Facile Synthesis of Magnetic Photocatalyst Ag/BiVO$_4$/Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ and Its Highly Visible-Light-Driven Photocatalytic Activity

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Abstract: Ag/BiVO$_4$/Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ was synthesized with a dip-calcination in situ synthesis method. This work was hoped to provide a simple method to synthesis three-phase composite. The phase structure, optical properties and magnetic feature were confirmed by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectrometer (XPS), transmission electron microscopy (TEM), ultraviolet-visible diffuse reflectance spectrophotometer (UV-vis DRS), and vibrating sample magnetometer (VSM). The photocatalytic activity was investigated by Rhodamine B (RhB) photo-degradation under visible light irradiation. The photo-degradation rate of RhB was 94.0~96.0% after only 60 min photocatalytic reaction under visible light irradiation, revealing that it had an excellent visible-light-induced photocatalytic activity. In the fifth recycle, the degradation rate of Ag/BiVO$_4$/Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ still reached to 94.0%. Free radical tunnel experiments confirmed the dominant role of •O$_2$ in the photocatalytic process for Ag/BiVO$_4$/Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$. Most importantly, the mechanism that multifunction Ag could enhance photocatalytic activity was explained in detail.

Keywords: Ag/BiVO$_4$/Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$; photocatalytic activity; magnetic property; wastewater treatment; reaction mechanism

1. Introduction

Semiconductor photocatalysts have been paid more attention in the application of research of clean energy exploration and environmental pollutants removal. These photocatalysts possess superior physicochemical and magneto-optical properties [1–4]. Non-toxic bismuth vanadate (BiVO$_4$), with good light absorption and high ionic conductivity [5–8], has attracted strong interest from scientists. Although the visible-light sensitivity and photocatalytic activity of monoclinic scheelite BiVO$_4$ (m-BiVO$_4$) are the largest among three crystals including additionally tetragonal zircon and tetragonal scheelite [9–12], the light absorption and the catalytic property of m-BiVO$_4$ can be further improved by various strategies. The photocatalytic activity can be greatly improved when the photo-generated electrons and holes are efficiently separated. BiVO$_4$-based composites with a high separation efficiency of photo-generated electrons and holes have been developed to enlarge the quantum efficiency of BiVO$_4$ and the photocatalytic activity of BiVO$_4$. Meanwhile, doping noble metal in photocatalysts is an effective way of promoting the efficient separation of photo-generated electrons and holes. Researchers have reported that the electron–hole separation in doping compounds was
strengthened by the charge transfer between semiconductor and noble metal [13–17]. Ag is the most promising noble metal because of the low cost and strong electron trapping ability. Ag-doped catalyst could induce surface plasmon resonance, involving in a better absorption of visible light [18].

For the convenience of recovery and separation of photocatalysts after reaction, magnetic photocatalysts have been fabricated in recent years [19–22]. Magnetic photocatalysts could be recovered with an external magnetic field, and a high recovery ratio would be conducive to promote their industrial application. In our previous research, both the soft-magnetic Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$/Bi$_2$O$_3$ [21] and hard-magnetic SrFe$_{12}$O$_{19}$/BiVO$_4$ [22] with photocatalytic properties were prepared with dip-calcination method. Further exploration is necessary to synthesize m-BiVO$_4$-based composite with high photocatalytic activity as well as large recovery ratio. In this work, Ag was doped in BiVO$_4$/Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ with in situ synthesis method. The photocatalytic activity of Ag/BiVO$_4$/Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ was investigated under sunlight irradiation. Further insights are focused on characteristic structure, magnetic property, and photocatalytic mechanism of Ag/BiVO$_4$/Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$.

In fact, fabrication of Ag/BiVO$_4$/Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ was a continuation of our research about the syntheses and application of BiVO$_4$/Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ [19]. The RhB degradation reaction using BiVO$_4$/Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ as photocatalyst was very slow (take 3 h). The incorporation of Ag could enhance the photocatalytic activity of BiVO$_4$/Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$.

2. Experimental

2.1. Synthesis of Ag/BiVO$_4$/Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$

Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ was prepared according to the literature [19,21].

The precursor of BiVO$_4$ was produced by the chemical co-precipitation way [22]. 486 mg Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ was dispersed into the precursor of BiVO$_4$ and dried at 80 °C for 12 h. BiVO$_4$/Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ (15.0 wt %) (marked BiVO$_4$/Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$) was gained after roasting at 450 °C for 3 h. After dip-roasting, 600 mg BiVO$_4$/Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ was put into 50 mL AgNO$_3$ solution (10 mmol/L) under stirring conditions at room temperature for 2 h to form dispersion solution A. 1.0 g polyvinylpyrrolidone (PVP) was added into 50 mL ethanol to obtain the solution B. The dispersion solution A mixed with the solution B. Then the mix solution was heated in water-bath at 70 °C for 4 h. The as-formed mixture was filtered, and washed with water and ethanol, respectively. 12.0 wt % Ag/BiVO$_4$/Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ (marked Ag/BiVO$_4$/Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$) was obtained after the filtration residues was dried at 50 °C for 12 h.

2.2. Material Characterization

The structure of samples was determined by X-ray diffractometer (Shimadzu, XRD-6000, Kyoto, Japan), Fourier transform infrared spectroscopy (FTIR, Perkin-Elmersystem 2000, Perkin Elmer, Waltham, MA, USA). The ultraviolet-visible diffuse reflectance spectrophotometer (UV-vis DRS, TU1901, Beijing Purkinje, Beijing, China) was employed to examine the light absorption performance of the as-obtained composites. Their morphologies were observed by transmission electron microscopy (TEM, FEI, Tecnai G2 F20, Hillsboro, OR, USA). The element content was analyzed by X-ray photoelectron spectrometer (XPS-XSAM800, Kratos, Manchester, UK) with a base pressure $2 \times 10^{-7}$ Pa and X-ray gun180 W (12 kV, 15 mA). The magnetic properties were investigated using a vibrating sample magnetometer (VSM, Lakeshore 7410, LakeShore, Carson, CA, USA).

2.3. Measurement of the Photocatalytic Performance

The photocatalytic activity of the as-prepared composites was investigated by the photodegradation of simulated dye wastewater (Rhodamine B, RhB) under visible light irradiation. 100 mg photocatalyst was put into 100 mL RhB solution of 5 mg/L. Then the suspension liquid was placed in dark for 0.5 h with stirring to reach the adsorption–desorption equilibrium. A 500 W
Xe lamp, equipping with UV cut-off filter, was used as the visible light source ($\lambda \geq 420$ nm). At the given irradiation time intervals, a series of the reaction solution was sampled and measured the absorption with the UV-vis spectrophotometer (TU-1901). The photocatalytic mechanism of Ag/BiVO$_4$/Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ was explored by holes-radical trapping experiments with p-benzoquinone (BZQ, $\bullet$O$_2^{-}$ radical scavenger), EDTA-Na$_2$ (hole scavenger), and tert-butanol (t-BuOH, $\bullet$OH radical scavenger).

The repeatability of the photocatalyst was detected by cycling tests. After each cycle, the catalyst was separated by an external magnetic field, then washed and dried for the next cycle.

3. Results and Discussion

3.1. Synthesis Condition and Structure Identification

The appropriate mass ratio of Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ and BiVO$_4$ was essential for BiVO$_4$/Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$. Thus, the composite possessed not only a good magnetization but also a high photocatalytic activity. By the comparison experiments, it is found that the composite held the largest magnetic property without the reduction of photocatalytic activity when 15.0 wt % Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ was loaded in BiVO$_4$ by the dip-calcination approach. The doping quantity of Ag was not only closely related to the photocatalytic activity but also affected the cost of Ag/BiVO$_4$/Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$. PVP was confirmed as an efficient stabilizer and reductant in the synthesis process of Ag/BiVO$_4$/Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$. Its suitable dosage was 1.0 g in 50 mL ethanol solution. With a series of tests, the optimized doping dosage of Ag in the magnetic composite was determined to be 12.0 wt %.

XRD patterns of Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$, BiVO$_4$, BiVO$_4$/Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$, and Ag/BiVO$_4$/Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ were illustrated in Figure 1. It was noticed that each diffraction peak of Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ was indexed to the franklinite (cubic spinel) phase [23] which belonged to the Fd-3m (227) space group with a lattice size of 0.8474 nm. Three peaks at 28.9°, 35.2°, and 46.0° were clearly attributed to the iconic twin peaks of monoclinic scheelite BiVO$_4$ (JCPDS 14-0688) [9]. The lattice parameters of the prepared BiVO$_4$ was $a = 5.1175$ nm, $b = 11.6697$ nm, and $c = 5.1084$ nm. The peak at 28.9° (121) was used to calculate the average crystallite size that was 27.2 nm, while the average size of BiVO$_4$/Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ was 12.0 wt %.

Thus, the composite possessed not only a good magnetization but also a high photocatalytic activity. Therefore, the optimized doping dosage of Ag in the magnetic composite was determined to be 12.0 wt %.

Figure 1. XRD patterns of Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$, BiVO$_4$, BiVO$_4$/Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$, and Ag/BiVO$_4$/Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$. This result confirmed the coexistence of Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$, while the V-O vibration absorption peaks of BiVO$_4$ was at 734.3 cm$^{-1}$ and 823.4 cm$^{-1}$. This result confirmed the coexistence of Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ and BiVO$_4$ in the composites. The absorption peaks at 2341.7 cm$^{-1}$ and 3433.6 cm$^{-1}$ were ascribed to CO$_2$ and the surface adsorption H$_2$O. There were not observable characteristic peaks of Ag in Figures 1 and 2 due to its low content [24].

Figure 1. XRD patterns of Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$, BiVO$_4$, BiVO$_4$/Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$, and Ag/BiVO$_4$/Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$.
To discern the element contents in Ag/BiVO$_4$/Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ and determine their valence states, XPS study was carried out. The binding energy peaks of Ag, O, V, Bi, Fe, Zn, and Mn were recorded in Figure 3. The peaks of O, V, Bi, Fe, Mn, and Zn elements were clearly observed in Figure 3a. Further comparing the fully scanning XPS spectra, it can be seen that the characteristic profile of Ag$_{3d}$ was obvious in Ag/BiVO$_4$/Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ while Ag peak in BiVO$_4$/Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ was not observed. Thus, it was deduced that the doping Ag in BiVO$_4$/Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ was successful [25]. The peaks at the binding energy of 373.9 eV and 367.9 eV in Figure 3b was severally ascribed to Ag$_{3d_{3/2}}$ and Ag$_{3d_{5/2}}$ [19], revealing the existence of Ag$^+$. In Figure 3c, the peaks of O$_{1s}$, V$_{2p_{3/2}}$, and V$_{2p_{1/2}}$ were located at 530.5 eV, 516.5 eV, and 523.4 eV, which were assigned to O$_2^-$ and V-O bands. There were peaks of Bi$_{4f_{5/2}}$ and Fe$_{4f_{7/2}}$ at 164.1 eV and 158.3 eV in Figure 3d, indicating the presence of bismuth species of Bi$^{3+}$ in BiVO$_4$. Figure 3f displayed peaks at the binding energy of 641.5 eV (Mn$_{2p_{3/2}}$) and 653.1 eV (Mn$_{2p_{1/2}}$). The high resolution spectra of Fe$_{2p}$ as well as Zn$_{2p}$ were shown in Figure 3e,g. These peaks verified the presence of Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$, which was consistent with the results of XRD and FTIR detection [26]. So, Ag/BiVO$_4$/Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ was successfully assembled by in situ wet-chemistry synthesis method. This synthesis approach was simple, low cost, and environmentally friendly.
Figure 3. XPS spectra of the magnetic composite (a) fully scanned spectra of BiVO$_4$/Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ and Ag/BiVO$_4$/Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$; (b–g) narrow scan spectrum of Ag3d, O1s and V2p, Bi4f, Fe2p, Mn2p, and Zn2p of Ag/BiVO$_4$/Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$.

The morphological analysis of Ag/BiVO$_4$/Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ was studied with transmission electron microscopy (TEM), and the results were displayed in Figure 4. By comparative experiments, it was demonstrated that the surface property of Ag/BiVO$_4$/Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ was significantly improved when the appropriate dosage of polyvinylpyrrolidone (PVP) was used in the fabrication process of the composite. The improvement in properties resulted from the surface activity of PVP and the full uniform dispersion of Ag ions in the reaction solution. In addition, ethanol (solvent) further promoted the complete interface reaction of the ions with BiVO$_4$/Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ particles. Namely, PVP could prompt the formation of nano-structural particles through in situ wet-chemistry method.
was directly related to the electrons and Ag⁺ transformation between the conduction band and the
valence band of BiVO₄ [17]. Second, Ag particles had darkened color to enhance absorption of the
visible light. The significant enhancement of optics properties would be conducive to bringing high
photocatalytic activity.

The band-gap energy (Eₔ) for Ag/BiVO₄/Mn₁₋ₓZnxFe₂O₄ shifted to red light region, leading to the main absorption edge around 400 nm. First, the red shift can be discovered from Figure 5a that the maximum absorption edge of Ag/BiVO₄/Mn₁₋ₓZnxFe₂O₄ was about 2.36 eV. The incorporation of Mn₁₋ₓZnxFe₂O₄ appeared to strengthen the absorption and sensitivity response for visible light. Third, Ag particles could produce a strong surface plasmon resonance absorption. The band-gap energy (Eₔ) for Ag/BiVO₄/Mn₁₋ₓZnxFe₂O₄ was about 2.25 eV. Eₔ values of BiVO₄ and BiVO₄/Mn₁₋ₓZnxFe₂O₄ in Figure 4b were about 2.36 eV. The incorporation of Mn₁₋ₓZnxFe₂O₄ did not change the optical properties of BiVO₄ [18]. The relatively low Eₔ of Ag/BiVO₄/Mn₁₋ₓZnxFe₂O₄ appeared to strengthen the absorption and sensitivity response for visible light. The significant enhancement of optics properties would be conducive to bringing high photocatalytic activity.

Figure 4. TEM images of Ag/BiVO₄/Mn₁₋ₓZnxFe₂O₄.

It was noted in Figure 4a,b that the bright surface sphere of BiVO₄ attached the dark particles of Mn₁₋ₓZnxFe₂O₄. A small amount of Ag granular particles uniformly dispersed in the spherical surface in Figure 4c,d. As estimated from the images of BiVO₄/Mn₁₋ₓZnxFe₂O₄, the average size of Ag granular particles was about 30 nm. The granular nanostructure particle of Ag favored production of rich active sites in the photocatalyst.

3.2. Light Absorption Property and Magnetic Property

UV-vis diffuse reflectance spectrophotometry was a suitable and important technique to determine the light absorption for semiconductor photocatalysts [27]. Figure 5 showed UV-vis diffuse reflectance spectra (UV-vis DRS) of BiVO₄, BiVO₄/Mn₁₋ₓZnxFe₂O₄, and Ag/BiVO₄/Mn₁₋ₓZnxFe₂O₄. It can be discovered from Figure 5a that the maximum absorption edge of Ag/BiVO₄/Mn₁₋ₓZnxFe₂O₄ shifted to red light region, leading to the main absorption edge around 400 nm. First, the red shift was directly related to the electrons and Ag⁺ transformation between the conduction band and the valence band of BiVO₄ [17]. Second, Ag particles had darkened color to enhance absorption of the visible-light for BiVO₄/Mn₁₋ₓZnxFe₂O₄. Third, Ag particles could produce a strong surface plasmon resonance absorption. The band-gap energy (Eₔ) for Ag/BiVO₄/Mn₁₋ₓZnxFe₂O₄ appeared to strengthen the absorption and sensitivity response for visible light. The significant enhancement of optics properties would be conducive to bringing high photocatalytic activity.
Ag/BiVO$_4$/Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ and pure Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$. The saturation magnetization (Ms) of Ag/BiVO$_4$/Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ in Figure 6 was 10.04emu/g. It was noted that large Ms was conducive towards the separation and recovery with an external magnet. Compared with Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$, the Ms of Ag/BiVO$_4$/Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ was declined by 87.5% due to the decrease of magnetic content per unit mass. More importantly, Ms of Ag/BiVO$_4$/Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ was larger than that (7.01emu/g) of Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$/B$_2$O$_3$ [21]. The magnetic property was conducive to the stable activity of Ag/BiVO$_4$/Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$. The result revealed that the as-prepared magnetic photocatalyst was easily recovered by an external magnet. Therefore, it was concluded that Ag/BiVO$_4$/Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ with good magnetic property possessed a high recovery rate.

3.3. Photocatalytic Activity

It was well-known that the photocatalytic ability was vital to photocatalytic materials, which was the base property for their industrial application. Generally, the photocatalytic activity was assessed with the degradation reaction of dyes.

3.3.1. Visible-Light-Driven Photocatalytic Activity

The photocatalytic performance of the samples under visible light irradiation was evaluated with the RhB photodegradation, and the result was shown in Figure 7. There was only a little degradation...
rate in the blank test (without any photocatalyst), indicating the poor self-degradation of RhB. The degradation rate for BiVO$_4$ and BiVO$_4$/Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ was approximately 45.0% after 60 min reaction. The same degradation rate proved that the introduction of Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ did not cause the activity loss of BiVO$_4$. Figure 7 indicates that the degradation rate for Ag/BiVO$_4$/Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ reached to 96.0% under the same condition. The setting time was only 60 min in this photodegradation test of RhB. Hence, the photocatalytic property of Ag/BiVO$_4$/Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ was obviously higher than that of BiVO$_4$ and BiVO$_4$/Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$. It meant that only 12.0 wt % Ag brought outstanding improvement in photocatalytic ability of BiVO$_4$/Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$.

![Figure 7. The degradation rates of RhB with the three photocatalysts.](image)

In fact, most degradation tests are very slow (may take several hours) despite the improvements in visible light absorption of the photocatalyst. Here, the as-prepared Ag/BiVO$_4$/Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ has a highly photocatalytic efficiency. This can be explained with the following three aspects: (1) Ag produced the surface plasmon resonance (plasma energy), which was transferred to BiVO$_4$, leading to more formation of photo-excited electrons and holes. It was helpful to the enhancement of photocatalytic activity; (2) Ag particles acted as holes and accepted photo-produced electrons from the conduction band of BiVO$_4$, extending the wavelength range and preventing the recombination of electrons and holes. The transformation or conversion of the charged particles in the interface was strengthened. In other words, the presence of Ag particles boosted the quantum efficiency for BiVO$_4$/Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$; (3) Owing to the nanostructure of Ag particles, Ag/BiVO$_4$/Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ possessed a relatively large specific surface area, which increased the efficient sites and further yielded a high photocatalytic activity [19,25]. Thus, nanostructure Ag particles ensured high photocatalytic property of Ag/BiVO$_4$/Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$.

Ag/BiVO$_4$/Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ was recovered with an external magnet in the end of the photocatalytic degradation test. 88~91 mg (after washing and drying) Ag/BiVO$_4$/Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ could recover from initial dosage of 100 mg in each cycle. The average recovery rate of magnetic Ag/BiVO$_4$/Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ was 89%, which was larger than the literature report value (85.0%) [28]. It is worth mentioning that the recovery method was quick with low energy consumption. The high recovery rate effectively avoided the leftover of catalysts in the water solution. Namely, Ag/BiVO$_4$/Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ demonstrated itself as an environmentally friendly photocatalytic material and showed perspective industrial application in removal water-soluble contaminants.

The repeatability and stability were necessary in the practical photocatalytic application [27]. Cycling tests were employed to evaluate the photocatalytic stability of Ag/BiVO$_4$/Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$,
and the degradation rate of RhB was described in Figure 8. It was clear that the degradation rate during the five cycles was severally 96.0%, 96.0%, 95.0%, 94.0% and 94.0%, which revealed photocatalyst efficiency of Ag/BiVO₄/Mn₁₋ₓZnₓFe₂O₄ barely decreased in the test process. Experiment results exhibited excellent photocatalytic stability. What is more, 94.0% of the degradation rate during the five cycles was very larger than that of the reference report [13]. So, magnetic photocatalyst Ag/BiVO₄/Mn₁₋ₓZnₓFe₂O₄ possessed promising prospect in the photo-decomposition organic dyes (industrial wastewater) field.

![Figure 8. Cycling tests of Ag/BiVO₄/Mn₁₋ₓZnₓFe₂O₄.](image)

3.3.2. Photocatalytic Mechanism

Radical scavengers were used to study active species in photocatalytic reaction, the result was displayed in Figure 9. In details, the degradation rate of RhB in Ag/BiVO₄/Mn₁₋ₓZnₓFe₂O₄-EDTA-Na₂ (h⁺ scavenger) lowed and reached to 28.0%, which was significantly lower than that of Ag/BiVO₄/Mn₁₋ₓZnₓFe₂O₄. Under the same condition, the degradation rate steeply went down when BZQ (●O₂⁻ scavenger) in place of EDTA-Na₂ was added into the reaction solution, the rate was only 11.0%. However, the introduction of t-BuOH (●OH scavenger) caused a large decrease in the degradation of about 60.0%. Namely, the change of the degradation rate in Ag/BiVO₄/Mn₁₋ₓZnₓFe₂O₄-t-BuOH was the smallest among three radical scavenger tests. The results illustrated that free radicals were major active species, and that ●O₂⁻ played the domination role though ●OH and h⁺ took part in the photocatalytic reaction.

![Figure 9. The photodegradation rate of RhB with Ag/BiVO₄/Mn₁₋ₓZnₓFe₂O₄ and different scavengers.](image)
The electron transition occurred between valence band and conduction band, generating the photoelectrons and holes when the photon energy was higher than $E_g$ of the semiconductor. The possible transition of photo-induced electron and hole was used to express the photocatalytic process under light irradiation. The photocatalytic mechanism of Ag/BiVO$_4$/Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ was described in Figure 10. In detail, $e^-$ transferred to the surface of Ag particle, the dissolved oxygen (O$_2$) could capture the electron and form the super oxygen radical ($\bullet$O$_2^-$) through the Fermi level surface resonance. The adsorbed H$_2$O in the surface of Ag/BiVO$_4$/Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ could be oxidized by holes (h$^+$), yielding hydroxyl free radical ($\bullet$OH). Both $\bullet$O$_2^-$ and $\bullet$OH had a large oxidation ability and decomposed RhB into CO$_2$ and H$_2$O. At the same time, holes themselves prompted the degradation-oxidized of RhB [26]. Thus, the doping Ag was favorable to drive more $\bullet$O$_2^-$ and $\bullet$OH radicals, strengthening the degradation of RhB in visible light irradiation.

![Figure 10. Photocatalytic mechanism scheme of Ag/BiVO$_4$/Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$.](image)

In fact, we used Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ as magnetic substrate in order to simplify separation after photocatalytic reaction for BiVO$_4$. The UV-vis DRS shown the incorporation of Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ did not enhance the optical properties of BiVO$_4$. Noble metal-doping and graphene-loading were good ways to improve optical properties and enhance photocatalytic activity for single phase semiconductor. Here, we chose Ag-doping to boost the photocatalytic activity of BiVO$_4$/Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$. In addition, we will use graphene to modify BiVO$_4$/Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$. These studies will help to choose a better way (the above mentioned) for enhancing photocatalytic activity via comparing their photocatalytic activity and reaction kinetics, and then apply these findings to other signal semiconductors.

4. Conclusions

Ag/BiVO$_4$/Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ was fabricated with the dip-calcination and in situ wet-chemistry synthesis method that was simple and environmentally-friendly. Element contents and their valence states in Ag/BiVO$_4$/Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ were detected, indicating Ag granular particles dispersed in the spherical surface of BiVO$_4$. The presence of Ag particles boosted the quantum efficiency, and further enhanced the photocatalytic activity. Under visible light irradiation ($\lambda \geq 400$nm), the degradation rate of RhB using Ag/BiVO$_4$/Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ after only 60 min reaction reached to 96.0%, which was greater than that of Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$/BiVO$_4$ and pure BiVO$_4$. Most importantly, the degradation rate was close to 94.0% during the fifth recycle. We hope this research can promote the industrial application of BiVO$_4$.

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