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# The enhanced properties in photocatalytic wastewater treatment: Sulfanilamide (SAM) photodegradation and $Cr^{6+}$ photoreduction on magnetic Ag/ZnFe<sub>2</sub>O<sub>4</sub> nanoarchitectures



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## ABSTRACT

Ag/ZnFe<sub>2</sub>O<sub>4</sub> nanoarchitectures composed of ZnFe<sub>2</sub>O<sub>4</sub> nanoparticles loading onto Ag nanowires were fabricated by hydrothermal method. The Ag/ZnFe<sub>2</sub>O<sub>4</sub> nanocomposites possessed excellent performance in simulated photocatalytic wastewater treatment like sulfanilamide (SAM) photodegradation and Cr<sup>6+</sup> photoreduction. The improvement of photoactivity could be ascribed to the successful formation of Schottky interface between ZnFe<sub>2</sub>O<sub>4</sub> nanoparticles and Ag nanowires and the enhanced light absorption ability in visible light region with modified energy band structures, which make further efforts to the ameliorate separation and improved mobility of photo-induced charge carriers with enhanced performance in photocatalysis. The Ag/ZnFe<sub>2</sub>O<sub>4</sub> nanocomposites exhibited outstanding photoactivity than single component and more importantly, the unique magnetic properties enabled the Ag/ZnFe<sub>2</sub>O<sub>4</sub> photocatalysts to be recycled easily with the aid of external magnetic field, which make it possible for practical applications. © 2021 Elsevier B.V. All rights reserved.

## 1. Introduction

ZnFe<sub>2</sub>O<sub>4</sub>, as a magnetic semiconductor material, has been widely investigated due to the special magnetic behavior with excellent stability and photo response capability. Ascribe to the theoretical band position ( $E_{VB}$  = 0.38 eV,  $E_{CB}$  = -1.54 eV), a relatively more negative conduction band (CB) position makes it possible to realize the photocatalytic or photoelectrochemical water splitting to generate hydrogen on ZnFe<sub>2</sub>O<sub>4</sub>, which could be utilized to develop new energy resources and alleviate energy crisis [1–3]. However, the poor photocatalytic efficiency resulted by the short hole transport length limited the application without further modification. In recent years, many strategies have been made such as coupling with other semiconductors [4–7], noble metal loading [8,9] to conquer these limitations. These methods facilitated the generation, separation, and migration of photo-excited charge carriers after light irradiation accompanied with the improvement of photocatalytic performance. Among various strategies, noble metal was considered as a thriving way to broaden the light absorption, inhibit the recombination of

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https://doi.org/10.1016/j.jallcom.2021.159085 0925-8388/© 2021 Elsevier B.V. All rights reserved. photo-excited carriers with prolonged lifetime when composing with other semiconductors to form Schottky barrier [10,11].

In the previous studies, noble metal nanoparticles were always loaded, reduced, or deposited onto the semiconductors by various methods. Zhang et al. prepared Ag activated ZnFe<sub>2</sub>O<sub>4</sub> nanocomposites with Ag loading onto ZnFe<sub>2</sub>O<sub>4</sub> hollow spheres with excellent acetone gas sensing properties [12]. Huerta-Aguilar et al. reduced HAuCl<sub>4</sub> onto ZnFe<sub>2</sub>O<sub>4</sub> to form Au/ZnFe<sub>2</sub>O<sub>4</sub> nanocomposites and applied it in the degradation of paracetamol [13]. Zhu et al. fabricated Ag/ferrite nanocomposites via wet impregnation method and exhibited good properties in 4-chlorophenol photodegradation [14]. These nanocomposites showed excellent separation efficiency during photocatalysis process. The loading of noble metal could effectively improve the light adsorption, and the Schottky barrier formed between metal and semiconductor can also promote the charge migration and separation, which was also conducive to the enhanced performance in photocatalysis [15]. According to our previous study, noble metal nanostructures with relatively larger size were also suitable for light adsorption according to the Mie's theory, and the obtained "reversed" nanostructures like Au/TiO<sub>2</sub> and Au/ZnO nanoarchitectures exhibited good properties in photocatalysis such as H<sub>2</sub>-generation, dye degradation and methanol oxidation [16,17]. Based on the above analysis, we fabricate the magnetically separable Ag/ZnFe<sub>2</sub>O<sub>4</sub> nanostructures through hydrothermal method with different amount of ZnFe<sub>2</sub>O<sub>4</sub> loading and Ag nanowires acted as supporter in this study. The as-prepared Ag/ZnFe<sub>2</sub>O<sub>4</sub> nanocomposites showed significantly enhanced photocatalytic activity in sulfanilamide (SAM) degradation and Cr<sup>6+</sup> photoreduction. In addition, the Ag/ZnFe<sub>2</sub>O<sub>4</sub> nanocomposites retained the magnetic separable properties, which was necessary for practical application. Furthermore, the possible mechanism of charge separation in Ag/ZnFe<sub>2</sub>O<sub>4</sub> during photocatalysis process were also discussed. The Ag/ZnFe<sub>2</sub>O<sub>4</sub> nanocomposites could be considered potentially for water purification due to the outstanding performance in simulated wastewater treatment process.

## 2. Experimental section

## 2.1. Preparation of Ag nanowires

Ag nanowires were prepared via a hydrothermal method according to the following steps: 0.5 g AgNO<sub>3</sub> and 1.0 g polyvinylpyrrolidone (PVP) were dissolved into 40 mL mixed solution containing 37 mL ethylene glycol (EG) and 3 mL glycerol. After 500 µL 0.5 mg/mL NaCl/EG solution was added into the mixture, the whole reaction system was transferred into the 50 mL Teflon-lined stainless-steel autoclave and reacted at 120 °C for 3 h. The gray mixture after the reaction was washed and centrifuged with absolute ethanol for several times. The Ag nanowires were obtained after drying at 60 °C overnight.

#### 2.2. Preparation of $Ag/ZnFe_2O_4$ nanoarchitectures

Ag/ZnFe<sub>2</sub>O<sub>4</sub> nanoarchitectures with ZnFe<sub>2</sub>O<sub>4</sub> nanoparticles decorated Ag nanowires were fabricated as described below: 1 mmol Zn(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O, 2 mmol FeCl<sub>2</sub> and certain amount of Ag nanowires were dispersed in 30 mL deionized water with continuous stirring for 2 h. After 1 mL ethylenediamine was added into the solution, the whole mixture was stirred for another 1 h and transferred into 50 mL Teflon-lined stainless-steel autoclave and reacted at 160 °C for 6 h. The Ag/ZnFe<sub>2</sub>O<sub>4</sub> nanocomposites were obtained after the products washed, centrifuged, and dried at 60 °C. Pure ZnFe<sub>2</sub>O<sub>4</sub> nanoparticles were synthesized under identical conditions except for the addition of Ag nanowires. For simplicity, we denote Ag/ZnFe<sub>2</sub>O<sub>4</sub> samples with 5%, 10%, 15%, 20% and 25% Ag content as AgZFO5, AgZFO10, AgZFO15, AgZFO20 and AgZFO25. The pure ZnFe<sub>2</sub>O<sub>4</sub> sample was denoted as ZFO.

## 2.3. Characterizations

X-ray diffraction patterns (XRD) was acquired to investigate the crystal structure of Ag/ZnFe<sub>2</sub>O<sub>4</sub> samples on D8 Bruker advanced X-ray diffractometer. Scanning electron microscope (SEM, Hitachi S-4800) and Transmission electron microscope (TEM, JEOL, JEM-2100) were employed to observe the microstructure and morphology of the samples. X-ray photoelectron spectrum (XPS) was carried out on Thermo Fischer ESCALAB 250Xi X-ray photoelectron spectrometer under an Al K<sub> $\alpha$ </sub> radiation (*hv* = 1486.6 eV). UV–Vis diffuse reflectance spectra were achieved from Shimadzu UV-2500 spectrophotometer with BaSO<sub>4</sub> as reference. The magnetism properties of pure ZnFe<sub>2</sub>O<sub>4</sub> and Ag/ZnFe<sub>2</sub>O<sub>4</sub> nanocomposites were analyzed on VSM-7407 vibrating sample magnetometer (Lake Shore, USA). The electron spin resonance (ESR) signals of spin-trapped O2<sup>-</sup> radicals were acquired from Bruker model ESR JES-FA300 spectrometer. The electrochemical measurements were investigated by CHI-760E electrochemical workstation with 0.5 M Na<sub>2</sub>SO<sub>4</sub> solution as electrolyte. The as-prepared samples were regarded as working electrode. Ag/AgCl and platinum were selected as reference electrode and counter electrode, respectively. The PL spectra and time-resolved photoluminescence (TRPL) spectra of samples were recorded on an FL3-TCSPC fluorescence spectrophotometer and time-resolved fluorescence spectrum (Edinburgh FLS9800) with an excitation wavelength of 280 nm, respectively.

# 2.4. Photocatalytic wastewater treatment: SAM degradation and $Cr^{6+}$ reduction

The catalytic activity through Ag/ZnFe<sub>2</sub>O<sub>4</sub> nanocomposites was conducted by SAM photodegradation and Cr<sup>6+</sup> reduction. Typically, 20 mg sample was dispersed in 50 mL 20 mg/L SAM or Cr<sup>6+</sup> aqueous solution. The pH of Cr<sup>6+</sup> solution was adjusted to 2 with H<sub>2</sub>SO<sub>4</sub> (1 M). Before light irradiation, the adsorption-desorption equilibrium was established after the mixture was stirred in dark for 1 h. Then a 300 W Xe lamp with 400 nm cut-off was used to illuminate the photodegradation system. About 4 mL solution was withdrawn at a given time interval and then centrifuged to separate solid catalyst for further analysis. The photocatalytic activity was estimated according to the maximum absorption wavelength ( $\lambda_{max} = 258$  nm) of SAM [18] and the colored Cr(VI)-diphenylcarbazide method ( $\lambda_{max} = 540$  nm) [19] monitored on UV–Vis spectrometer (UV-1201).

## 3. Results and discussion

## 3.1. XRD analysis

The crystallographic structure of as-obtained Ag/ZnFe<sub>2</sub>O<sub>4</sub> nanocomposites were studied by XRD (Fig. 1). Pure ZnFe<sub>2</sub>O<sub>4</sub> exhibited diffraction peaks at 31.8°, 35.5°, 42.7°, 47.5°, 56.6°, 62.8° and 68.1°, which confirmed the cubic structure of ZnFe<sub>2</sub>O<sub>4</sub> (JCPDS No. 22-1012). After ZnFe<sub>2</sub>O<sub>4</sub> sample were loaded onto Ag nanorods, the diffraction peaks of ZnFe<sub>2</sub>O<sub>4</sub> remained the same except for four additional peaks positioned at 38°, 44°, 66° and 77° corresponding to the metallic Ag (JCPDS No. 65-2871). The purity of Ag/ZnFe<sub>2</sub>O<sub>4</sub> nanocomposites were evident because no other peaks were observed apart from the above-mentioned peaks. As is known to all, Ag element could react with Fe<sup>3+</sup> to generate Ag<sup>+</sup> ions, but in our fabrication process, ZnFe<sub>2</sub>O<sub>4</sub> was obtained from zinc acetate {Zn(CH<sub>3</sub>COO)<sub>2</sub>:2H<sub>2</sub>O} and ferrous chloride (FeCl<sub>2</sub>), which could prevent the formation of Ag<sup>+</sup> ions and destroy the structure of Ag nanowires. Moreover, the existence of metallic Ag also suggested the stability of Ag during the preparation procedure and the feasible route to prepare Ag/ZnFe<sub>2</sub>O<sub>4</sub> nanocomposites.

## 3.2. Morphological analysis

The Ag/ZnFe<sub>2</sub>O<sub>4</sub> nanocomposites with ZnFe<sub>2</sub>O<sub>4</sub> loading onto Ag nanowires were fabricated through continuous hydrothermal strategies and the morphology of obtained Ag/ZnFe<sub>2</sub>O<sub>4</sub> samples were viewed by SEM and TEM. From Fig. 2A we could find that uniform



Fig. 1. XRD patterns of as-obtained samples.



Fig. 2. SEM images of Ag nanowires (A); AgZFO5 (B); AgZFO10 (C); AgZFO15 (D); AgZFO20 (E) and AgZFO25 (F).

Ag nanowires accompanied with clean surface were prepared via hydrothermal method. After Ag nanowires were composed with ZnFe<sub>2</sub>O<sub>4</sub>, the small nanoparticles were clearly observed and anchored on the surface of Ag nanowires with high dispersion as indicated in Fig. 2B–F. With the increase of Ag content, it can be seen clearly on the SEM pictures that the amounts of nanoparticles attached to the Ag nanowires were also decreased, indicating the feasibility of the experimental procedure. In addition, when the loading amount of ZnFe<sub>2</sub>O<sub>4</sub> particles exceeded the optimal amount, the exceeded ZnFe<sub>2</sub>O<sub>4</sub> particles will also agglomerate itself rather than forming a composite to generate Ag/ZnFe<sub>2</sub>O<sub>4</sub> interface (Fig. 2B and C). It can be seen from the photocatalytic experiments that the photocatalytic performance of the Ag/ZnFe<sub>2</sub>O<sub>4</sub> composite decreases when the optimal amount of  $ZnFe_2O_4$  particles is exceeded. This may be discussed in the following photocatalytic experiment sections. Otherwise, the HRTEM of AgZFO15 sample depicted in Fig. S1C revealed the successful construction of interfacial attachment between Ag nanowires and ZnFe<sub>2</sub>O<sub>4</sub>. The lattice spacing distance between the adjacent lattice fringes was 0.254 nm, which belonged to the (331) crystalline planes of ZnFe<sub>2</sub>O<sub>4</sub> (JCPDS No. 65-3111). Meanwhile, the HRTEM analysis could also suggested the fabrication of Ag/ZnFe<sub>2</sub>O<sub>4</sub> nanocomposites instead of physical mixture. Moreover, the intimate hybrid structure of Ag/ZnFe<sub>2</sub>O<sub>4</sub> was conducive to the charge separation during the photocatalytic procedure, thus improving the photocatalytic efficiency.

## 3.3. XPS analysis

The surface elemental composition of Ag/ZnFe<sub>2</sub>O<sub>4</sub> nanocomposites were employed by XPS technique as shown in Fig. 3. The full scan of pure ZnFe<sub>2</sub>O<sub>4</sub> and Ag/ZnFe<sub>2</sub>O<sub>4</sub> were similarity except for some cases. Simultaneously, the fine scan of Zn 2*p*, Fe 2*p*, O 1 *s* and Ag 3*d* were recorded to confirm the chemical states of different elements. In fine scan of Zn 2*p*, two obvious peaks centered at binding energies of 1020.9 eV and 1044.0 eV could be identified to Zn 2*p*<sub>3/2</sub> and Zn 2*p*<sub>1/2</sub>, respectively, indicating the existence of Zn<sup>2+</sup> in Ag/ZnFe<sub>2</sub>O<sub>4</sub> nanocomposites [20–22]. Four bands shown in Fig. 3(c) located at 710.6, 724.7, 718.8 and 732.8 eV, which could be indexed to Fe 2*p*<sub>3/2</sub>, Fe 2*p*<sub>1/2</sub> and their satellite peaks, indicating the presence of Fe<sup>3+</sup> oxidation state in Ag/ZnFe<sub>2</sub>O<sub>4</sub> samples [23,24]. For O 1*s* fine spectrum, the divided peaks situated at 530.8 and 529.5 eV could ascribed to the absorbed oxygen and lattice oxygen of Fe–O and Zn–O bonds, respectively [25,26]. It should be noted that the binding energy of O 1s was slightly shifted to higher values compared to that of pure  $ZnFe_2O_4$  (530.9 and 529.7 eV for 5% Ag/ZnFe\_2O\_4, respectively) which could attribute to the interactions between Ag and  $ZnFe_2O_4$ . Moreover, the existence of Ag<sup>0</sup> species in Ag/ZnFe<sub>2</sub>O<sub>4</sub> nanocomposites was proved according to the Ag 3*d* fine spectra (Fig. S2). The photoelectron peaks situated at 374.2 eV and 368.2 eV were observed to be the evidence of metallic Ag with no other oxidation state of Ag due to the slitting energy of Ag 3*d* doublet was 6.0 eV [27–29], also represented the stability of Ag during the fabrication process of Ag/ZnFe<sub>2</sub>O<sub>4</sub> nanocomposites.

## 3.4. UV-Vis analysis

UV-Vis measurement was conducted to analyze the optical properties of Ag/ZnFe<sub>2</sub>O<sub>4</sub> nanocomposites. Due to the smaller band gap energy ( $E_g = 2.00 \text{ eV}$ ) measured by Kubelka-Munk formalism, pure ZnFe<sub>2</sub>O<sub>4</sub> exhibited a certain absorption capacity in the whole spectral region (200-800 nm). As depicted in Fig. 4A, Ag nanowire exhibited relative lower light absorption ability from 200 nm to 800 nm than that of ZnFe<sub>2</sub>O<sub>4</sub>. So, after Ag and ZnFe<sub>2</sub>O<sub>4</sub> were combined, the absorption spectrum of Ag/ZnFe<sub>2</sub>O<sub>4</sub> could shift due to the change of the ratio of the two components, which would further affect the band gap energy [30]. Despite all this, the obtained Ag/ZnFe<sub>2</sub>O<sub>4</sub> nanoarchitectures showed enhanced light absorption ability in visible light region (400-600 nm). The band gap energy of different samples was also calculated and listed in Table 1. The UV-Vis analysis suggested that the Ag/ZnFe<sub>2</sub>O<sub>4</sub> nanocomposites displayed better performance in light absorption ability, which could contribute to the efficient use of solar energy and benefit to the improvement of photocatalytic performance.

## 3.5. Photocatalytic wastewater treatment

As an antibiotic which was usually used for human and veterinary science and difficult to be disposed of, sulfanilamide (SAM) was chemically stable due to the aromatic ring with heteroatoms, amino group, and sulfonic group [31,32]. So, in this study, SAM was first opted as a simulated pollutant to measure the photoactivity of Ag/ZnFe<sub>2</sub>O<sub>4</sub> nanocomposites, which was photo-stable under visible light illumination on account of the negligible change in UV–Vis absorbance (< 5%). A comparison of different photocatalysts for SAM



Fig. 3. XPS spectra of ZFO and AgZFO15 samples: (A) full scan; (B) Zn 2p; (C) Fe 2p and (D) O 1s.

photodegradation was presented in Fig. 5A. Pristine  $ZnFe_2O_4$  nanoparticles exhibited lower performance during SAM photodegradation process, indicating the suppressed carrier separation rate and efficiency. However, after coupling with Ag nanowires, the Ag/ZnFe\_2O\_4 nanocomposites showed enhanced photoactivity during SAM photocatalytic degradation, especially for AgZFO15 sample, which could increase the degradation efficiency from 48.4% to 98.4% in 2 h. The photocatalytic degradation kinetics of SAM followed firstorder reaction, and the corresponding reaction rate constants (k) with different sacrificial agents were calculated and listed in Fig. 5B. As we mentioned above, Ag could trap electrons due to the Schottky barriers formed in the Ag/ZnFe<sub>2</sub>O<sub>4</sub> interfaces and the photo-excited electrons on ZnFe<sub>2</sub>O<sub>4</sub> surface could transferred to Ag, which accelerate the charge separation on ZnFe<sub>2</sub>O<sub>4</sub> and help the carriers to participate in photocatalytic reactions [33–35]. Besides, the effective Ag/ZnFe<sub>2</sub>O<sub>4</sub> interface was also affected by excessive loadings, the



Fig. 4. UV-Vis spectrum of as-fabricated Ag/ZnFe<sub>2</sub>O<sub>4</sub> samples (A) and the Kubelka-Munk transformed function of different samples (B).

Table 1

Band gap energy of as-prepared $Ag/ZnFe_2O_4$ samples.	
Sample	Band gap energy (eV)
ZFO	2.00
AgZFO5	2.01
AgZFO10	2.01
AgZFO15	2.02
AgZFO20	2.02
AgZFO25	2.03

charge separation efficiency could decrease due to the photo-excited electrons had the tendency to recombine with holes on agglomerated ZnFe<sub>2</sub>O<sub>4</sub> nanoparticles rather than transferring to Ag due to the excess amount of ZnFe<sub>2</sub>O<sub>4</sub> onto Ag nanowires. Therefore, the optimal amount of Ag in Ag/ZnFe<sub>2</sub>O<sub>4</sub> was necessary to obtain the best photocatalytic performance. To further confirm the photoactivity of as-fabricated Ag/ZnFe<sub>2</sub>O<sub>4</sub> nanoarchitecture, Cr<sup>6+</sup> photoreduction reaction was also conducted according to the colored Cr(VI)-diphenylcarbazide (DPC) method. From Fig. S4A we could find the concentration of Cr<sup>6+</sup> ions were decreased dramatically after light illumination according to the peaks centered at around 540 nm. The poor efficiency of ZnFe<sub>2</sub>O<sub>4</sub> for Cr<sup>6+</sup> photoreduction was also improved after combining with Ag nanowires. The reaction rate constant (k) of Ag/ZnFe<sub>2</sub>O<sub>4</sub> sample in Cr<sup>6+</sup> photoreduction were 0.0095, 0.0132, 0.0146, 0.0119 and 0.0081 min<sup>-1</sup>, which was 3.96, 5.5, 6.08, 4.96, and 3.38 times higher than that of pure  $ZnFe_2O_4$  (0.0024 min<sup>-1</sup>) (Fig. 6A and B). As is known to all, Ag could exhibit the surface plasmonic resonance (SPR) effect due to its intrinsic property. Based

on the traditionally SPR effect theory, the electrons could transfer from noble metal (Ag) to semiconductors ( $ZnFe_2O_4$ ). However, electrons would transfer from lower work function one (ZnFe<sub>2</sub>O<sub>4</sub>,  $\Phi_{\rm s}$  = ~2.07 eV) to the higher one (Ag,  $\Phi_{\rm m}$  = 4.26 eV). The band gap energy of ZnFe<sub>2</sub>O<sub>4</sub> was estimated as 2.00 eV according to the UV-Vis analysis and shown in Table 1. When the above two materials (Ag and  $ZnFe_2O_4$ ) form a composite and illuminated by visible light, the photogenerated electrons will transfer from the conduction band (CB) of  $ZnFe_2O_4$  to Ag due to the Schottky barriers in order to achieve Fermi level equilibration when ZnFe<sub>2</sub>O<sub>4</sub> and Ag get into contact [13,36–38]. Therefore, the surface plasmon resonance (SPR) effect of nano Ag in this composite system is very weak to realize the transfer of photogenerated electrons from Ag to ZnFe<sub>2</sub>O<sub>4</sub> due to the existence of Schottky barrier formed between ZnFe<sub>2</sub>O<sub>4</sub> and Ag [39], and the proposed schematic illustration of electron-hole transfer during the photocatalysis process on Ag/ZnFe<sub>2</sub>O<sub>4</sub> system under the visible light irradiation was illustrate in Fig. 7. Therefore, the as-fabricated Ag/ZnFe<sub>2</sub>O<sub>4</sub> nanocomposites could be primarily considered as an effective catalyst for wastewater treatment due to the excellent performance in SAM photodegradation and Cr<sup>6+</sup> photoreduction.

During the photodegradation process, the photo-excited charge carriers could generate and separated to react with the adsorbed  $H_2O$  or  $O_2$  to form active species contributing to the catalysis progress. The active species during photocatalysis process was investigated by capturing experiment with the addition of sacrificial agent. In this study, TEOA, t-BuOH and BQ were selected to realize  $h^+$ , OH and  $O_2^-$  quenching, respectively [40,41]. Because of the addition of quenching agents, the photocatalytic activity of AgZFO15



Fig. 5. Photocatalytic SAM degradation performance (A, B) over different samples and photocatalytic performance with different sacrificial agent on AgZFO15 (C, D).



Fig. 6. Photocatalytic Cr<sup>6+</sup> reduction performance (A, B) over different samples and photocatalytic performance with different sacrificial agent on AgZFO15 (C, D).



**Fig. 7.** Schematic illustration of electron-hole transfer during the photocatalysis process on Ag/ZnFe<sub>2</sub>O<sub>4</sub> system under the visible light irradiation ( $E_v$ : energy in vacuum;  $\Phi_m$ : work function of Ag;  $\Phi_s$ : work function of ZnFe<sub>2</sub>O<sub>4</sub>;  $F_m$ : Fermi level of Ag;  $F_s$ : Fermi level of ZnFe<sub>2</sub>O<sub>4</sub>;  $F_m$ : Fermi level of equilibrium position; VB: valance band of ZnFe<sub>2</sub>O<sub>4</sub>; CB: conduction band of ZnFe<sub>2</sub>O<sub>4</sub>).

sample exhibited a decreasing trend. We could clearly find that the degradation performance of SAM evidently reduced from 98.4% to 11.6% due to the addition of BQ, which suggested the importance of  $\cdot O_2^-$  during SAM photodegradation. Comparatively, the lower effect

of  $\cdot$ OH and h<sup>+</sup> were also evidenced by the photodegradation efficiency were reduced to 34.0% and 67.9% in the presence of t-BuOH and TEOA (Fig. 5C and D). It should be noted that, the active species during Cr<sup>6+</sup> photoreduction was also-O<sub>2</sub><sup>-</sup> due to the degrade efficiency was decreased from 82.7% to 23.6%, which also suggested the importance of  $\cdot$ O<sub>2</sub><sup>-</sup> during Cr<sup>6+</sup> photoreduction process (Fig. 6C and D). Moreover, the high-intensity of DMPO-  $\cdot$ O<sub>2</sub><sup>-</sup> signals obtained from ESR spectra exhibited in Fig. S5 could also demonstrate the generation of  $\cdot$ O<sub>2</sub><sup>-</sup> during the photocatalytic process, indicating the successful formation of Ag/ZnFe<sub>2</sub>O<sub>4</sub> anoarchitectures and effective Schottky barriers in Ag/ZnFe<sub>2</sub>O<sub>4</sub> system.

The reusability and stability were all crucial factors in practical use during photocatalysis process [42,43]. The cycling test of SAM photodegradation and Cr<sup>6+</sup> photoreduction with AgZFO15 sample were displayed in Fig. S3 and Fig. S4B. The photocatalytic performance exhibited no obvious decrease after 3 cycles with photocatalytic efficiency from 98.4% to 95.2% for SAM photodegradation and 82.7-80.1% for Cr<sup>6+</sup> reduction, respectively, which could indicate the stability and the possibility during a longer operation time. Besides, pure ZnFe<sub>2</sub>O<sub>4</sub> sample exhibited a magnetic saturation (Ms) value of 70.26 emu/g. Because of the content of Ag nanowires existed in AgZFO15 nanocomposites was as high as 15%, the Ms value of AgZFO15 nanocomposites was decreased to 58.65 emu/g. The hysteresis loop of AgZFO15 sample illustrated in Fig. S6 also proved that the AgZFO15 sample could be separated magnetically. Thus, it was convinced that the Ag/ZnFe<sub>2</sub>O<sub>4</sub> nanocomposites could be a separable and effective photocatalyst for contaminants treatment based on the results of photocatalytic reaction.



Fig. 8. Photocurrent response under visible light irradiation (A) and EIS plots of different Ag/ZnFe<sub>2</sub>O<sub>4</sub> samples (B).



Fig. 9. PL (A) and TRPL (B) spectra of ZFO and AgZFO15 samples.

## 3.6. Photoelectrochemical properties

The photoelectrochemical measurements were performed to gain deep understanding into the separation and migration of photoexcited carriers during photocatalysis [44-46]. Fig. 8A displayed the transient on-off photocurrent response of ZnFe<sub>2</sub>O<sub>4</sub> and Ag/ZnFe<sub>2</sub>O<sub>4</sub> nanocomposites after deposited onto FTO electrodes. Bulk ZnFe<sub>2</sub>O<sub>4</sub> was responsive to visible light illumination with average photocurrent density of 0.11  $\mu$ A cm<sup>-2</sup>. Obviously, affected by the formation of Schottky barriers between Ag/ZnFe<sub>2</sub>O<sub>4</sub> interface, the AgZFO serious samples exhibited good sensitivity to the visible light irradiation, suggesting the effective charge generation and separation after being a composite. The AgZFO15 sample exhibited average photocurrent density of 2.45 times higher compared to that of pure  $ZnFe_2O_4$  (0.27  $\mu A \text{ cm}^{-2}$ ). This result was also corresponding to the SAM photodegradation and Cr<sup>6+</sup> photoreduction experiment, indicating the enhanced mobility and longer lifetime of photoinduced charge carriers were accountable for the improvement of photoactivity. Moreover, the conclusion of photocurrent tests could also contribute to the existence of the interface between two components.

To explore the interfacial charge transfer of  $Ag/ZnFe_2O_4$  samples, the electrochemical impedance spectroscopy (EIS) study was also carried out and depicted in Fig. 8B [47,48]. The results indicated that compared to pure  $ZnFe_2O_4$ , the  $Ag/ZnFe_2O_4$  nanocomposites exhibited a smaller semicircle in the Nyquist plots, representing the lower resistance of  $Ag/ZnFe_2O_4$  samples and photo-excited carriers could be separated effectively and speedy transferred during the photocatalysis process. Overall, the existence of metallic Ag could promote the charge separation and transformation and made it possible for  $Ag/ZnFe_2O_4$  nanocomposites to achieve a higher rate of photocatalysis.

## 3.6.1. PL and TRPL analysis

Solid-state photoluminescence (PL) and time-resolved photoluminescence (TRPL) spectra were conducted to further evaluate the lifetime of photo-induced charge carriers. From Fig. 9A we could find that AgZFO15 exhibited lower PL emission peak compared to the ZFO sample, indicating the improved separation of photo-excited charge carriers. Furthermore, TRPL decay curve of ZFO and AgZFO15 sample were also collected. As shown in Fig. 9B, the fluorescence lifetime of AgZFO15 was longer than that of ZFO sample, which could also reveal the higher separation ability of photogenerated electron-hole pairs on Ag/ZnFe<sub>2</sub>O<sub>4</sub> nanoarchitectures.

## 3.7. Possible mechanism

According to the former analysis, the possible mechanism during photocatalytic progress was illustrated in Fig. 10. Under the light irradiation,  $ZnFe_2O_4$  could adsorb photo irradiation to generate charge carriers. Due to the Schottky barriers between  $ZnFe_2O_4$  and Ag, the photo-induced electrons could migrate from CB of  $ZnFe_2O_4$  to



Fig. 10. Schematic illustrations of charge transfer-separation for waste water treatment during photocatalysis process on Ag/ZnFe<sub>2</sub>O<sub>4</sub> nanoarchitecture under visible light irradiation.

Ag, which could contribute to the separation of charge carriers, facilitate the prolonged lifetime to take part in the photocatalytic procedures. The holes and electrons could react with adsorbed H<sub>2</sub>O and O<sub>2</sub> to form active species such as·OH and·O<sub>2</sub><sup>-</sup>, which will further take part in photocatalytic process and both displayed decisive roles.

## 4. Conclusions

Herein, we reported the fabrication of Ag/ZnFe<sub>2</sub>O<sub>4</sub> nanocomposites with ZnFe<sub>2</sub>O<sub>4</sub> nanoparticles decorated onto Ag nanowires. The as-synthesis Ag/ZnFe2O4 nanocomposites showed enhanced properties in simulated wastewater treatment process like SAM photodegradation and Cr<sup>6+</sup> photoreduction. The best performance was reflected in AgZFO15, with a SAM photodegradation rate constant of 0.0330 min<sup>-1</sup> and a Cr<sup>6+</sup> photoreduction rate constant of 0.0146 min<sup>-1</sup>. The enhanced separation efficiency of photo-induced carriers caused by Schottky interface generated between Ag and ZnFe<sub>2</sub>O<sub>4</sub> and the appropriate content of two components were responsible for the enhanced photoactivity. This work offered a new strategy into the energy conversion of magnetic nanocomposites and unusual fabrication procedures to prepare composite nanostructures containing noble metals. Likewise, the Ag/ZnFe<sub>2</sub>O<sub>4</sub> nanocomposites could be utilized in wastewater treatment and energy fields due to the high photoactivity, high stability and magnetic separable properties.

## **CRediT** authorship contribution statement

Tianyu Liu: Methodology, Formal analysis, Investigation, Data curation, Writing - original draft, Writing - review & editing. Chongxi Wang: Experimental, Validation. Wei Wang: Formal analysis, Funding acquisition. Guojiang Yang: Validation. Zhiying Lu: Validation. Peng Xu: Formal analysis. Xiaonan Sun: Formal analysis. Jintao Zhang: Resources, Supervision, Funding acquisition.

## **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### **Appendix A. Supporting information**

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jallcom.2021.159085.

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