionized water and stirred for 30 min. Then put the transparent solution into a drying oven for 12 h at 80 °C. Then the mixture was underwent a two-step high temperature calcination process at 500 and 1000 °C for 10 and 120 min, respectively.

ZFO/SnO<sub>2</sub> composites with different SnO<sub>2</sub> mole ratios (5%, 10%, and 15%) were fabricated by performing the same process as single catalyst and were designed as ZFO-SnO<sub>2</sub> (5%), ZFO-SnO<sub>2</sub> (10%), and ZFO-SnO<sub>2</sub> (15%), respectively.

### 2.2.3. Characterization

X-ray diffraction (XRD) patterns were collected at a diffractometer (Miniflex 600, Rigaku) using the radiation source of Cu K $\alpha$ . The size values of crystallite were calculated by the Debye-Scherrer equation [29]. A field emission scanning electron microscope (JEOL, JSM-7001FA) was performed to study the surface morphologies of samples. X-ray photoelectron spectroscopic (XPS) measurements were performed at an X-ray photoelectron spectrometer (JEOL, JPS-9200), which was operated at 10 kV and 10 mA using Mg K $\alpha$  source. All the binding energies data in XPS spectra were calibrated with C 1s as the reference (284.8 eV). UV-Vis absorption spectra were collected on a UV-Vis spectrophotometer (JASCO 770) equipped with an integrating sphere attachment.

### 2.2.4. Photocatalytic and photo-Fenton activity measurements

The MB aqueous solution degradation experiments were performed to evaluate the photocatalytic degradation performance of as-obtained catalysts. Typically, the powder

photocatalysts of 50 mg were dispersed in a beaker containing 50 mL MB aqueous solution (20 ppm). To obtain adsorption equilibrium, the mixture solution in a shade cloth was magnetically stirred for 30 min. A Xe lamp as simulated solar light was applied to irradiate right above from the aqueous. During degradation process, 3 mL of the solution was drawn every 15 min. After centrifugation, the residual solution was analyzed by a UV-Vis spectrophotometer (JASCO, V-630). For photo-Fenton reaction, 100  $\mu\text{L}$   $\text{H}_2\text{O}_2$  (34 wt%) was added into the solution after stirring in the dark. The degradation efficiency can be obtained from the following Equation (2.3)

$$\frac{C_0 - C}{C_0} \times 100\% \quad (2.3)$$

where  $C_0$  and  $C$  are the concentration of MB after stirring in the dark and under irradiation, respectively.

## 2.3. Results and discussion

### 2.3.1. The effect of SCS precursor on product composition

XRD patterns of S500ZFO and G500ZFO are shown in Figure 2.3. For solution precursor SCS synthesis, the final products include  $\text{ZnFe}_2\text{O}_4$  and impure phase  $\text{ZnO}$ . For gel precursor SCS synthesis, the final product only includes pure  $\text{ZnFe}_2\text{O}_4$  phase with high crystallinity without any impurities. Therefore, SCS synthesis with gel precursor is beneficial to pure phase samples production.

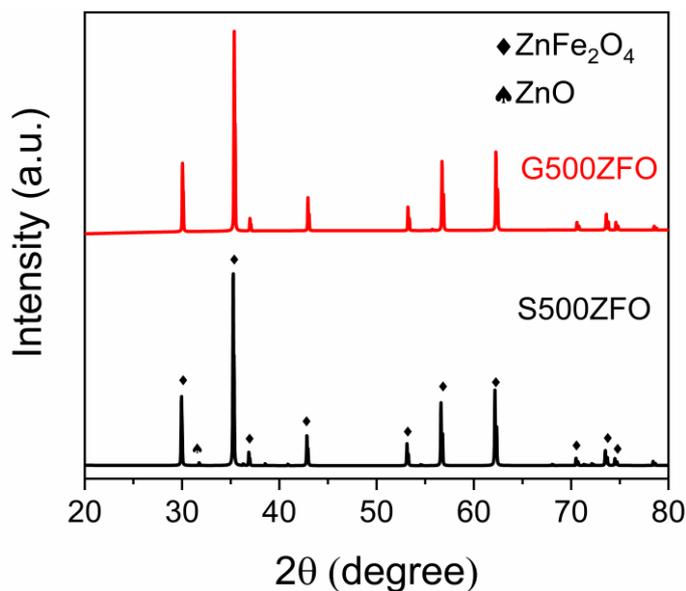


Figure 2.3 XRD patterns of solution and gel precursor samples

The possible reasons for this result were checked by testing temperature-time curves, as shown in Figure 2.4. For SCS synthesis process using solution precursor, there are two processes including water evaporation and combustion process. However, there is only combustion synthesis for gel precursor SCS synthesis process. Specifically, the highest temperature points for S500ZFO and G500ZFO are 350 and 460 °C, respectively. The high combustion temperature for G500ZFO is beneficial to the formation of pure phase product.

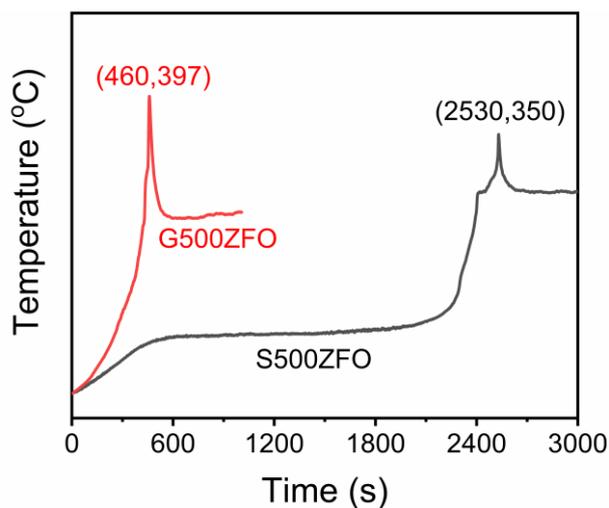


Figure 2.4 Temperature vs. time curves of solution-precursor and gel-precursor samples during SCS ignition process.

### 2.3.2. Crystalline structure and component composition

XRD patterns demonstrated in Figure 2.5 confirmed the composition of obtained catalysts. The diffraction peaks of ZFO can be ascribed to the crystal planes of cubic spinel  $\text{ZnFe}_2\text{O}_4$  (PDF#01-082-1049) [30]. These sharp and strong peaks indicate high crystallinity of samples due to the high calcination temperature during the SCS process. The sharp diffraction peaks of pure  $\text{SnO}_2$  also indicate its high crystallinity and tetragonal  $\text{SnO}_2$  phase (JCPDS NO. 01-071-5324) [31]. There is the coexistence of diffraction peaks from ZFO and  $\text{SnO}_2$  in the composites, indicating the successful formation of ZFO/ $\text{SnO}_2$  composite. With increasing the amount of  $\text{SnO}_2$ , the diffraction peaks intensity of  $\text{SnO}_2$  increased, while that of ZFO decreased. A new peak appeared at  $33.26^\circ$  in the ZFO/ $\text{SnO}_2$  composites. This peak can be ascribed to the (104) plane of  $\text{Fe}_2\text{O}_3$  (JCPDS NO. 01-087-1166) [32], which is similar to the literature [17]. Meanwhile, the stability of catalysts can be affected by the crystallite size. Sample with smaller crystallite size often provides a more stable crystallite phase [33]. Based on the Debye-Scherrer equation [29], the average crystallite sizes of ZFO are estimated to be 116, 98, 89, and 93 nm in the ZFO, ZFO- $\text{SnO}_2$  (5%), ZFO- $\text{SnO}_2$  (10%), and ZFO- $\text{SnO}_2$  (15%) samples, respectively. Likewise, the average crystallite size of pure  $\text{SnO}_2$  is estimated to be 42 nm. In the composites, the addition of  $\text{SnO}_2$  resulted in the crystallite size of ZFO decreased and showed the smallest size when the addition amount of  $\text{SnO}_2$  is 10% in the ZFO- $\text{SnO}_2$  (10%) sample.

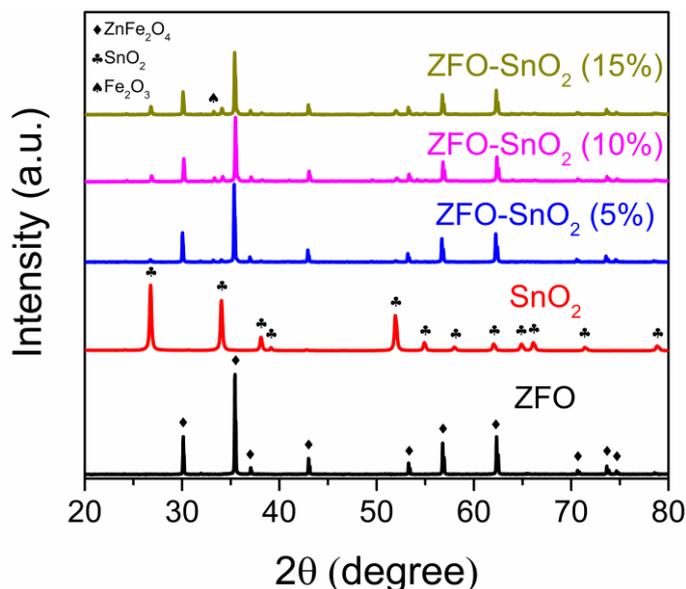


Figure 2.5 XRD patterns of ZFO, SnO<sub>2</sub>, and ZFO-SnO<sub>2</sub> composites.

### 2.3.3. Surface morphology

The morphology and elemental distribution of samples were examined by the FE-SEM and EDS shown in Figure 2.6. The morphology image in Figure 2.6 shows that ZFO with smooth surface is aggregated of some nanoparticles due to the high calcination temperature. Compared to pure ZFO, ZFO/SnO<sub>2</sub> composites show decreased particle size shown in Figure 2.6b-d, which is possibly due to the incorporation of SnCl<sub>4</sub> as new nucleation sites during the SCS process. The particle size of the composite is decreased with an increase in the amount of SnO<sub>2</sub>, resulting in the smallest particle size in ZFO-SnO<sub>2</sub> (10%). An excess amount of SnO<sub>2</sub> may lead to a greater particle size shown in Figure 2.6d. As shown in Figure 2.6e, SnO<sub>2</sub> has a smaller particle size around 40 nm compared to ZFO. The above SEM results agree with the XRD results. To clearly identify the formation configuration of the ZFO/SnO<sub>2</sub> composite, EDS measurements were performed to characterize the individual elemental mappings of ZFO-SnO<sub>2</sub> (10%) sample. As shown in Figure 2.6g-j, all the elements are uniformly distributed, indicating the homogeneous distribution of ZFO and SnO<sub>2</sub> in ZFO/SnO<sub>2</sub> composites.

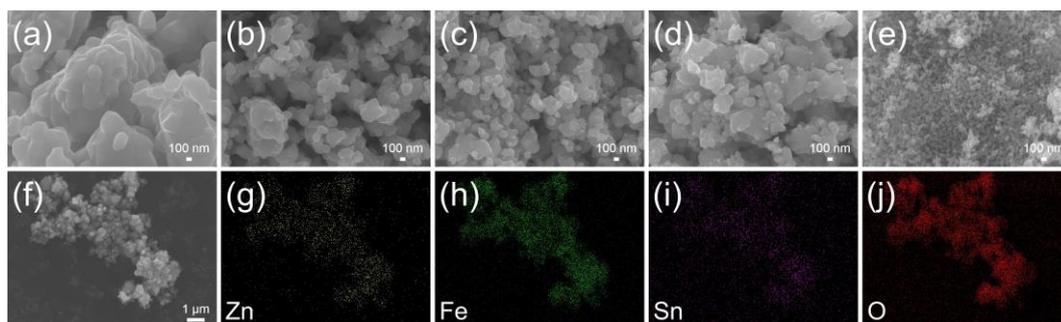


Figure 2.6 SEM images of (a) ZFO, (b) ZFO-SnO<sub>2</sub> (5%), (c) ZFO-SnO<sub>2</sub> (10%), (d) ZFO-SnO<sub>2</sub> (15%), and (e) SnO<sub>2</sub>. EDS elemental mapping images of (f) ZFO-SnO<sub>2</sub> (10%) at (g) Zn, (h) Fe, (i) Sn, and (j) O.

#### 2.3.4. Surface state analysis

The surface chemical composition and state of the obtained species were studied by XPS. Their detailed XPS spectra of Zn, Sn, and Fe elements in the ZFO-SnO<sub>2</sub> (10%) and O element of all samples are shown in Figure 2.7. As shown in Figure 2.7a, two peaks of binding energies at 1021.4 and 1044.4 eV of Zn 2p spectrum are corresponding to Zn 2p<sub>3/2</sub> and Zn 2p<sub>1/2</sub>, respectively [34]. Figure 2.7b exhibits two expected peaks of Sn 2d<sub>5/2</sub> and Sn 2d<sub>3/2</sub> in the ZFO-SnO<sub>2</sub> (10%) sample and the corresponding binding energies are 486.2 and 494.8 eV, respectively, which is demonstrated as Sn(IV) state [35]. For Fe 2p spectrum in Figure 2.7c, two peaks with binding energies at around 711.0 and 724.7 eV can be ascribed to Fe 2p<sub>3/2</sub> and Fe 2p<sub>1/2</sub>, respectively. There are two shakeup accompanying satellite signals (at around 717.5 and 724.1 eV), confirming the Fe(III) chemical state within the catalyst, which are consistent with the previous report [36]. The spectrum of Fe 2p<sub>3/2</sub> can be deconvoluted into two peaks, the peaks with lower and higher binding energies are corresponding to octahedral and tetrahedral sites, respectively [37]. The chemical state of O element is significant important for the photocatalytic properties of catalyst. Broad peaks of O 1s spectra for all samples can be observed in Figure 2.7d. O 1s spectrum can be deconvoluted into two distinct peaks at approximately 529.9 and 531.3 eV corresponding to the metal-oxygen bonds from lattice (O<sub>L</sub>) and oxygen vacancy/defect (O<sub>V</sub>), respectively,

with different states for oxygen atoms [38]. On one hand,  $O_V$  in metal oxide semiconductors is usually incorporated into the photocatalysts to improve photocatalytic properties due to the adventitious energy levels and improved charge concentration [39-41]. On the other hand, unsuitable  $O_V$  incorporation may bring about defects state on the surface. These defects states will provide sites for the recombination of charge carriers, which is disadvantage for the efficient charge separation [42-44]. The ratios of  $O_L$  and  $O_V$  are calculated according to their area ratios in O 1s spectra. The number of  $O_V$  ratios in ZFO and  $SnO_2$  may lead to a high charge recombination under irradiation, resulting in poor photocatalytic properties. The incorporation of  $SnO_2$  results in a slight decrease of  $O_V$  ratio, which contributes to the improved photocatalytic properties discussed below.

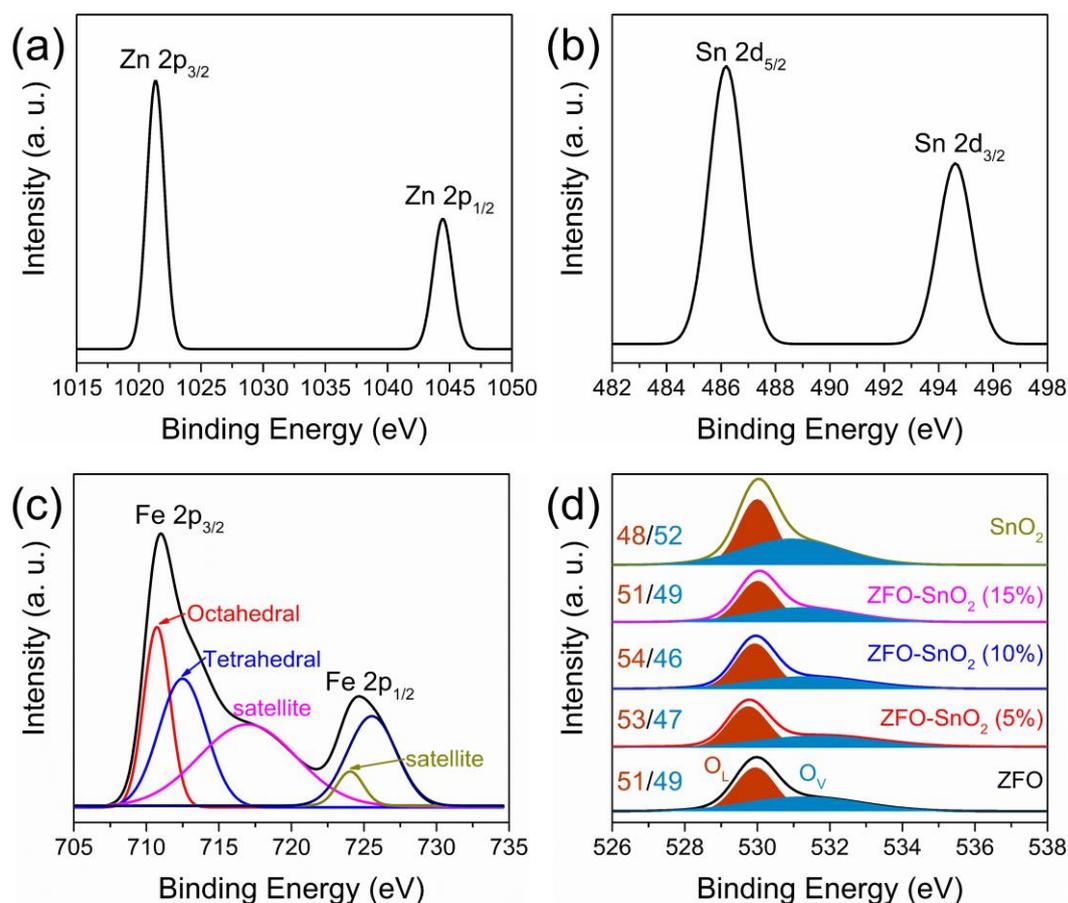


Figure 2.7 High-resolution XPS spectra of typical elements (a) Zn 2p, (b) Sn 3d, and (c) Fe 2p in the ZFO-SnO<sub>2</sub> (10%). (d) The fine structures of the XPS O 1s spectra for all samples. The area ratios of lattice-related (O<sub>L</sub>, orange) and vacancy-related (O<sub>v</sub>, blue) peaks are marked.

### 2.3.5. Optical properties

The optical absorption properties of the fabricated catalysts were characterized through UV-Vis absorption spectra shown in Figure 2.8. The absorption onsets for ZFO and SnO<sub>2</sub> are approximately 650 and 500 nm, respectively. Compared to pure ZFO, ZFO/SnO<sub>2</sub> composites show a decrease in the long-wavelength range and ZFO-SnO<sub>2</sub> (10%) sample shows the lowest absorbance position. This may be because of the decreased charge trapping effect on the sample surface due to the shallow energy level impurities [45].

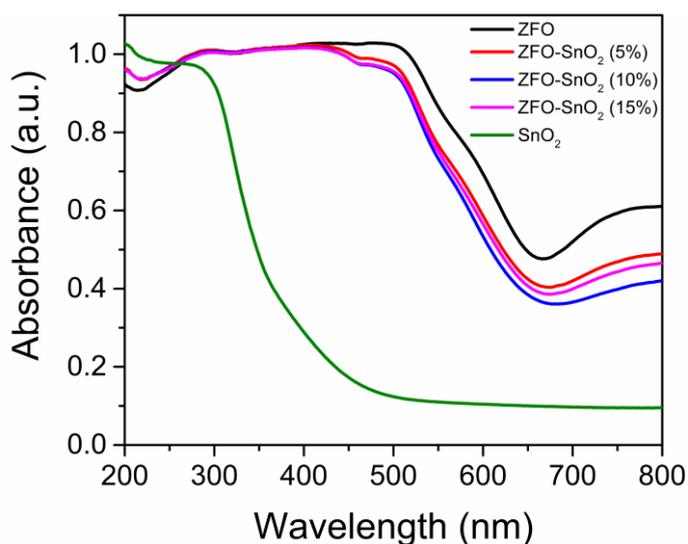


Figure 2.8 UV-Vis absorption spectra of ZFO, SnO<sub>2</sub> and ZFO-SnO<sub>2</sub> composites.

The energy band alignments over ZFO/SnO<sub>2</sub> composite were investigated before studying the photocatalytic properties of samples. Both direct ( $E_g^d$ ) and indirect ( $E_g^i$ ) bandgap energy values of ZFO, SnO<sub>2</sub>, and ZFO/SnO<sub>2</sub> composites were calculated with the help of Tauc plots through Equation (2.4) [46]:

$$(\alpha h\nu)^{1/n} = A(h\nu - E_g) \quad (2.4)$$

where  $\alpha$  is the absorption coefficient,  $h$  is the Planck constant,  $\nu$  is the photon's frequency,

$A$  is a constant,  $E_g$  is the optical bandgap energy of catalyst, and the  $n$  values are  $1/2$  and  $2$  for the direct and indirect transition bandgaps, respectively. As shown in Figure 2.9a, the  $E_g^d$  values for ZFO and  $\text{SnO}_2$  are 1.99 and 2.62 eV, respectively. ZFO and  $\text{SnO}_2$  show relatively small  $E_g^i$  values (1.22 and 1.86 eV) shown in Figure 2.9b. For the ZFO/ $\text{SnO}_2$  composites, the  $E_g^d$  and  $E_g^i$  values in Figure 2.9c and d both show slightly increase, demonstrating 2.05 and 1.24 eV, respectively.

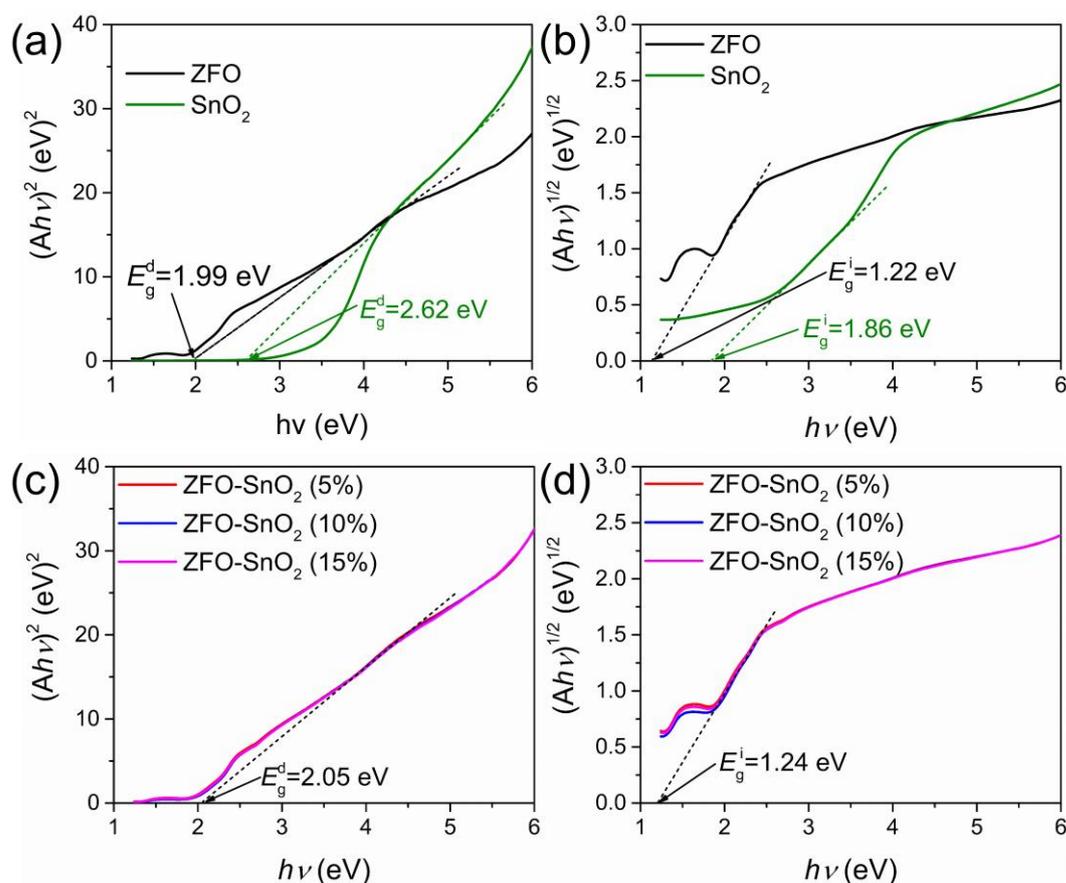


Figure 2.9 (a) Direct bandgap values estimation for ZFO and  $\text{SnO}_2$ , (b) Indirect bandgap values estimation for ZFO and  $\text{SnO}_2$ . (b) Direct bandgap values and (c) indirect bandgap values estimation for ZFO/ $\text{SnO}_2$  composites.

### 2.3.6. Band alignment analysis

For the analysis of the band alignment over ZFO/ $\text{SnO}_2$  composite, high-resolution XPS spectra at 0 eV surrounding were carried out and the valence band maximum (VBM) values

for single ZFO and SnO<sub>2</sub> samples were calculated via band XPS using a liner extrapolation method. From Figure 2.10, it can be seen that the VBM values of ZFO and SnO<sub>2</sub> were 0.90 and 2.60 eV, respectively. Figure 2.11a and b exhibited the core-level XPS spectra of Zn 2p and Sn 2d. After forming composite, the binding energies of Zn 2p<sub>3/2</sub> and Sn 2d<sub>5/2</sub> were shifted from 1021.4 to 1021.3 eV and from 486.1 to 486.2 eV, respectively. According to the bandgap values, VBM values, and core-level positions summarized in Table 2.1, the valence band offset ( $\Delta E_V$ ) between ZFO and SnO<sub>2</sub> was calculated by the following equations [47]:

$$\Delta E_V(\text{ZFO/SnO}_2) = (E_{\text{Zn}2\text{p}_{3/2}} - E_{\text{VBM}})_{\text{ZFO}} - (E_{\text{Sn}2\text{d}_{5/2}} - E_{\text{VBM}})_{\text{SnO}_2} - \Delta E_{\text{CL}} \quad (2.5)$$

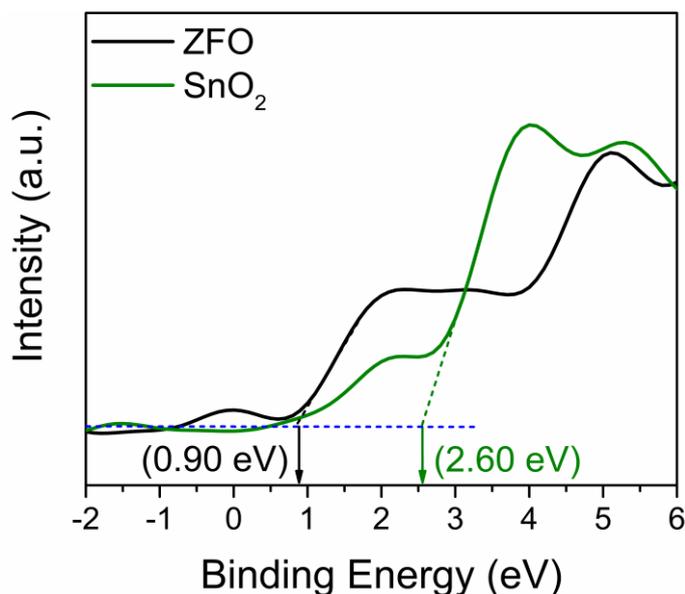
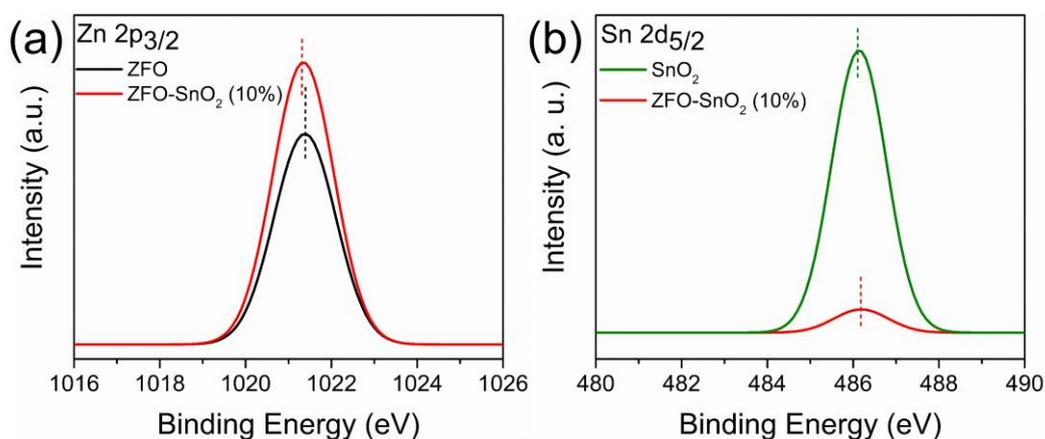
$$\Delta E_{\text{CL}} = (E_{\text{Zn}2\text{p}_{3/2}} - E_{\text{Sn}2\text{d}_{5/2}})_{\text{ZFO/SnO}_2} \quad (2.6)$$

where,  $(E_{\text{Zn}2\text{p}_{3/2}} - E_{\text{VBM}})_{\text{ZFO}}$  is the energy difference between Zn 2p<sub>3/2</sub> and VBM in the pure ZFO,  $(E_{\text{Sn}2\text{d}_{5/2}} - E_{\text{VBM}})_{\text{SnO}_2}$  is the energy difference between Sn 2d<sub>5/2</sub> and VBN in the SnO<sub>2</sub>, and  $\Delta E_{\text{CL}}$  is the energy difference between two core levels in the ZFO/SnO<sub>2</sub> composite. In addition, the  $E_g^d$  values of ZFO and SnO<sub>2</sub> are selected for calculation. Similarly, the conduction band offset ( $\Delta E_C$ ) can be calculated by Equation (2.7). Hence, the measured  $\Delta E_V$  and  $\Delta E_C$  are found to be 1.90 and 1.27 eV, respectively.

$$\Delta E_C(\text{ZFO/SnO}_2) = E_g^d(\text{ZFO}) + \Delta E_V(\text{ZFO/SnO}_2) - E_g^d(\text{SnO}_2) \quad (2.7)$$

Table 2.1 Bandgap values, VBM and core level binding energy of ZFO, SnO<sub>2</sub> and ZFO/SnO<sub>2</sub> composite samples.

Samples	ZFO	SnO <sub>2</sub>	ZFO/SnO <sub>2</sub>
Direct band gap, Eg (eV)	1.99	2.62	2.05
Indirect band gap, Eg (eV)	1.22	1.86	1.24
VBM (eV)	0.90	2.60	—
Zn 2p <sub>3/2</sub> (eV)	1021.4	---	1021.3
Sn 2d <sub>5/2</sub> (eV)	---	486.1	486.2

Figure 2.10 Valence band XPS spectra for ZFO and SnO<sub>2</sub>Figure 2.11 (a) Zn 2p<sub>3/2</sub> core level peaks for ZFO and ZFO-SnO<sub>2</sub> (10%), (b) Sn 2d<sub>5/2</sub> core level peaks for SnO<sub>2</sub> and ZFO-SnO<sub>2</sub> (10%).

### 2.3.7. Photocatalytic MB degradation

MB degradation experiments were performed to investigate the photocatalytic performance of as-fabricated catalysts. Figure 2.12 shows the MB degradation and the corresponding kinetics under different experimental conditions within 60 min. First, photocatalytic degradation and rate constants of ZFO, SnO<sub>2</sub>, and ZFO/SnO<sub>2</sub> composites were carefully investigated to determine the optimization amount of SnO<sub>2</sub> in ZFO/SnO<sub>2</sub>

composites. As shown in Figure 2.12a, single ZFO and SnO<sub>2</sub> catalyst can reach only 32.3% and 37.0% removal of MB under irradiation for 60 min, respectively. Compared to the single catalyst, composite catalysts show superior photocatalytic degradation performance. Specially, ZFO-SnO<sub>2</sub> (10%) shows the highest photocatalytic degradation efficiency (68.7%) in the composites. Herein, the process of MB degradation was analyzed by a pseudo-first-order kinetic reaction model, which can be described as the equation,  $-\ln C_0/C=kt$  [48]. The kinetic curves are presented in Figure 2.12b and the corresponding rate constants  $k$  are shown in Figure 2.12e. The rate constant values of single ZFO and SnO<sub>2</sub> are 0.00640 and 0.00747 min<sup>-1</sup>, respectively. Composites often showed enhanced reaction rate constant compared to single catalyst. Moreover, ZFO-SnO<sub>2</sub> (10%) catalyst shows the highest photocatalytic degradation rate constant of 0.01970 min<sup>-1</sup> in the composites, about 3.08 and 2.64 times higher than that of single ZFO and SnO<sub>2</sub>, respectively. According to Figure 2.12a and b, ZFO-SnO<sub>2</sub> (10%) is selected as a sample of the composite to further investigate its degradation property under H<sub>2</sub>O<sub>2</sub> condition.

The photocatalytic and photo-Fenton MB degradation of ZFO and ZFO-SnO<sub>2</sub> (10%) samples were performed. As shown in Figure 2.12c, the MB degradation efficiency was only 10.1% under irradiation without any catalysts and H<sub>2</sub>O<sub>2</sub>, indicating that MB solution had a good photo-stability under irradiation. The addition of photocatalyst could slightly enhance the degradation efficiencies of MB due to its inferior properties of samples as mentioned above. Only 33.3% of MB was removed under irradiation by adding H<sub>2</sub>O<sub>2</sub> due to the limited oxidation power of H<sub>2</sub>O<sub>2</sub> [49]. When there was only catalyst and H<sub>2</sub>O<sub>2</sub>, its degradation efficiencies were 33.8% and 40.9% for ZFO/H<sub>2</sub>O<sub>2</sub> (Dark) and ZFO-SnO<sub>2</sub> (10%)/H<sub>2</sub>O<sub>2</sub> (Dark) conditions, respectively. This is because of the limited dark Fenton reaction of catalysts under experimental conditions [50]. Interestingly, the light-catalysts-

H<sub>2</sub>O<sub>2</sub> systems usually show enhanced degradation efficiencies compared to the light-catalysts, catalysts-H<sub>2</sub>O<sub>2</sub>, and light-H<sub>2</sub>O<sub>2</sub> systems. Typically, the ZFO/H<sub>2</sub>O<sub>2</sub> and ZFO-SnO<sub>2</sub> (10%)/H<sub>2</sub>O<sub>2</sub> shown improved MB degradation efficiencies of 65.8% and 95.2% within 60 min, respectively. To further study the improvement of MB degradation efficiencies for ZFO-SnO<sub>2</sub> (10%), the plots of ln(C<sub>0</sub>/C) versus reaction time are shown in Figure 2.12d, and the corresponding rate constant k collected in Figure 2.12e were calculated according to the slope of the curves. Usually, the rate constants of light-catalysts-H<sub>2</sub>O<sub>2</sub> systems are faster than that of light-catalysts and catalysts-H<sub>2</sub>O<sub>2</sub> systems. Specially, the light ZFO/H<sub>2</sub>O<sub>2</sub> condition shows MB degradation rate constant of 0.01783 min<sup>-1</sup>, which is approximately 2.61 and 2.79 times higher than that of ZFO/H<sub>2</sub>O<sub>2</sub> (Dark) and light ZFO conditions, respectively. While, the light ZFO-SnO<sub>2</sub> (10%)/H<sub>2</sub>O<sub>2</sub> condition shows the rapidest MB degradation rate constant of 0.05301 min<sup>-1</sup>, which is approximately 6.44 and 2.69 times higher than that of ZFO-SnO<sub>2</sub> (10%)/H<sub>2</sub>O<sub>2</sub> (Dark) and light ZFO conditions, respectively.

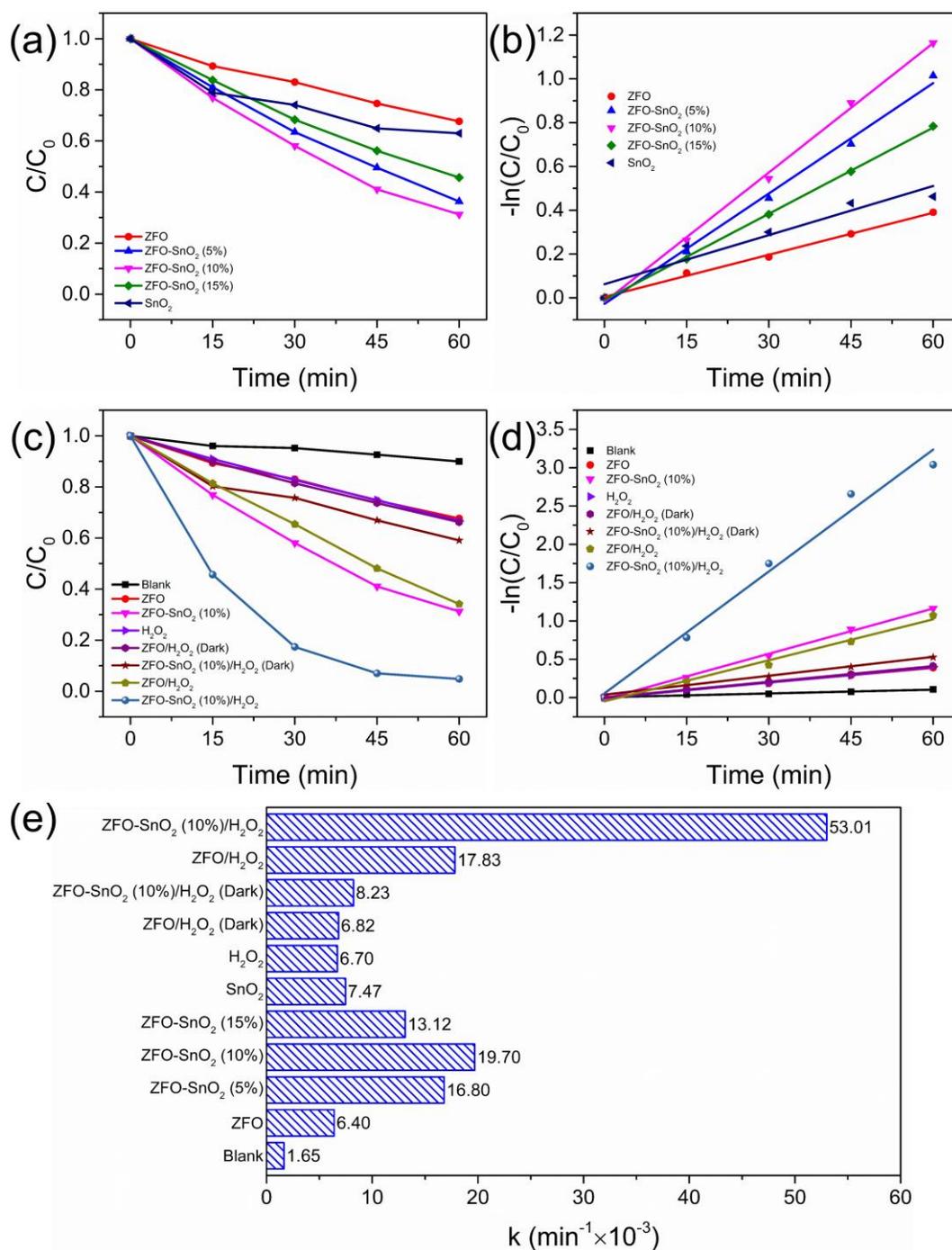


Figure 2.12 (a) Photocatalytic degradation and (b) the corresponding degradation kinetics of MB in optimization of SnO<sub>2</sub> number of ZFO/SnO<sub>2</sub> composites. (c) Degradation and (d) the corresponding degradation kinetics of MB in blank, catalysts, H<sub>2</sub>O<sub>2</sub>, catalysts/H<sub>2</sub>O<sub>2</sub> (Dark), and catalysts/H<sub>2</sub>O<sub>2</sub> conditions.

(e) Rate constant  $k$  of MB degradation.

The band alignment of ZFO/SnO<sub>2</sub> composite and the corresponding schematic for the MB degradation process are shown in Figure 2.13. When the single photocatalyst (ZFO or SnO<sub>2</sub>) was irradiated in the solution of MB, electron-hole pairs were generated in the bulk of semiconductor (Equations (2.8) and (2.9)). After separation and diffusion, few parts of photogenerated hole (h<sup>+</sup>) will transfer to the surface and react with H<sub>2</sub>O or the surface-adsorbed OH group to form ·OH (Equations (2.10) and (2.11)). However, only a few parts of photogenerated holes (h<sup>+</sup>) and electrons (e<sup>-</sup>) can be efficiently utilized due to the rapid recombination of charges in ZFO sample [51] and relatively large bandgap of SnO<sub>2</sub> semiconductor as mentioned above. Therefore, the photocatalytic degradation efficiencies of ZFO and SnO<sub>2</sub> were relatively low. According to the band alignment of ZFO/SnO<sub>2</sub> composite in Figure 2.13, the electrons in the conduction band (CB) and holes in the valence band (VB) will transfer in the opposite direction. This efficient configuration of band alignment will lead to a superior charge separation efficiency in ZFO/SnO<sub>2</sub> composites, resulting in more charges are utilized in the MB degradation process compared to single catalyst conditions [52]. Therefore, ZFO/SnO<sub>2</sub> composites show relatively superior photocatalytic degradation efficiencies than single catalyst. The addition of H<sub>2</sub>O<sub>2</sub> is beneficial for MB degradation. The activity of H<sub>2</sub>O<sub>2</sub> can be activated by Fe(II) through Equation (2.12) called dark Fenton reaction. However, the dark Fenton degradation efficiency was relatively low due to the limited cycle from Fe(III) to Fe(II). Meanwhile, Fe(III) on the surface of the photocatalyst can capture few parts of photogenerated e<sup>-</sup> to form Fe(II) (Equation (2.13)). Under condition of H<sub>2</sub>O<sub>2</sub>, photogenerated e<sup>-</sup> can be captured by H<sub>2</sub>O<sub>2</sub> through Equation (2.14). On one hand, the H<sub>2</sub>O<sub>2</sub> can produce more ·OH and OH<sup>-</sup>. On the other hand, the consumption of e<sup>-</sup> will also promote the separation efficiency of charge carrier pairs. Importantly, more and more Fe(II) and ·OH will be produced under

irradiation through the reaction of Fe(III) and OH<sup>-</sup> (Equation (2.15)). The increase of Fe(II) will also promote the reaction of Equation (2.12) to produce more ·OH. Finally, the increase of ·OH will promote MB degradation (Equation (2.16)). According to the abovementioned analysis, ZFO-SnO<sub>2</sub> (10%) photo-catalysts shows the highest MB degradation efficiency with the addition of H<sub>2</sub>O<sub>2</sub> under irradiation.

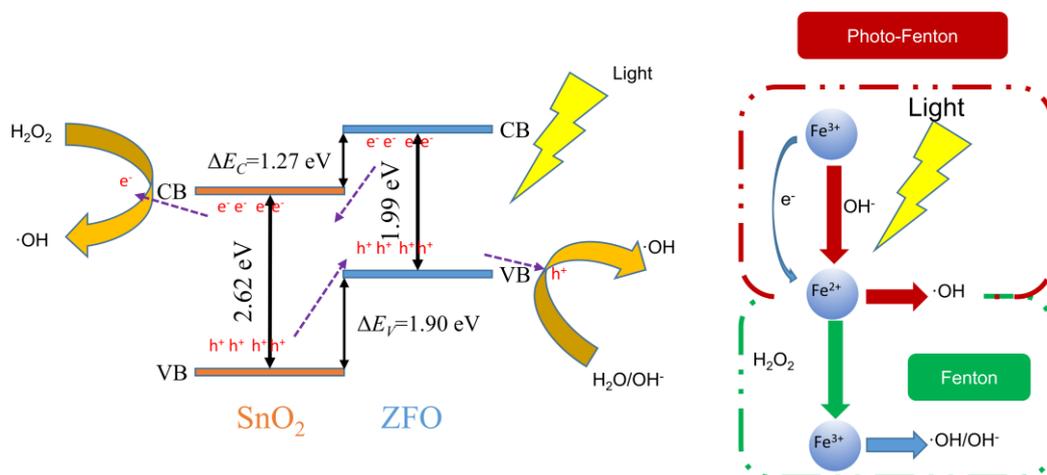
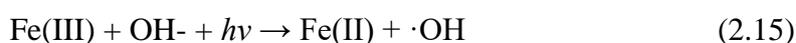
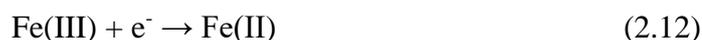
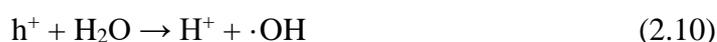


Figure 2.13 Schematic illustration for charge separation and transfer over ZFO/SnO<sub>2</sub> composite and MB degradation mechanism under light irradiation.

## 2.4. Conclusions

In summary, we have successfully fabricated the ZFO/SnO<sub>2</sub> composites through a facile solution combustion synthesis method for MB aqueous solution degradation. The characterizations of crystallite structure and morphology revealed that ZFO/SnO<sub>2</sub> composites showed relatively small crystallite and particle size, resulting in higher active surface area. The introduction of SnO<sub>2</sub> significantly improved the photocatalytic MB degradation efficiency of pure ZFO catalyst. Specifically, ZFO-SnO<sub>2</sub> (10%) catalyst exhibited the highest photocatalytic degradation rate constant of 0.01970 min<sup>-1</sup> in the composites, approximately 3.08 and 2.64 times higher than that of single ZFO (0.00640 min<sup>-1</sup>) and SnO<sub>2</sub> (0.00747 min<sup>-1</sup>), respectively. The improvement of photocatalytic degradation performance was due to enhanced charge separation efficiency in the ZFO/SnO<sub>2</sub> composite based on the band alignment analysis. ZFO-SnO<sub>2</sub> (10%) with H<sub>2</sub>O<sub>2</sub> showed the highest photo-Fenton degradation rate constant of 0.05301 min<sup>-1</sup> and could remove 95.2% of MB within 60 min under irradiation. This work also provides an available strategy for constructing a ZFO based composite for high efficiency photocatalytic dye degradation.

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**Chapter 3 Effect of Fuels and Fuel Ratios on Photocatalytic  
Performance of  $\text{CaFe}_2\text{O}_4$  by Solution Combustion Synthesis**

### 3.0. Brief summary

CaFe<sub>2</sub>O<sub>4</sub> (CFO) was fabricated by solution combustion synthesis (SCS) method using different fuels (urea and glucose) and fuel ratios (0.5, 1.0, and 1.5). CFO-Glucose shows a smaller crystallite size than CFO-Urea sample. CFO-1.0 presents the smallest crystallite size among various fuel ratios products. CFO-1.0 photocatalyst presents the best photocatalytic MB degradation with a kinetic constant of 0.00372 min<sup>-1</sup> compared to CFO-Urea (0.00123 min<sup>-1</sup>), CFO-0.5 (0.00176 min<sup>-1</sup>), and CFO-2.0 (0.00249 min<sup>-1</sup>). Based on the PL and XPS characterizations, the efficient photocatalytic performance of CFO-1.0 is attributed to the efficient charge separation and suitable photocatalyst surface state.

### 3.1. Introduction

Ternary metal oxide materials, such as perovskite type oxides (ABO<sub>3</sub>) [1, 2], spinel type oxide (AB<sub>2</sub>O<sub>4</sub>) [3, 4], scheelite type oxides (ABO<sub>4</sub>) [5] and other complex oxides [6], have attracted significant attentions in recent years. The preparation of ternary metal oxide materials used for solar energy conversion and solar-induced environmental remediation (such as solar photovoltaic, solar-induced photoelectrochemical water splitting and photocatalytic contaminant degradation) becomes increasingly important [7-9]. Among them, spinel ferrites are a promising family of ternary metal oxides that have recently drawn increasing attention for applications of solar energy conversion and solar-induced environmental remediation [10, 11]. CaFe<sub>2</sub>O<sub>4</sub> (CFO) has received the most extensive research as an emerging photo-induced catalyst due to its appropriate band gap for full spectrum, abundant constituent elements and long-term photo stability under solar irradiation [12-15].

Compared to several conventional synthesis methods such as hydrothermal [16-18], co-precipitation [19-22] and mechanical ball-milling [23], solution combustion synthesis

(SCS) [24-26] indicates significant advantages for preparation of calcium ferrite, owing to its simple equipment and experimental procedure, relatively low calcination temperatures, high purity and high homogeneity degree, etc. Fuel kinds and fuel ratios of SCS have a great effect on the final product. Sheng reported that single phase of  $K_{0.5}Na_{0.5}NbO_3$  products can be successfully prepared in a one-step SCS by adjusting the glycine-nitrate ratio and also shown that the stoichiometric or slightly fuel-excess condition is good for the single step production [27]. However, there is not enough research on the influence of fuel type and fuel ratio on CFO.

Here, we study the synthesis of CFO by SCS process using different fuels (urea and glucose) and different fuel ratios (0.5, 1.0, 2.0). We amply investigate the effect of fuels and fuel ratios of SCS on the morphology, crystal phase composition, photocatalytic MB degradation activity of as-prepared CFO samples.

## **3.2. Experimental**

### *3.2.1. Materials*

All raw reagents used in this chapter were commercially available and used without further purification. Calcium nitrate tetrahydrate ( $Ca(NO_3)_2 \cdot 4H_2O$ , 98.0%), iron nitrate enneahydrate ( $Fe(NO_3)_3 \cdot 9H_2O$  99.0%), urea ( $NH_2CONH_2$ , 99.0%), and glucose ( $C_6H_{12}O_6$ , 98.0%) were used as raw materials.

### *3.2.2. Solution combustion synthesis of $CaFe_2O_4$ by different fuels and fuel ratios*

In a typical synthesis procedure, 1.446 g  $Ca(NO_3)_2 \cdot 4H_2O$ , 4.897 g  $Fe(NO_3)_3 \cdot 9H_2O$  and 2.427 g urea or 1.838 g glucose were dissolved in 30 mL of distilled water. After constant stirring with the speed of 400 rpm for 30 min at room temperature, a transparent and uniform solution precursor was formed in the alumina crucible. The solution precursor was directly put in a oven at 100 °C for 12 h, then 500 °C for 10 min. After cooling down to

room temperature and fully grinding, the samples were performed calcination process at 1000 °C for 2 h. The final products using urea and glucose as precursor are named as CFO-Urea and CFO-Glucose, respectively. To investigate the effect of fuel ratios, 0.919, 1.838, and 3.677 g glucose were added into the solution and the corresponding final products are named as CFO-0.5, CFO-1.0, and CFO-2.0, respectively. Then do the same procedure as above.

### *3.2.3. Materials characterization*

The phase composition and crystal structure of the as-prepared samples were characterized by X-ray diffraction (XRD) analysis using an X-ray diffractometer (Rigaku Miniflex) with Cu K $\alpha$  radiation. The morphology and microstructure of the as-prepared samples were inspected by a scanning electron microscopy (SEM, JEOL, JSM-7400F). A measuring device (GRAPHTEC midi LOGGER GL220) coupled with a K-type thermocouple was used to measure and record temperature changes over time during the ignition process. Further detailed morphology and microstructure of the as-fabricated samples were studied through transmission electron microscopy (TEM) using JEM-2000FX (JEOL, Japan) at operating voltage of 200 kV. The surface chemical state analysis was carried out at an X-ray photoelectron spectrometer (JEOL, JPS-9200) operated at 10 kV and 10 mA. A UV-Vis spectrometer (JASCO V-770) equipped with an integrating sphere attachment was performed to test the optical properties of samples. The photoluminescence (PL) spectra were collected through a luminescence spectrometer (JASCO FP-8600).

### *3.2.4. Photocatalytic performance characterization*

The photocatalytic performance of as-fabricated CFO samples was characterized by MB solution degradation experiments. Typically, 50 mL MB solution (20  $\mu$ L/L) was chosen as

degradation target. Before irradiation, the solution containing as-fabricated photocatalysts of 50 mg was magnetically stirred for 30 min in the dark to achieve adsorption-desorption equilibrium. A simulated solar light (HAL-320W, Asahi spectra) as a light source was used to provide an irradiation intensity of 100 mW/cm<sup>2</sup> from the top of the solution. Approximately 3 mL solution was taken every 30 min and centrifuged to remove the catalyst. The absorption spectra of the residual solution were collected by UV-Vis spectrometer (JASCO V-770). The peak intensity at 664 nm was chosen to indicate the concentration of solution.

### **3.3. Results and discussion**

#### *3.3.1. Crystalline structure and surface morphology*

Powder XRD is used to identify the phase composition, crystal structure and crystallinity of the as-prepared materials. Figure 3.1 shows the XRD patterns of CFO photocatalysts synthesized by SCS method with different fuel kinds and fuel ratios. These sharp and strong peaks present great crystallinity of as-fabricated photocatalysts by virtue of a facile SCS method. As shown in Figure 3.1(a), all diffraction peaks of CFO-Urea and CFO-Glucose are perfectly matched to crystal plane of CaFe<sub>2</sub>O<sub>4</sub> phase (JCPDS NO. 03-065-1333). Diffraction patterns of CFO photocatalysts with different fuel ratios are shown in Figure 3.1(b) and Figure 3.1(c) (enlarged view of corresponding part). When the fuel is insufficient ( $\Phi = 0.5$ ), the final product (CFO-0.5) is only pure CaFe<sub>2</sub>O<sub>4</sub> phase. However, when the fuel is excess, the impure phases were formed like Ca<sub>2</sub>Fe<sub>2</sub>O<sub>5</sub> (JCPDS NO. 01-071-2264) and Fe<sub>2</sub>O<sub>3</sub> (JCPDS NO. 01-087-1166). The simple synthesis process of CFO by SCS method as follows. As the temperature increases, metal nitrates are converted into corresponding metal oxides (CaO and Fe<sub>2</sub>O<sub>3</sub>) then metal oxides form final products (CFO). When the fuel is excess, part CaFe<sub>2</sub>O<sub>4</sub> is formed first and then CaO will continue react with CaFe<sub>2</sub>O<sub>4</sub> to

form  $\text{Ca}_2\text{Fe}_2\text{O}_5$ . The average crystallite sizes of photocatalysts were calculated from the top three intensity planes of (302), (210), and (410) in  $\text{CaFe}_2\text{O}_4$  based on the Debye-Scherrer equation [28]. CFO-Urea and CFO-Glucose present average crystallite sizes of 97.83 and 73.19 nm, respectively. Samples obtained at different fuel ratios also show different crystallite sizes of 75.41, 73.19, and 97.38 nm for CFO-0.5, CFO-1.0, and CFO-2.0, respectively. The sample of CFO-1.0 (CFO-Glucose) shows the smallest crystallite size.

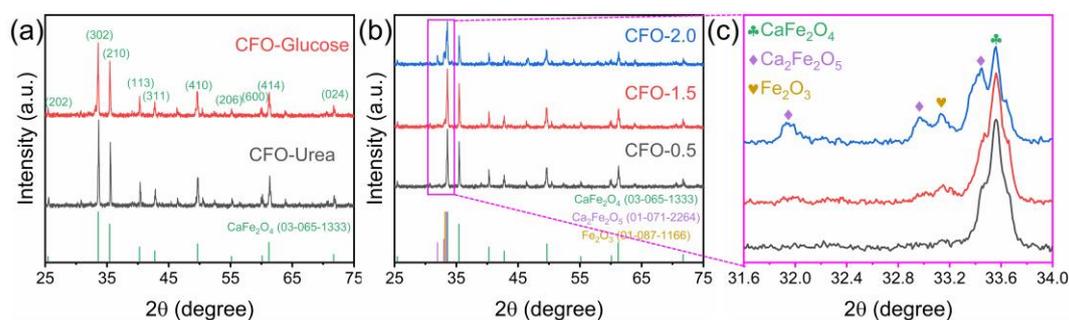


Figure 3.1 XRD of CFO samples prepared by different conditions

The typical surface figures of CFO are shown in Figure 3.2. It can be clearly seen that all samples are gathered together by small particles due to the high calcination temperature. Based on the XRD results, we can know that the average crystal sizes are below 100 nm. However, it is hard to see the clear crystallite sizes differences in SEM results. Therefore, all CFO samples are composed of multiple crystallites.

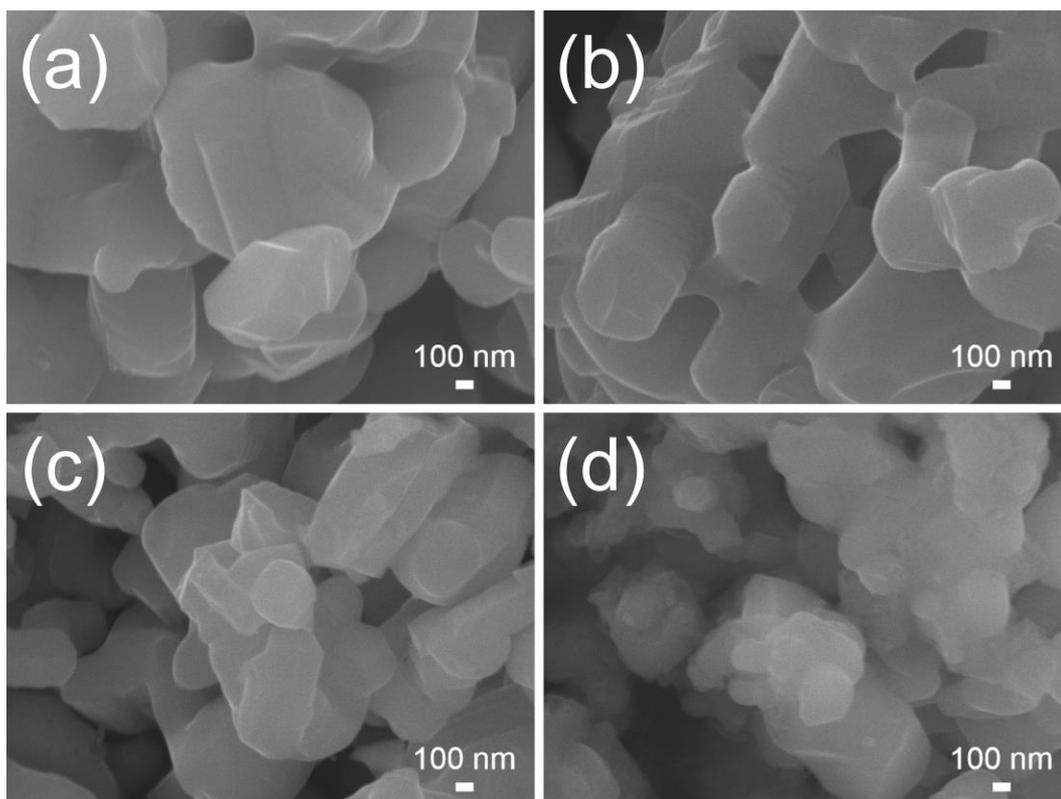


Figure 3.2 SEM figures of (a) CFO-Urea, (b) CFO-Glucose (CFO-1.0), (c) CFO-0.5, and (d) CFO-2.0

EDS was performed to indicate the elemental mappings of CFO-1.0 and CFO-2.0 in Figure 3.3. The molar ratios of Ca, Fe, and O for CFO-1.0 and CFO-2.0 are 17:45:38 and 19:39:42, respectively. Compared to CFO-1.0, CFO-2.0 shows a higher molar ratio of Ca due to the presence of  $\text{Ca}_2\text{Fe}_2\text{O}_5$ .

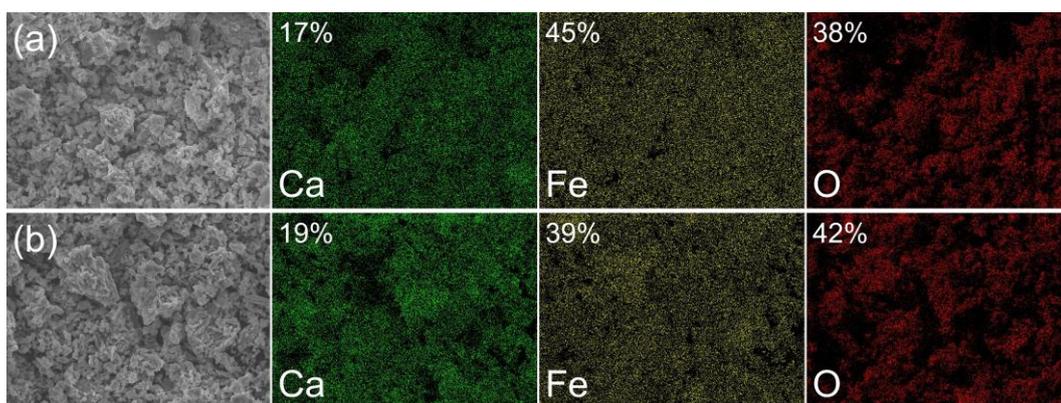


Figure 3.3 EDS elemental mappings of (a) CFO-1.0 and (b) CFO-2.0

### 3.3.2. Optical properties based on UV-Vis and PL results

The optical properties of the as-fabricated CFO photocatalysts were investigated by UV-Vis absorption spectra in Figure 3.4. CFO-Urea and CFO-Glucose show similar absorption onsets at wavelength of 650 nm in Figure 3.4(a). Compared to CFO-Urea, there is an absorption improvement above 650 nm for CFO-Glucose. CFO samples obtained at different fuel ratios also show different absorbance performance. CFO-0.5 sample presents lower absorbance ability than CFO-1.0 sample in the absorbance range of 500 to 650 nm. CFO-1.0 and CFO-2.0 show similar absorbance in the range of 500 to 650 nm. The absorbance above 650 nm of CFO-1.0 is higher than that of CFO-2.0. All bandgaps of photocatalysts were calculated through the Tauc plots [29]. As shown in Figure 3.4(c) and (d), the bandgap values for CFO-Urea, CFO-Glucose, CFO-0.5, CFO-1.0, and CFO-2.0 are 1.91, 1.90, 1.92, 1.90, and 1.91 eV, respectively.

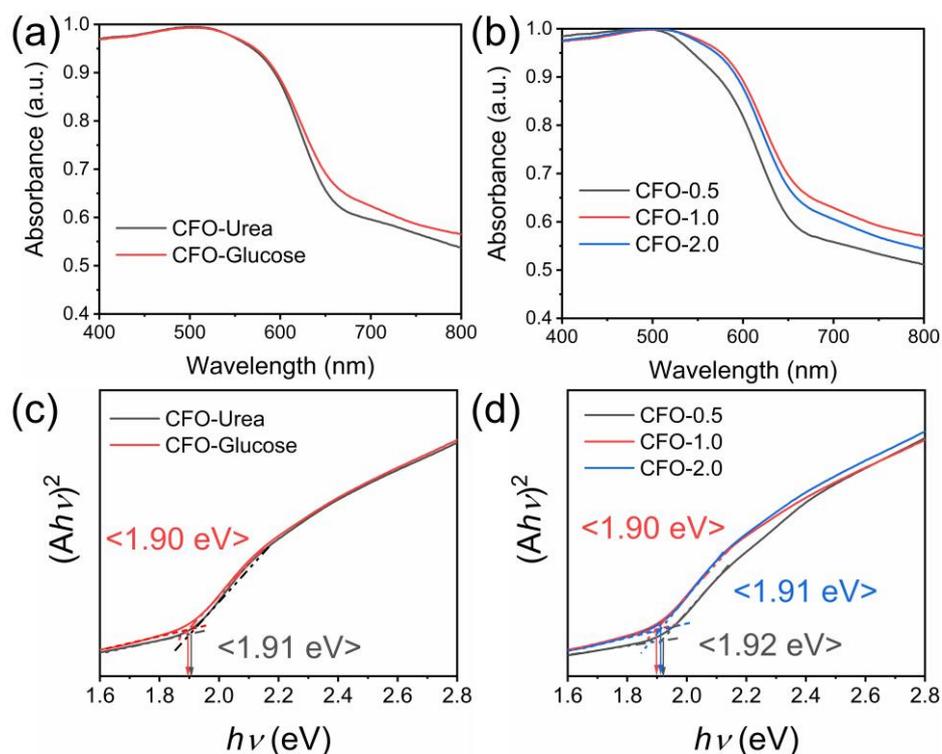


Figure 3.4 UV-Vis spectra of all CFO samples

PL emission spectra were obtained to show the charge recombination and separation behaviors of CFO samples. There are three main peaks at 467, 557, and 620 nm, respectively. The intensity of the PL spectra provides the information about photo-induced charge recombination. The higher the peak intensity, the more serious the charge recombination. The peak intensity of CFO-Urea is higher than that of CFO-Glucose, which means the more serious charge recombination of CFO-Urea than that of CFO-Glucose. In all photocatalysts obtained from various fuel ratios, CFO-1.0 exhibits the lowest peak intensity, which means that CFO-1.0 presents the best charge separation efficiency.

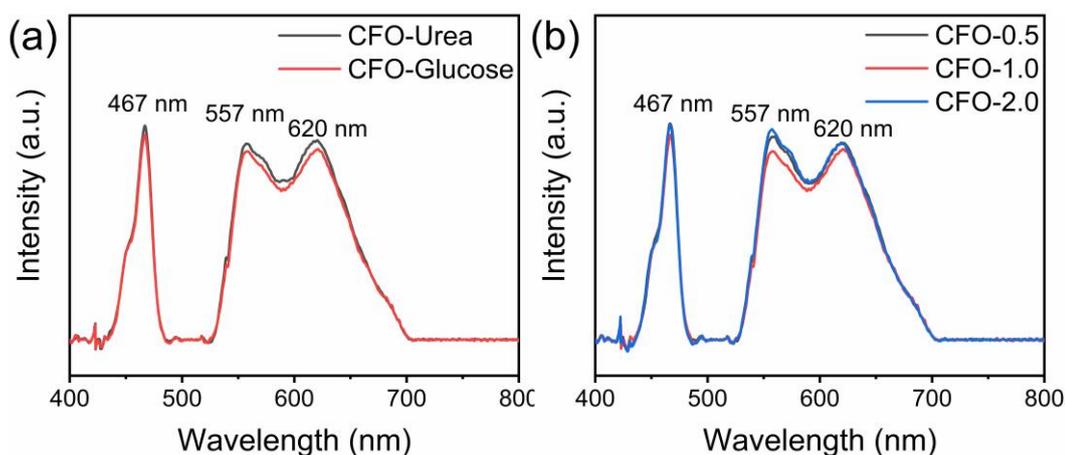


Figure 3.5 PL spectra of all CFO samples

### 3.3.3. Surface state analysis based on XPS data

XPS data were collected to investigate the surface chemical composition and electronic valence state of CFO samples. The presence of Ca and Fe was confirmed by Figure 3.6(a) and (b), respectively. It is well known that the relative content of oxygen vacancy play a significant role in photocatalytic applications. The peaks related to metal-oxygen bonds from lattice ( $O_L$ ) and oxygen vacancy ( $O_V$ ) are two important factors influenced the photocatalytic performance of photocatalysts. The higher ratio of  $O_V$  in CFO-Urea than CFO-Glucose, resulting in lower photocatalytic performance of CFO-Urea than CFO-Glucose, as shown in Figure 3.6(c). Meanwhile, CFO-1.0 shows the lowest ratio of  $O_V$

among samples prepared through different fuel ratios, as shown in Figure 3.6(d).

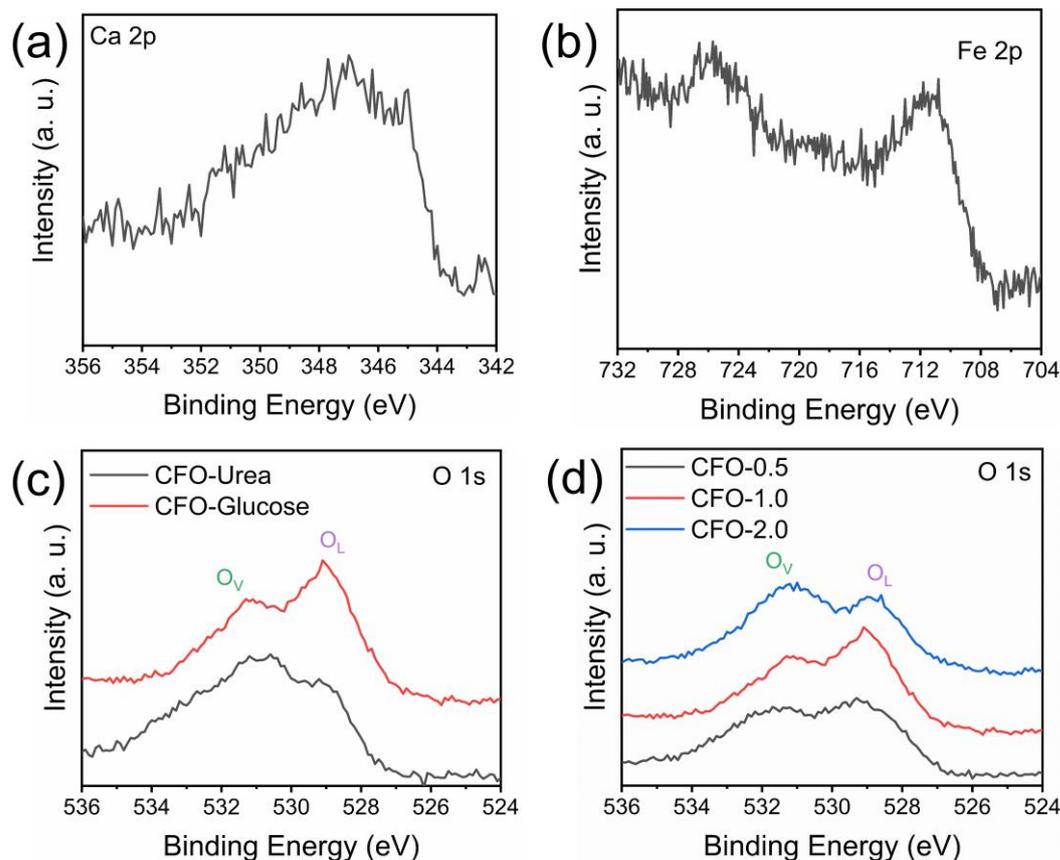


Figure 3.6 High-resolution XPS spectra of CFO-1.0 (a) Ca 2p and (b) Fe2p. O 1s spectra of (c) different fuels and (d) different fuel ratios.

### 3.3.4. Photocatalytic dye degradation

MB solution degradation experiments under irradiation were performed to indicate the photocatalytic properties of all CFO samples. The related data were shown in Figure 3.7. The MB degradation of CFO-Glucose is faster than that of CFO-Urea in Figure 3.7(a). For photocatalysts with different fuel ratios, CFO-1.0 presents the fastest MB degradation speed. More details about kinetics were calculated by plotting  $-\ln(C/C_0)$  vs. time curves in Figure 3.7(c) and (d). Further, the kinetic constant  $k$  was calculated from the slope value of the kinetic curves. The kinetic constant values for CFO-Urea and CFO-Glucose are  $0.00123$  and  $0.00372 \text{ min}^{-1}$ , respectively. The kinetic constant of CFO-Glucose is three times that of CFO-Urea. Meanwhile, the kinetic constant of CFO-1.0 ( $0.00372 \text{ min}^{-1}$ ) is higher

than that of CFO-0.5 ( $0.00176 \text{ min}^{-1}$ ) and CFO-2.0 ( $0.00249 \text{ min}^{-1}$ ). This is maybe because of the efficient charge separation and surface recombination and suitable amount of oxygen vacancy in CFO-1.0 sample.

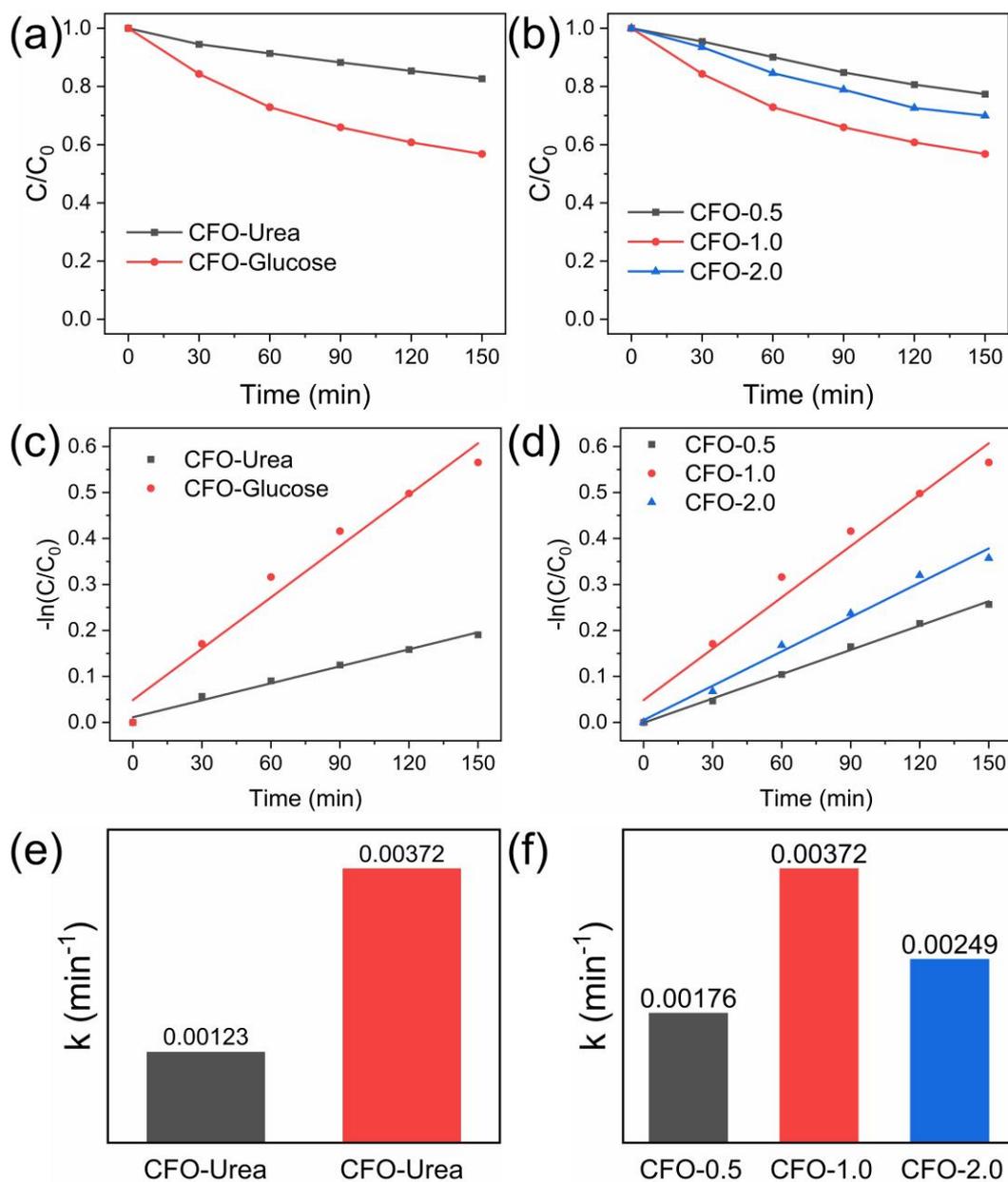


Figure 3.7 Photocatalytic degradation of MB by (a) different fuels samples and (b) different fuel ratios samples; (c) and (d) the kinetics fitting plots; (e) and (f) the kinetic constant  $k$ .

### 3.4. Conclusions

In summary, we have successfully fabricated CFO samples using urea and glucose as fuels, respectively. CFO-Glucose shows smaller crystallite sizes than CFO-Urea. We also fully investigated the effect of fuel ratios on the final products by SCS method using glucose as fuel. The XRD results clearly show that CFO-1.0 presents the smaller crystallite sizes. PL and XPS results show that CFO-1.0 present high separation efficiency and suitable amount of oxygen vacancy on the surface, resulting the best kinetic constant of  $0.00372 \text{ min}^{-1}$  among all CFO samples.

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**Chapter 4 Molten Salt-assisted Shape Modification of  $\text{CaFe}_2\text{O}_4$   
Nanorods for Highly Efficient Photocatalytic Degradation of  
Methylene Blue**

## 4.0. Brief summary

In this chapter,  $\text{CaFe}_2\text{O}_4$  nanorods (CFO NRs) and aggregated particles (CFO APs) were fabricated with and without the help of molten salt-assisted shape modification, respectively. CFO APs present inferior photocatalytic performance due to the plenty of grain boundaries which hinder photogenerated charges transfer and act as charge recombination sites. Molten salt-assisted modification can easily change the shape of CFO NRs and significantly suppresses the formation of grain boundaries, facilitating photogenerated charges separation and transfer for highly efficient photocatalytic degradation of methylene blue (MB). Surface state investigation indicates a decreased amount of unsuitable oxygen vacancies and defects in CFO NRs, which is beneficial in alleviating the recombination of photogenerated charges in CFO NRs. The CFO NRs show a ten-time increased kinetic constant of MB degradation from  $0.0013$  to  $0.013 \text{ min}^{-1}$  by virtue of the alleviative charge recombination.

## 4.1. Introduction

With the massive use of organic dyes in industrial production, the residue of coloring wastewater has become a severe environmental problem, which is threatening drinking water safety and human health [1]. Among the various technologies used for pigment degradation, the semiconductor-based photocatalytic degradation is emerging as a high-efficiency and environmentally friendly approach because it only uses photocatalyst and solar energy [2, 3]. Therefore, the research and development of highly efficient photocatalyst becomes an urgent task on account of environmental remediation [4].  $\text{TiO}_2$  as the first investigated photocatalyst has been widely used in various fields, such as environmental pollutant degradation [5], water splitting [6], hazardous elements reduction [7], air treatment [8] and  $\text{CO}_2$  reduction [9]. Nevertheless,  $\text{TiO}_2$  with wide bandgap (3.2eV)

only shows high photocatalytic efficiency under ultraviolet (UV) light irradiation which only accounts for 4% of the solar spectrum [10, 11]. Hence, it is necessary to develop visible-light-active and property stable semiconductor photocatalysts with narrow bandgap to take full advantage of solar irradiation.

In recent years, spinel ferrite ( $MFe_2O_4$ , M represent divalent metal atoms such as  $Ca^{2+}$ ,  $Zn^{2+}$ ,  $Ba^{2+}$ ,  $Co^{2+}$ ,  $Mg^{2+}$ ,  $Ni^{2+}$ , etc.) as an emerging visible-light-driven photocatalyst has been widely utilized as an attractive photocatalyst in many fields due to its relatively narrow bandgap (approximately 2.0 eV), low cost, and superior durability [12, 13]. Among them,  $CaFe_2O_4$  (CFO) is an extraordinary one because it is a p-type semiconductor [14]. A great number of studies showed that the p-n heterojunction structure in the semiconductor is beneficial for the effective separation of photogenerated charge carrier pairs by virtue of the built-in electric fields at the interface [15-18]. Although plenty of semiconductor photocatalysts have been well developed, studies on p-type semiconductor photocatalysts are still limited. CFO catalysts have been successfully synthesized by numerous synthesis methods such as solution combustion synthesis [19], pulsed laser deposition [20], solid-state reaction [21], co-precipitation method [22], and so on. Various modifications have been applied for the performance enhancement of photocatalysts, such as structure improvement by metal doping [23], charge separation enhancement by forming heterojunction [24-28], and surface state adjustment through co-catalyst deposition [29]. Some studies indicated that shape modification is a feasible method for the improvement of photocatalytic performance of photocatalysts due to the efficient charge separation or increased surface area [30, 31]. However, the performance improvement of CFO by shape modification is still rare.

In addition, the high fabrication temperature is still an important factor limiting the

practical application of CFO samples. On the one hand, high temperature calls for higher requirements on the reactor. On the other hand, at high calcination temperature, nanoparticles may aggregate together to form grain boundaries, which will hinder the transfer and separation of photogenerated charges and affect their photocatalytic properties [32]. The molten salt synthesis method presents unique advantages in catalyst preparation, especially for materials with higher synthesis temperatures [33]. This method can not only lower the liquid phase forming temperature by the incorporation of low melting point inorganic salts, but also easily modify samples with the specific morphologies, such as rods [34, 35], wires [36], plates [37], flowers [38], etc. Recently, Liu et al. reported the synthesis of rod-form CFO using a NaCl-KCl molten salt method [39]. However, the studying on the effect of molten salt synthesis method on the photocatalysts structure and photocatalytic property is still limited.

Herein, CFO catalyst precursors were first synthesized by a facile polymerizable complex method followed by molten salt-assisted shape modification. The photocatalytic degradation studies of methylene blue (MB) solution were conducted under simulated solar irradiation. Compared to CFO APs, the CFO NRs show a ten-time enhanced degradation kinetic constant from 0.0013 to 0.013 min<sup>-1</sup> by virtue of the single crystalline feature and the decreased amount of unsuitable oxygen vacancies and defects by detailed microstructural characterization and surface state investigation. The excellent enhancement of degradation performance paves the way for improving photocatalyst performance by molten salt-assisted shape modification.

## **4.2. Experimental**

### *4.2.1. Chemical reagents*

Calcium nitrate tetrahydrate (Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, 98.0%), iron nitrate enneahydrate

( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , 99.0%), citric acid monohydrate ( $\text{HOC}(\text{COOH})(\text{CH}_2\text{COOH})_2 \cdot \text{H}_2\text{O}$ , 99.5%), and ethylene glycol ( $\text{HOCH}_2\text{CH}_2\text{OH}$ , 99.0%) were purchased from Fujifilm Wako Pure Chemical Corporation. Potassium chloride ( $\text{KCl}$ , 99.5%) and sodium chloride ( $\text{NaCl}$ , 100%) were purchased from Kanto Chemical Co., Inc. All chemical reagents were directly used without further purification. During the whole fabrication process, deionized (DI) water was used.

#### 4.2.2. Preparation of catalysts

Target catalysts were fabricated by two processes, including the CFO precursor fabrication process via a polymerizable complex method and crystallinity improvement or shape modification process [39]. For CFO precursor fabrication, 20 mmol of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , 40 mmol of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , and 40 mmol of citric acid monohydrate were sequentially added to a mixed solution of DI (20 mL) and ethylene glycol (8 mL). After stirring for 30 min at ambient temperature, the transparent CFO precursor solution was formed. After water evaporation and polyesterification at 130 °C for 20 h, the transparent solution became a dark green sphere in the crucible, followed by calcination at 500 °C for 2 h. The as-fabricated CFO precursor was fully ground and reserved for the following process. To improve crystallinity, as-fabricated CFO precursor was calcined in air at 900 °C for 6 h in a crucible. Due to the high calcination temperature, CFO precursors were aggregated together to form CFO aggregated particles, named as CFO APs. For CFO nanorods (CFO NRs) fabrication, 1.119 g of CFO precursors were blended with 1.873 g of  $\text{KCl}$  and 1.461 g of  $\text{NaCl}$  and fully grounded. The mixture was spread flat in the crucible with a square bottom, the thickness of the sample was about 3 mm. Then performed the same calcination process as the CFO APs fabrication process. After cooling to room temperature, as-synthesized samples were washed by DI under strong stirring for 12 h.

After centrifugation and drying at 50 °C, pure CFO NRs was obtained. The overview of the synthetic process for CFO APs and CFO NRs is illustrated in Figure 4.1.

#### 4.2.3. Characterization

X-ray diffraction (XRD) patterns of as-fabricated catalysts were performed for the crystal structure study at a diffractometer (Miniflex 600, Rigaku) using Cu K $\alpha$  radiation ( $\lambda=1.54060$  Å). The surface morphology of samples was investigated by a scanning electron microscope (SEM) using JSM-7001FA (JEOL, Japan). Further detailed morphology and microstructure of the as-fabricated samples were studied through transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) using JEM-2000FX (JEOL, Japan) and JEM-2010F (JEOL, Japan) at both operating voltage of 200 kV, respectively. The selected area electron diffraction (SAED) patterns were obtained at JEM-2000FX (JEOL, Japan). The Brunauer-Emmett-Teller (BET) specific surface areas were obtained by Autosorb 6AG based on the nitrogen adsorption isotherms at 77 K. An exhaust treatment was performed at 120 °C for 4 h. The surface chemical state analysis was carried out at an X-ray photoelectron spectrometer (JEOL, JPS-9200) operated at 10 kV and 10 mA. A UV-Vis spectrometer (JASCO V-770) equipped with an integrating sphere attachment was performed to test the optical properties of samples. The photoluminescence (PL) spectra were collected through a luminescence spectrometer (JASCO FP-8600).

#### 4.2.4. Photocatalytic performance experiments

The photocatalytic performance of as-fabricated CFO APs and CFO NRs was characterized by MB solution degradation experiments. Typically, 50 mL MB solution (1 mg/L) was chosen as degradation target. Before irradiation, the solution containing as-fabricated photocatalysts of 50 mg was magnetically stirred for 30 min in the dark to

achieve adsorption-desorption equilibrium. A simulated solar light (HAL-320W, Asahi spectra) as a light source was used to provide an irradiation intensity of 100 mW/cm<sup>2</sup> from the top of the solution. Approximately 3 mL solution was taken every 30 min and centrifuged to remove the catalyst. The absorption spectra of the residual solution were collected by UV-Vis spectrometer (JASCO V-770). The peak intensity at 664 nm was chosen to indicate the concentration of solution. The residual relative amount was calculated according to the following Equation (4.1).

$$\text{Residual relative amount} = \frac{C}{C_0} \quad (4.1)$$

where  $C_0$  and  $C$  represent the concentration of MB solution after stirring in the dark and residual concentration during irradiation at various time intervals, respectively.

### **4.3. Results and discussion**

#### *4.3.1. Fabrication of CFO APs and CFO NRs*

As shown in Figure 4.1, CFO APs and CFO NRs were fabricated through two processes. CFO NRs were obtained by the NaCl and KCl molten salts-assisted shape modification method. CFO APs were just synthesized without adding molten salts. Compared with the conventional solid state approach with reaction temperature of 1100 °C [18], low-melting-point salt-assisted synthesis method can reduce the reaction temperature by 200 °C to 900 °C. XRD patterns of CFO APs and CFO NRs are presented in Figure 4.2. Both CFO APs and CFO NRs samples show sharp diffraction peaks, indicating the high crystallinity of as-fabricated samples. In addition, the background line noise was from the fluorescence of the Fe atoms [40]. All diffraction peaks can be perfectly matched to crystal plane of orthorhombic phase CaFe<sub>2</sub>O<sub>4</sub> (JCPDS NO. 03-065-1333). The (302)/(210) peak intensity ratios of CFO APs and CFO NRs are 1.29 and 2.15, respectively. The different (302)/(210)

peak intensity ratios of as-fabricated samples indicate different product shapes, showing that the addition of molten salt can promote the shape modification of CFO as discussed in the following SEM results.

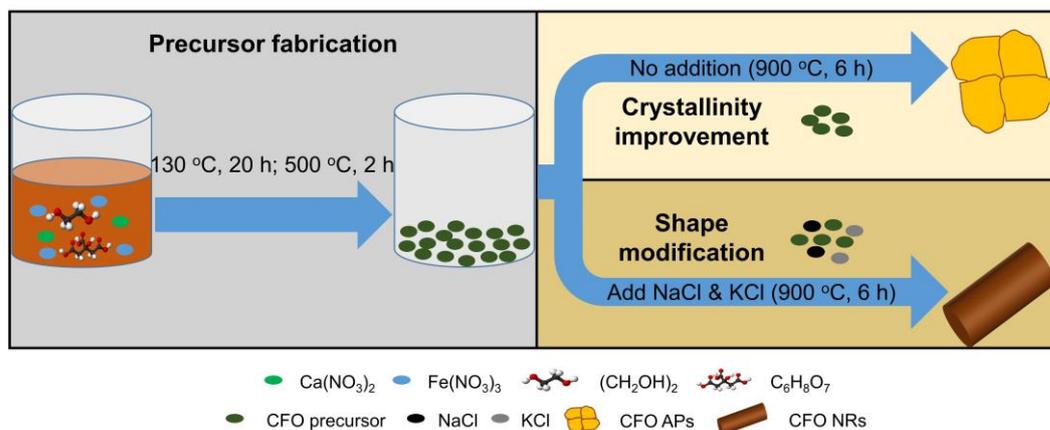


Figure 4.1 Schematics diagram of the synthesis process of CFO APs and CFO NRs.

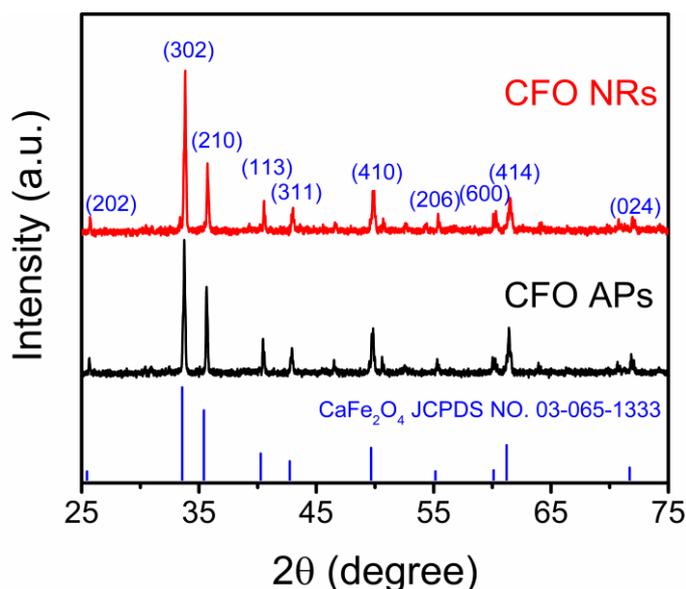


Figure 4.2 XRD patterns of CFO APs and CFO NRs.

#### 4.3.2. Surface morphology

The typical surface morphologies of CFO APs and CFO NRs are shown in Figure 4.3. As shown in Figure 4.3(a), CFO APs are aggregated together by few nanoparticles due to the high calcination temperature, which is constant with other materials fabricated at high calcination temperature [41, 42]. The high magnification inset in Figure 4.3(a) further

clearly indicates that the aggregation is formed by several nanoparticles with widths of 200 to 400 nm in different directions. The junction in CFO APs may act as the place of photogenerated charge carriers recombination, which will result in low charge migrate rate and inferior charge separation efficiency. In contrast, CFO NRs show straight nanorod morphology with a smooth surface, as shown in Figure 4.3(b) and the lengths are about several micrometers. The widths of the CFO NRs are also about 200 to 400 nm as shown in the high magnification inset of Figure 4.3(b). In summary, as-fabricated CFO APs and CFO NRs catalysts have similar widths but different lengths under the same calcination temperature. Figure 4.4 shows the photos of CFO APs and CFO NRs before and after the calcination process. There is almost no difference except color for CFO APs by a conventional high temperature calcination method without the introduction of molten salts, indicating no molten phase formed during the calcination process. In contrast, obvious region changes that few separated parts formed in final products can be seen for CFO NRs before and after calcination process, which indicates that molten phases were formed during the high temperature calcination process. As mentioned above, the introduction of molten salt has two main effects. On the one hand, the addition of low melting point inorganic salt can easily form the liquid phase to improve the mobility during calcination process. On the other hand, the introduction of molten KCl and NaCl facilitates the formation of nanorods by changing the energy of specific crystal surface of CFO NRs [39].

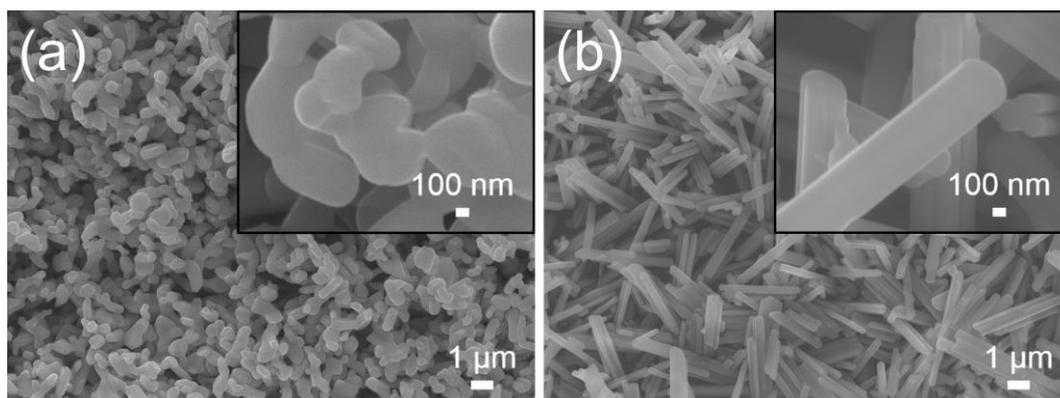


Figure 4.3 SEM images of (a) CFO APs and (b) CFO NRs. Insets are the corresponding images under high magnification.

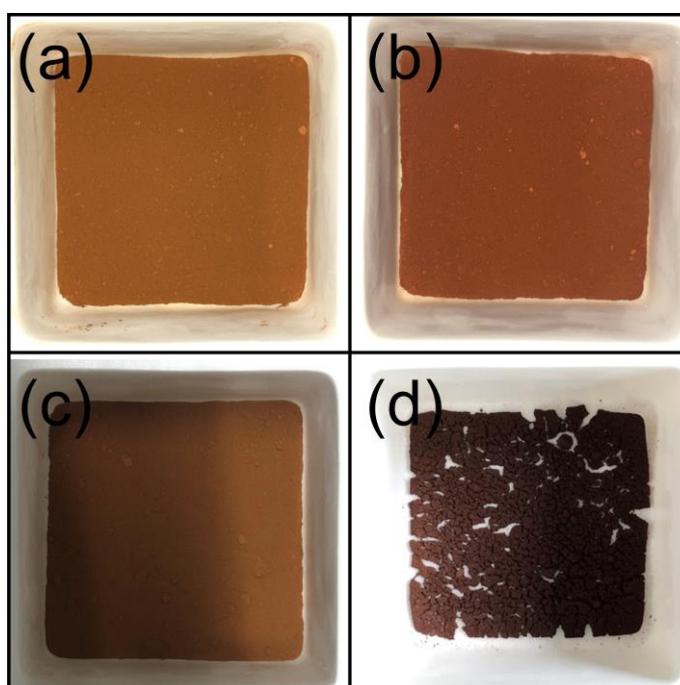


Figure 4.4 Optical pictures of CFO APs (a) before and (b) after calcination synthesis process and CFO NRs (c) before and (d) after calcination synthesis process.

#### 4.3.3. Microstructure characterization

The detailed microstructure characterizations were further performed by TEM, HRTEM and SAED, as shown in Figure 4.5. Figure 4.5(a) demonstrates the typical image of CFO APs. It can be clearly seen that some nanoparticles gather together due to high calcination temperature. Figure 4.5(b) shows the HRTEM image of CFO APs. The lattice spacing values of 0.535 and 0.267 nm correspond to the (002) and (302) planes of CFO APs,

respectively. In addition, a clear grain boundary in CFO APs can be seen from HRTEM image. The grain boundary may hinder the photogenerated charge transfer and act as the recombination site. In contrast, CFO NRs in Figure 4.5(c) show a nanorod morphology with smooth surface. Meanwhile, the HRTEM images in Figure 4.5(d) and (e) clearly show that there are almost no obvious grain boundaries not only at the ends of the CFO NRs but also at the main body of the CFO NRs. The lattice spacing of 0.253 nm corresponds to (210) plane of  $\text{CaFe}_2\text{O}_4$ , indicating the growth direction of CFO NRs is along [210] direction. In addition, the SAED patterns obtained at f, g, and h parts (both ends and main body) of CFO NRs in Figure 4.5(c) show uniform patterns in Figure 4.5(f-h), which means that the as-fabricated CFO NRs are single crystalline. These features of grain boundary free and single crystalline of CFO NRs provide a free path for the charge carrier transfer and show an alleviative charge recombination. In summary, compared with the traditional method (high temperature calcination without molten salt) for improving crystallinity, the molten salt method can not only enhance the crystallinity, but also modify its shape.

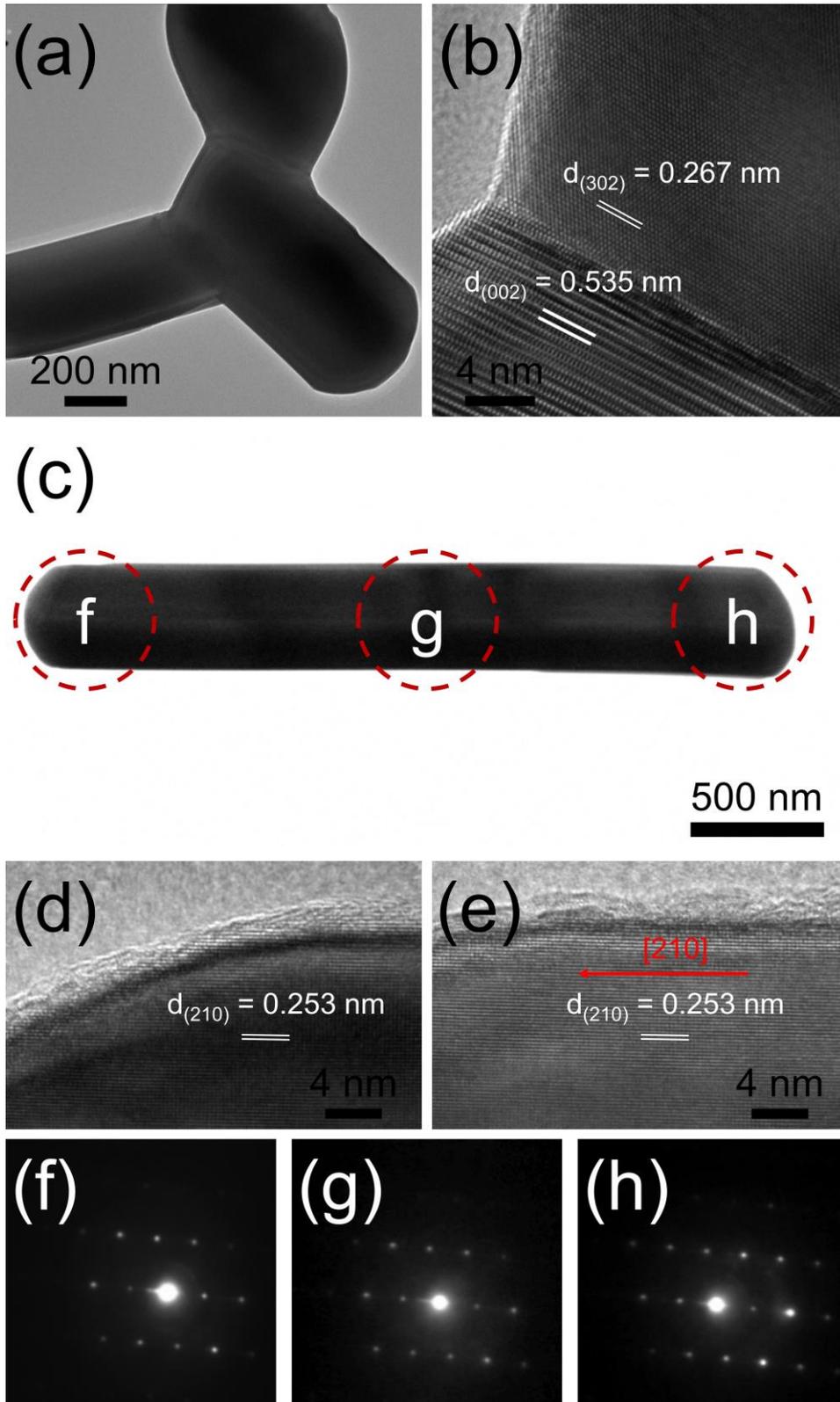


Figure 4.5 TEM images of (a) CFO APs and (c) CFO NRs. HRTEM images of (b) CFO APs, (d) the end and (e) the main body of CFO NRs. (f-h) SAED patterns of the selected parts in (c).

#### 4.3.4. Surface area and pore characterization

The surface area and pore characterization of CFO APs and CFO NRs were investigated by conducting the  $N_2$  adsorption and desorption isotherms as shown in Figure 4.6. As shown in Figure 4.6(a), the CFO APs possess a type IVa isotherm with a hysteresis loop of type H3, showing the presence of inter-particle voids between nanoparticles [43, 44]. However, the CFO NRs show a type III isotherm feature. The BET specific surface areas of CFO APs and CFO NRs are  $3.40$  and  $2.50 \text{ m}^2\text{g}^{-1}$ , respectively. Moreover, Barrett-Joyner-Halenda (BJH) method is used to determine the pore diameter distribution as shown in Figure 4.6(b). The average pore diameters of CFO APs and CFO NRs are  $2.88$  and  $1.49$  nm, respectively. The pore volumes for CFO APs and CFO NRs are  $0.0181$  and  $0.0127 \text{ cm}^3\text{g}^{-1}$ , respectively. As shown in Figure 4.3, CFO APs and CFO NRs are similar in width. The lengths of CFO NRs are longer than that of CFO APs. Therefore, CFO APs have more side surface than CFO NRs in terms of specific quality samples. Moreover, the pore volume of CFO APs is higher than that of CFO NRs. So, the surface areas of CFO APs are larger than that of CFO NRs.

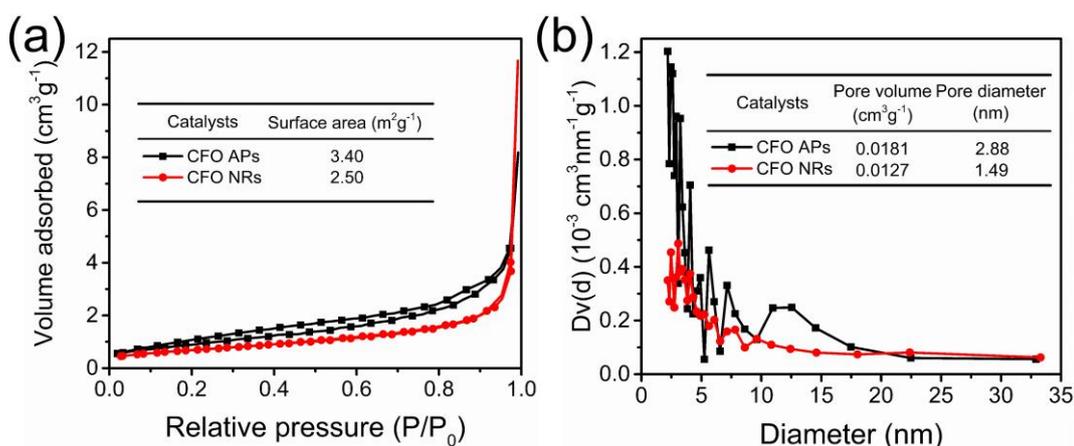


Figure 4.6 (a) The nitrogen adsorption-desorption isotherm and BET surface areas (inset). (b) BJH pore size distributions, pore volume (inset), and average pore diameter (inset) of CFO APs and CFO NRs.

#### 4.3.5. Surface state based on XPS

Further investigation on the surface chemical composition and electronic valence state of as-fabricated samples was conducted by XPS. All the XPS data were performed calibration according to the adventitious carbon signal located at 284.8 eV [45]. The presence of Fe, O, and Ca was confirmed by the wide scan XPS spectrum in Figure 4.7(a). As shown in Figure 4.7(b), there are two peaks located at 351.7 and 348.3 eV, corresponding to Ca 2p<sub>1/2</sub> and Ca 2p<sub>3/2</sub>, respectively, which is demonstrated as the oxidation state of +2 for Ca [46]. The Fe 2p spectra in Figure 4.7(c) present two main peaks located at around 723.8 and 710.6 eV can be assigned to Fe 2p<sub>1/2</sub> and 2p<sub>3/2</sub>, respectively. After deconvolution, two satellite peaks at around 723.5 and 716.9 eV can be clearly seen, representing the presence of Fe<sup>3+</sup> in both CFO APs and CFO NRs [47]. The two fitting peaks at 712.4 and 71.03 eV may be related to Fe at different sites [48]. Figure 4.7(d) presents the O 1s spectra of CFO APs and CFO NRs. It is well known that the state and relative content play a significant role in photocatalytic applications. Therefore, the deconvolution of O 1s spectrum was conducted to further investigate the effect of oxygen under various chemical states on photocatalytic performance. The deconvoluted peaks located at approximately 531.7 and 529.3 eV are related to the metal-oxygen bonds from lattice (O<sub>L</sub>) and oxygen vacancy/defect (O<sub>V</sub>), respectively [49]. The relative ratios based on the corresponding peak area values of O<sub>V</sub>/O<sub>L</sub> for CFO APs and CFO NRs are 42/58 and 39/61, respectively. The high ratio of O<sub>V</sub> in CFO APs may result in low photocatalytic performance because these unsuitable oxygen vacancies or defects can act as recombination sites of photogenerated hole and electron charge carriers [50, 51]. However, that value for CFO NRs was decreased, which was beneficial to the enhancement of photocatalytic performance as mentioned below.

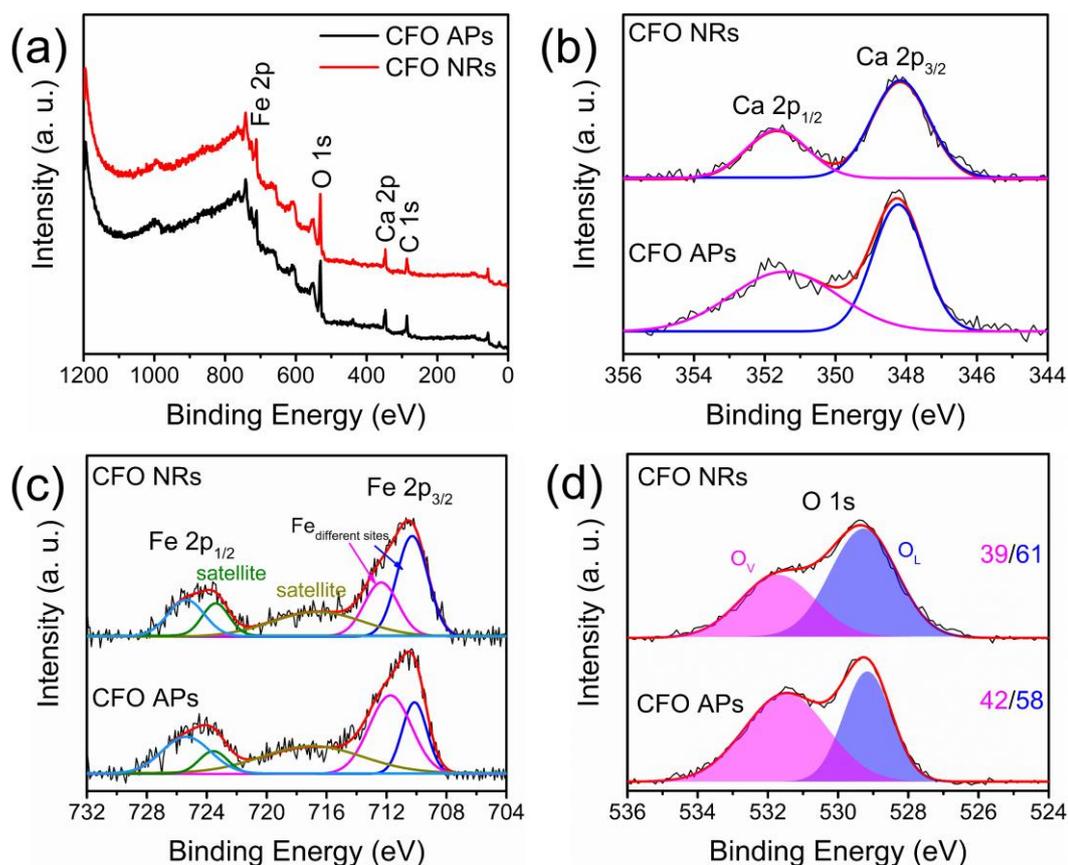


Figure 4.7(a) Wide XPS spectra; high-resolution XPS spectra of CFO APs and CFO NRs of typical elements (b) Ca 2p, (c) Fe 2p, and (d) O 1s. The area ratios of lattice-related ( $O_L$ , orange) and vacancy-related ( $O_V$ , blue) peaks are marked.

#### 4.3.6. Optical properties

UV-Vis absorption spectra in Figure 4.8 demonstrate the optical properties of the as-fabricated photocatalyst. Both CFO APs and CFO NRs show visible light absorption onsets at wavelength of 650 nm. It can be clearly seen that there is an absorption enhancement above 650 nm for CFO NRs compared to CFO APs. However, the lifting in this range has almost no effect on the photocatalytic performance of the sample [52]. The bandgaps of photocatalysts were calculated using the Tauc plots [53] through Equation (4.2).

$$(\alpha h\nu)^{1/n} = A(h\nu - E_g) \quad (4.2)$$

where  $\alpha$  represents the absorption coefficient,  $h$  represents the Planck constant,  $\nu$  represents the photon's frequency,  $A$  is a constant,  $E_g$  is the optical bandgap energy of catalyst, and the

n value is 1/2 for the direct transition bandgap. As shown in the inset of Figure 4.8, the  $E_g$  values for CFO APs and CFO NRs are 1.95 and 1.94 eV, respectively. These bandgaps are consistent with the previously reported values [44]. Meanwhile, the bandgap values for CFO APs and CFO NRs are similar. Therefore, the bandgap values change may not be the main reason for the photocatalytic performance enhancement as discussed below.

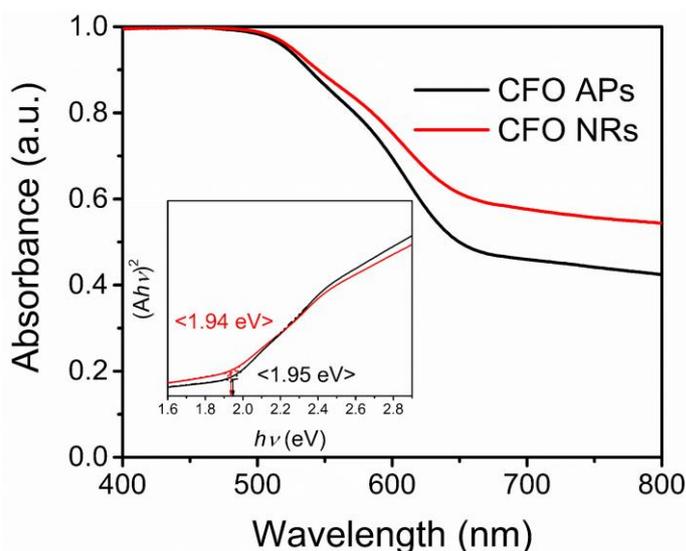


Figure 4.8 UV-Vis absorption spectra of CFO APs and CFO NRs (the inset is the corresponding direct bandgap obtained by the Tauc method).

To further investigate charge behavior of as-fabricated photocatalysts, PL emission spectra were obtained to show the separation efficiency of photogenerated charge carriers. This characterization can provide evidence for radiative recombination of photoexcited hole and electron pairs [54]. As presented in Figure 4.9, the peaks of CFO APs and CFO NRs located at 467 nm were selected for comparison. The intensity of the fluorescence peak of CFO APs was stronger than that of CFO NRs, which means more charge recombination occurs at CFO APs, resulting in relatively low photocatalytic performance of CFO APs as discussed below.

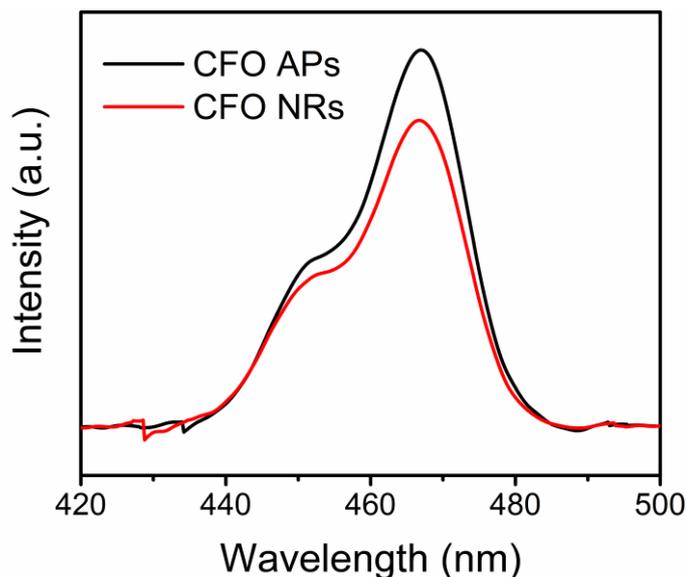


Figure 4.9 PL spectra of the photocatalysts.

#### 4.3.7. Photocatalytic performance

The photocatalytic performance of as-fabricated catalysts was investigated by MB solution degradation experiments under simulated sunlight irradiation (AM 1.5G). Figure 4.10 (a) shows the photocatalytic degradation of MB using CFO APs and CFO NRs within 120 min. The photocatalytic degradation efficiency can be calculated using the following Equation (4.3) [55].

$$\%degradation = \left(1 - \frac{C}{C_0}\right) \quad (4.3)$$

The photocatalytic degradation efficiency of CFO APs and CFO NRs are 14.1% and 77.2%, respectively. The analysis of MB degradation kinetics was further performed based on a pseudo-first-order reaction kinetics model as shown in Equation (4.4).

$$-\ln \frac{C}{C_0} = kt \quad (4.4)$$

where  $k$  and  $t$  are the apparent specific reaction time ( $\text{min}^{-1}$ ) and irradiation time (min), respectively.

Figure 4.10(b) presents the corresponding pseudo-first-order kinetics fitting plots and the

comparison of the degradation rate constant  $k$  (inset) of CFO APs and CFO NRs. The kinetic constant values of CFO APs and CFO NRs are  $0.0013$  and  $0.013 \text{ min}^{-1}$ , respectively. Compared to CFO APs, the reaction kinetic constant of CFO NRs catalysts produced by molten salt assisted calcination method enhanced 10 times. The reusability of CFO NRs for MB degradation was evaluated. Figure 4.11 shows the recycling performance of CFO NRs for MB degradation. In the 4th MB degradation recycling, CFO NRs also present a kinetic constant of  $0.011 \text{ min}^{-1}$  as good kinetic constant as the fresh one. The results show that the synthesized samples have good reusability.

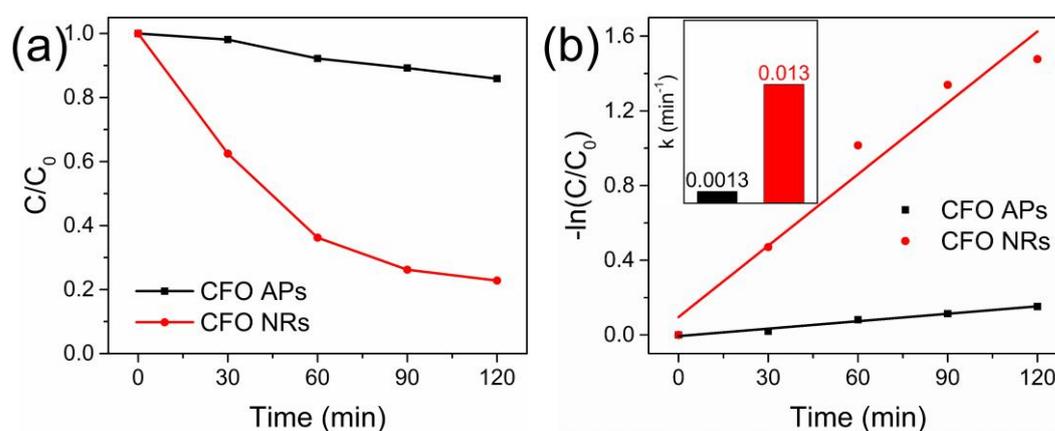


Figure 4.10 (a) Photocatalytic degradation of MB by as-prepared catalysts. (b) The corresponding pseudo-first-order kinetics fitting plots and comparison of the degradation rate constant  $k$  (inset).

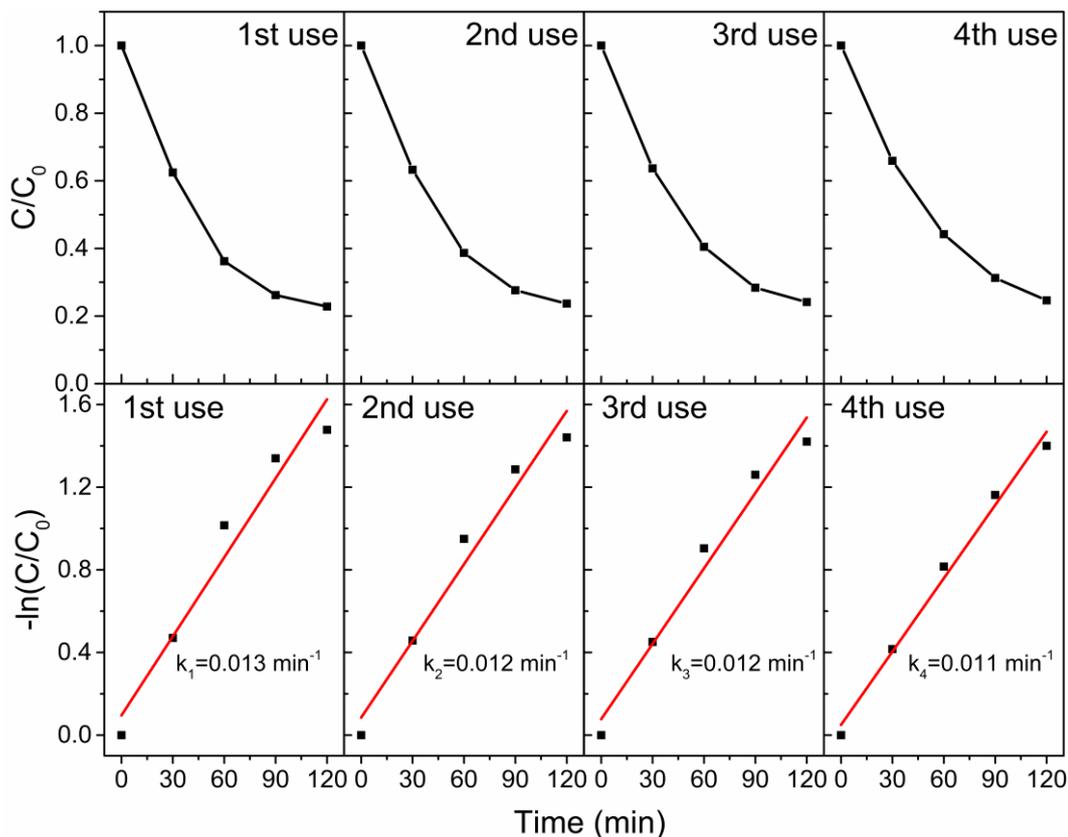


Figure 4.11 The reusability test results of (a) photocatalytic degradation and (b) kinetic constant.

To further understand the photocatalytic degradation process of MB solution and possible mechanism for the performance enhancement of CFO NRs, a brief schematic is presented in Figure 4.12. After irradiation, equal numbers of electrons and holes were formed in conduction band and valence band, respectively. The plenty of grain boundaries in CFO APs not only limit the transfer of charges, but also act as charges recombination sites. Only a small part of the photogenerated charges can be successfully transported to the surface. Meanwhile, the unsuitable oxygen vacancies and defects in CFO APs will also lead to high charges recombination. The two reasons mentioned above result in that only few charges can participate in the photocatalytic reaction, resulting inferior photocatalytic performance for MB degradation. On the contrary, CFO NRs present features of single crystalline without grain boundary and reduced oxygen defect amount by virtue of molten salt modification, which provide free path for charges separation and transfer. These

features enable more charges in CFO NRs can participate in the photocatalytic degradation process. These successfully separated and transferred holes ( $h^+$ ) and electrons ( $e^-$ ) can react with  $H_2O$  and  $O_2$  to form hydroxyl radicals ( $\cdot OH$ ) and superoxide radical ( $\cdot O_2^-$ ), respectively. These active radicals can effectively degrade the MB solution, resulting an enhanced degradation kinetic constant compared to CFO APs.

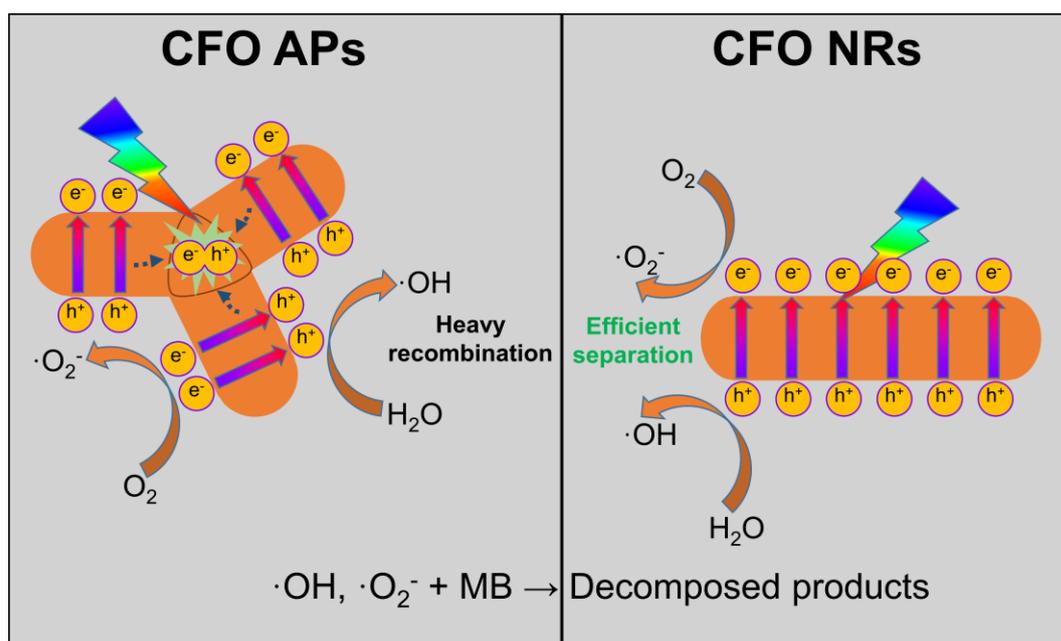


Figure 4.12 Mechanism schematic for MB photocatalytic degradation.

#### 4.4. Conclusions

In summary, we have successfully synthesized single crystalline CFO NRs via a molten salt method for efficient photocatalytic MB degradation. CFO APs show inferior photocatalytic performance due to the plenty of grain boundaries. The molten salt-assisted modification not only change the shape of CFO NRs but also suppress the formation of grain boundaries, which are beneficial to photogenerated charges separation and transfer. In addition, the charge recombination of CFO NRs is lower than that of CFO APs based on the PL results. After shape modification, the kinetic constant of photocatalytic MB degradation for CFO NRs is  $0.013 \text{ min}^{-1}$ , which is 10 times of the kinetic constant of CFO

APs ( $0.0013 \text{ min}^{-1}$ ). This study also provides a feasible route for efficient photocatalysts fabrication by molten salt assisted shape modification method and a further understanding of the performance enhancement.

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## **Chapter 5 Summary**

## 5.1. General conclusions

The research topic of this dissertation is the design and modification of spinel type ferrites ( $\text{ZnFe}_2\text{O}_4$  and  $\text{CaFe}_2\text{O}_4$ ) for highly efficient photocatalytic application. A facile SCS method was used to synthesized CFO and ZFO. A heterojunction of ZFO/ $\text{SnO}_2$  was made to enhance the photocatalytic properties of pure ZFO. A detailed study on the effect of fuels and fuel ratios on the final CFO product was performed. Moreover, a molten salt-assisted shape modification of  $\text{CaFe}_2\text{O}_4$  nanorods was fabricated for highly efficient photocatalytic degradation of methylene blue.

In Chapter 2, I successfully synthesized the ZFO/ $\text{SnO}_2$  composites through a facile solution combustion synthesis method for MB aqueous solution degradation. The characterizations of crystallite structure and morphology revealed that ZFO/ $\text{SnO}_2$  composites showed relatively small crystallite and particle size, resulting in higher active surface area. The introduction of  $\text{SnO}_2$  significantly improved the photocatalytic MB degradation efficiency of pure ZFO catalyst. Specifically, ZFO- $\text{SnO}_2$  (10%) catalyst exhibited the highest photocatalytic degradation rate constant of  $0.01970 \text{ min}^{-1}$  in the composites, approximately 3.08 and 2.64 times higher than that of single ZFO ( $0.00640 \text{ min}^{-1}$ ) and  $\text{SnO}_2$  ( $0.00747 \text{ min}^{-1}$ ), respectively. The improvement of photocatalytic degradation performance was due to enhanced charge separation efficiency in the ZFO/ $\text{SnO}_2$  composite based on the band alignment analysis. ZFO- $\text{SnO}_2$  (10%) with  $\text{H}_2\text{O}_2$  showed the highest photo-Fenton degradation rate constant of  $0.05301 \text{ min}^{-1}$  and could remove 95.2% of MB within 60 min under irradiation. This work also provides an available strategy for constructing a ZFO based composite for high efficiency photocatalytic dye degradation.

In Chapter 3, I have successfully fabricated CFO samples using urea and glucose as

fuels, respectively. CFO-Glucose shows smaller crystallite sizes than CFO-Urea. I also fully investigated the effect of fuel ratios on the final products by SCS method using glucose as fuel. The XRD results clearly show that CFO-1.0 presents the smaller crystallite sizes. PL and XPS results show that CFO-1.0 present high separation efficiency and suitable amount of oxygen vacancy on the surface, resulting the best kinetic constant of  $0.00372 \text{ min}^{-1}$  among all CFO samples.

In Chapter 4, I have successfully synthesized single crystalline CFO NRs via a molten salt method for efficient photocatalytic MB degradation. CFO APs show inferior photocatalytic performance due to the plenty of grain boundaries. The molten salt-assisted modification not only change the shape of CFO NRs but also suppress the formation of grain boundaries, which are beneficial to photogenerated charges separation and transfer. In addition, the charge recombination of CFO NRs is lower than that of CFO APs based on the PL results. After shape modification, the kinetic constant of photocatalytic MB degradation for CFO NRs is  $0.013 \text{ min}^{-1}$ , which is 10 times of the kinetic constant of CFO APs ( $0.0013 \text{ min}^{-1}$ ). This study also provides a feasible route for efficient photocatalysts fabrication by molten salt assisted shape modification method and a further understanding of the performance enhancement.

## **5.2. Future prospects**

Although some modifications have been made in improving the photocatalytic properties of ZFO and CFO for efficient dye degradation catalysts. There are also some spaces to enhance their properties, one of them is to modify the photocatalyst sample by Ag co-catalyst through photodeposition method.

### *5.2.1. Photo-deposition of Ag as a co-catalyst on CFO NRs*

A photodeposition setup is shown in Figure 5.1. The photodeposition process as follows.

CFO NRs of 300 mg was dispersed in a sealed vial with photodeposition precursor solution (H<sub>2</sub>O of 20 mL, methanol of 20 mL, and 0.01 M AgNO<sub>3</sub> of 10 mL). Before irradiation, the solution was bubbled with N<sub>2</sub> gas for 30 min to remove air and keep inert atmosphere. The deposition time is set as 12 h. After photodeposition, the product was washed with distilled water and dried in a drying oven at 50 °C for 12 h and named as CFO-NRs-12.

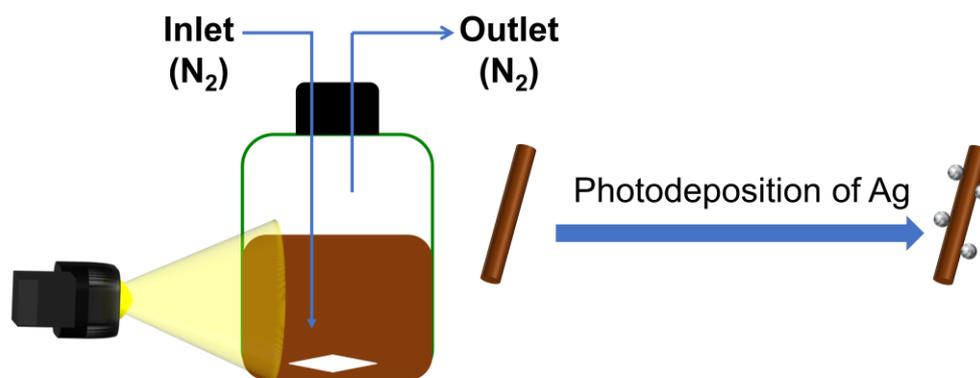


Figure 5.1 Photo-deposition of Ag on CFO NRs figure

### 5.2.2. Characterization of presence of Ag

Some tests are performed to show the presence of Ag on CFO-NRs by photodeposition. SEM and TEM figures were collected in Figure 5.2 and Figure 5.3, respectively. We can clearly see the presence of Ag on the CFO NRs sample. XPS data in Figure 5.4 also show the peaks from Ag. However, the amount of Ag is low. This result can also be seen from XRD figure in Figure 5.5. There are no Ag peaks shown in CFO-NRs-12 sample. However, there is no obvious change in the UV-Vis curves, as shown in Figure 5.6. This also means that the amount of Ag by photodeposition on CFO NRs-12 is not enough to affect the optical properties of CFO NRs-12 sample.

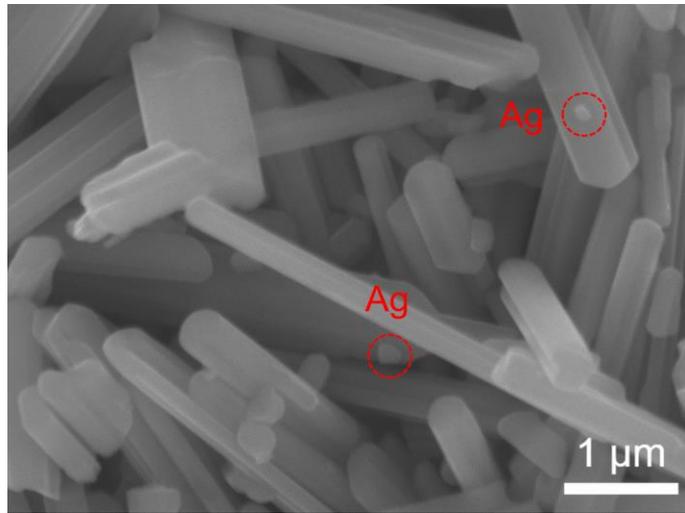


Figure 5.2 SEM figure of Ag deposited CFO NRs

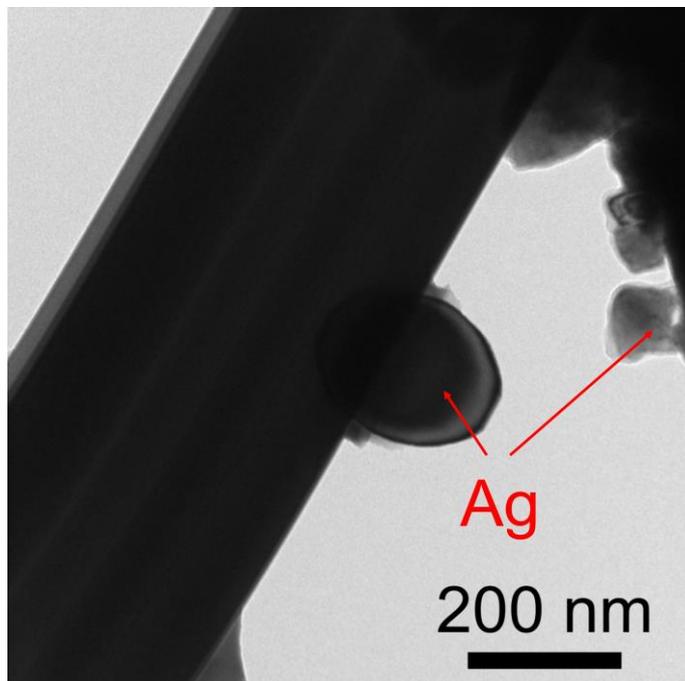


Figure 5.3 TEM figure of Ag deposited CFO NRs

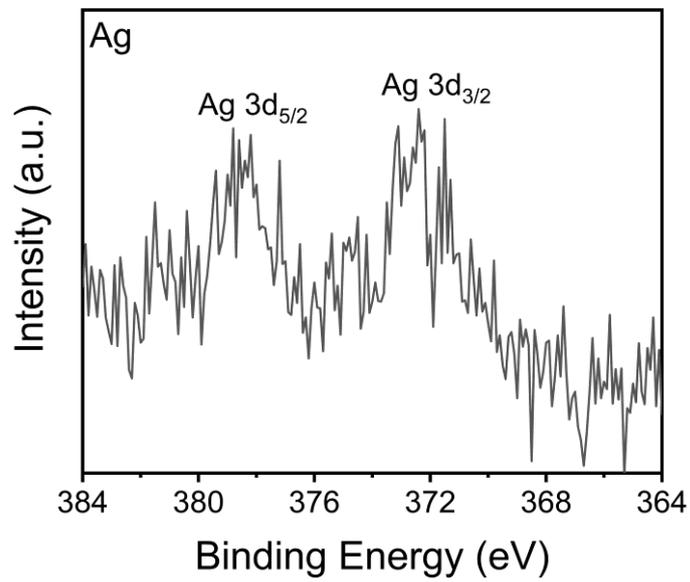


Figure 5.4 XPS of Ag deposited on CFO NRs

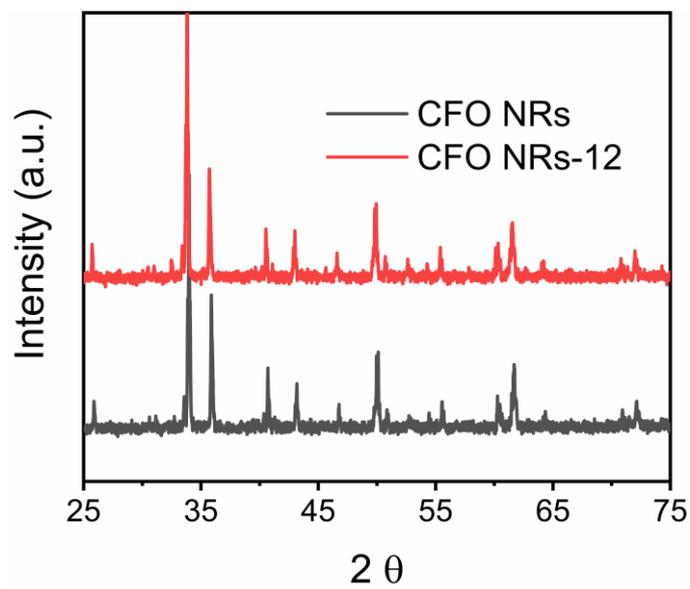


Figure 5.5 XRD patterns of CFO-NRs and CFO-NRs-12

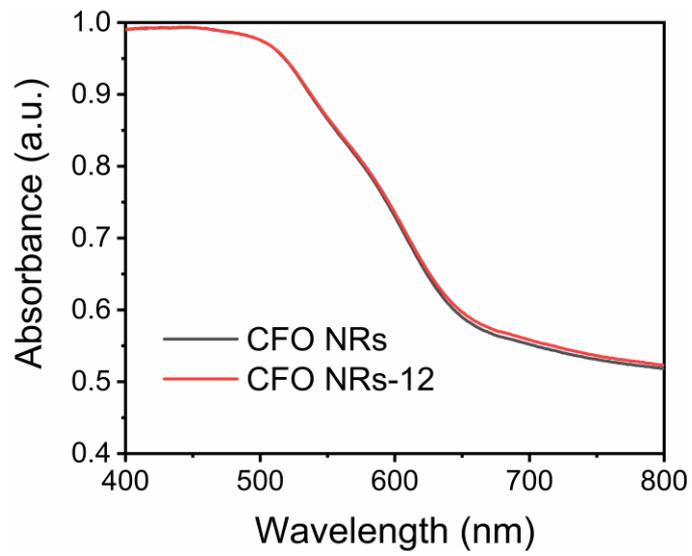


Figure 5.6 UV-Vis of CFO NRs and CFO NRs-12

### 5.2.3. Possible solution

It is a possible method to enhance the amount of Ag deposited on CFO NRs by increasing methanol volume and irradiation time



## Academic Achievements

### 1. Publications

- [1] **L. Guo**, N. Okinaka, L. Zhang, S. Watanabe. Facile synthesis of ZnFe<sub>2</sub>O<sub>4</sub>/SnO<sub>2</sub> composites for efficient photocatalytic degradation of methylene blue. *Materials Chemistry and Physics*. **2021** (262) 124273.
- [2] **L. Guo**, N. Okinaka, L. Zhang, S. Watanabe. Molten Salt-assisted Shape Modification of CaFe<sub>2</sub>O<sub>4</sub> Nanorods for Highly Efficient Photocatalytic Degradation of Methylene Blue. *Optical Materials*. **2021** (119) 111295.

### 2. Presentations

- [1] **L. Guo**, et al., "Facile Synthesis of ZnFe<sub>2</sub>O<sub>4</sub>/SnO<sub>2</sub> Composite for Enhanced Photocatalytic and Photo-Fenton Reaction" The 2019 annual winter meeting of The Iron and Steel Institute of Japan, Jan. 16-17, 2019, Hokkaido, Japan.
- [2] **L. Guo**, et al., "Facile Synthesis of ZnFe<sub>2</sub>O<sub>4</sub>/SnO<sub>2</sub> Composite for Enhanced Photocatalytic and Photo-Fenton Reaction" The 2020 annual autumn meeting of The Japan Institute of Metals and Materials, Sep. 15-18, 2020, Online.

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