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Magnetic field assisted $\alpha$-Fe$_2$O$_3$/Zn$_{1-x}$Fe$_x$O heterojunctions for accelerating antiviral agents degradation under visible-light

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**Abstract**

Reducing the recombination efficiency of photo-induced carriers has been found as an effective means to improve the degradation of antiviral agents. Given that the Lorentz forces can cause the abnormal charge to move in the opposite direction, external magnetic field improved $\alpha$-Fe$_2$O$_3$/Zn$_{1-x}$Fe$_x$O heterojunctions (FZHx) were developed to remove increasing antiviral agents that were attributed to the COVID-19 pandemic under visible light. The characterization of the mentioned FZHx in the external magnetic field indicated that FZHx had perfect photocatalytic activity for degrading antiviral agents. In the external magnetic field, the quantities of photo-generated carriers and free radicals ($\bullet$OH and $\bullet$O$_2^-$) derived from FZHx increased significantly, which improved antiviral agent removal by 30.0%. Though the band structure ($\alpha$-Fe$_2$O$_3$) is unlikely to change due to some orders of magnitude weaker of Zeeman energy in magnetic fields, which insignificantly impacts photocatalytic performance. However, this study proposed a strategy of negative magnetoresistance effects and heterojunctions to facilitate the separation and transfer of photo-induced carriers in magnetic fields. Based on the proposed strategy, spin oriented electrons were selected and accumulated on the conduction band, which contributed to the degradation of antiviral agents. Overall, this study presented novel insights into the improved degradation performance of antiviral agents by applying Fe-based heterojunctions in an external magnetic field.

1. Introduction

The novel severe acute respiratory syndrome corona virus 2 (SARS-CoV-2), initially discovered in December 2019, refers to a virus that has posed a global public health threat. In 2020, SARS-CoV-2 disease was termed COVID-19 (Corona Virus Disease 2019) by the World Health Organization (WHO) and caused a pandemic [1]. On the whole, the severity of COVID-19 has been indicated in its high infectivity (e.g., directly or indirect contact with viruliferous object surfaces/waste, airborne/respiratory droplets and oral-fecal transmission) as well as the absence of a safe and effective vaccine. Compared with the mentioned severities, employing considerable antiviral agents under the COVID-19 pandemic may more severely jeopardize the natural ecosystem and human health [2]. Antiviral pollution agents fail to trigger acute intoxication, whereas its bioaccumulation and chronic toxicity caused severe and irreversible harm. This threat above is inevitable to everyone, regardless of whether the demographic characteristics are. Accordingly, it is necessary to eliminate the threat of antiviral agent pollution due to COVID-19 transmission in water [3].

Photocatalysis technology is recognized as a promising program to reduce the water pollution (e.g., antiviral agent pollution) [4,5]. This technology is found to be more eco-friendly, sustainable, highly-efficient and low-cost. Thus, the development of new photocatalysts for improving photocatalytic performance has become a hotspot in this field. Over the past few years, most photocatalysts (e.g., TiO$_2$ [6], ZnO [7], ZnWO$_4$ [8], $\alpha$-Fe$_2$O$_3$ [9] and CdS [10]) have been modified and prepared for their prominent photocatalytic performance (e.g., catalytic degradation of a wide variety of organic dyes). To be specific, ferric oxide ($\alpha$-Fe$_2$O$_3$) refers to a significant photocatalyst that helps simultaneously carry out energy conversion and environmental remediation. A smaller band gap of $\alpha$-Fe$_2$O$_3$ (2.3 eV) is found to be beneficial since it can absorb visible light [11]. However, its photocatalytic activity is too poor to cope with organic pollutant. Given the mentioned facts, many references have reported the construction of heterojunction for improving
2. Experimental section

2.1. Chemicals

Iron(III) nitrate nonahydrate (Fe(NO₃)₃·9H₂O, AR 99.8%) and zinc acetate ((CH₃COO)₂Zn·2H₂O, AR 99.9%) originated from Chendu Chron Chemicals Corporation. Corporation. Potassium hydroxide (KOH, AR 99.8%) was provided by Jiangsu Zhenjiang Chemicals Factory. Above chemical reagents were analytically pure without being further purified. Ribavirin was purchased from Guangzhou Baiyunshan Pharmaceutical General Factory (C₈H₁₂N₂O₃, LR > 90.0%). Chloroquine Phosphate and Arbidol originated from Renhe Pharmaceutical Incorporated Company (C₂₀H₂₂ClN₂O₈P₂, LR > 90.0%; C₂₂H₂₃BrN₂O₅S·HCl·H₂O, LR > 90.0%).

2.2. Synthesis

1) α-Fe₂O₃: According to Fig. 1a, pure α-Fe₂O₃ was prepared with the chemical precipitation method. First, 0.01 mol powder of Fe(NO₃)₃·9 H₂O was dissolved in deionized water (40 mL). Second, potassium hydroxide (KOH, 0.03 M, 30 mL) was added into the iron nitrate solution and then stirred for 1 h. Subsequently, the pH of the mixed system was kept at ~10.0. Next, the intermediate products were kept at 180 °C for 16 h. Lastly, the samples were washed to neutral and then calcined at 300 °C for ~2 h. The final sample was termed α-Fe₂O₃ (af).

2) α-Fe₂O₃/Zn₁-xFeₓO heterojunctions: The samples of α-Fe₂O₃/Zn₁-xFeₓO heterojunctions were synthesized using the facile protocol presented in Fig. 1b. First, 0.005 mol of (CH₃COO)₂Zn·2 H₂O powder and different molars radio (Fe to Zn is 0, 0.02, 0.04 and 0.06 mol) of Fe(NO₃)₃·9 H₂O powder were dissolved in deionized water (40 mL). Subsequently, KOH solution (0.01 mol, 30 mL) was progressively introduced into the above solution and then stirred for 1 h. The pH value of the solution was kept at 10.0. Next, the intermediate products were introduced into the Tetra-tert-butyl orthotitanate (25 mL) and kept at 180 °C for 16 h. Lastly, the samples were washed to neutral and then calcined at 300 °C for ~2 h. The final sample was termed FZHx (The different atomic ratios of Fe/Zn (2%, 4%, or 6%) simplified as FZH1, FZH2 or FZH3).

2.3. Characterisation

X-ray diffraction (XRD) patterns were recorded on a PANalytical X’Pert PRO with Cu Kα radiation (λ = 1.5406 Å, at 40 kV and 40 mA). A Carl Zeiss Ultra 55 was used for scanning electron microscopy (SEM). X-ray photoelectron spectroscopy (XPS) analyses were conducted by applying a Thermo Fisher Scientific K-Alpha. Transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDX) were conducted with a Carl Zeiss LIBRA 200 FE. A Shimadzu SolidSpec-3700 was adopted to record Ultraviolet-visible (UV-vis) spectra. Vibrating sample magnetometer (VSM) patterns were recorded on America LakeShore Company. Fluorescence spectrophotometer (PL) spectra were recorded with a F-4600, Shanghai Devos. Electrochemical workstation measurements were recorded on a Shanghai Chenhua CHI760E. Electron paramagnetic resonance spectrometer (EPR) tests were performed by German bruk A300. Total organic carbon analyzer (TOC) was tested by Shimazu TOC-V WP.

2.4. Photocatalytic experiments

The photocatalytic activities achieved by αf and FZHx in the magnetic field and the same samples in the absence of the magnetic field were assessed to determine their ability to degrade antiviral agents (Ribavirin, Chloroquine Phosphate, and Arbidol) in aqueous solution under visible light. The antiviral agents achieved the concentrations of ~30 mg·L⁻¹ (Ribavirin), 10 mg·L⁻¹ (Chloroquine Phosphate) and 30 mg·L⁻¹ (Arbidol), and they were irradiated at an intensity of 5.0 mW cm⁻² under a Xe lamp with λ > 420 nm. Furthermore, the pH was maintained at ~7.0 at the ambient temperature (25 °C) in a heterogeneous system. First, the catalysts of 0.1 g were placed into a 50 mL antiviral agent solution. Before the irradiation with the illuminant, all samples were ultrasonicated for ~50 min to achieve an equilibrium of dispersion and adsorption, and subsequently kept in the dark for...
~20 min to achieve an equilibrium on the surface of the photocatalysts. Next, a Xe lamp was placed ~5 cm above the beaker, and ten fixed permanent magnets (20 mT) were set on both sides. During the photo-reactions, ~3 mL of the antiviral agent supernatant liquid was sampled per 10 min and then tested at 206, 228, 257 nm. Next, the photocatalytic experiment of αF and FZHx was repeated in the absence of the external magnetic field. Eq. (1) was adopted to determine the degradation rate:

\[ \text{Removal rate} = \left(1 - \frac{C_t}{C_0}\right) \times 100\% \] (1)

Where \( C_0 \) and \( C_t \) (mg L\(^{-1}\)) respectively denote the initial and post-degradation concentrations of the aqueous antibiotic solutions.

3. Results and discussion

3.1. Morphology and structure

Fig. 2 illustrates the XRD patterns of αF and FZHx. The XRD peaks belonged to α-Fe\(_2\)O\(_3\) (JCPDS No.33-0664) and ZnO (JCPDS No.36-1451). All samples were more significantly crystallized, and no other diffraction peaks were identified. It was therefore indicated that the purity of αF and FZHx was higher than that of the other phases. However, at higher concentrations, the diffraction peaks of αF were not identified in the sample of FZH3. Moreover, the higher dispersion and the lower crystallinity exhibited by α-Fe\(_2\)O\(_3\) were the significant factors [22]. The dominant diffraction peaks of FZHx were located at 31.7°, 34.4°, 36.2°, 47.5°, 56.6°, 62.8°, 66.3°, 66.3°, 69.0° and 76.9°, which respectively complied with (100), (002), (101), (102), (110), (103), (200), (122), (201), and (202) crystal faces. The crystallite size \( D \) values were determined by employing the Scherrer’s equation [23], as expressed in Eq. (2).

\[ D = \frac{K \lambda}{B \cos \theta} \] (2)

After the calculation, the crystallite sizes were estimated as 36.70 nm (αF), 44.84 nm (FZH1), 35.99 nm (FZH2) and 34.36 nm (FZH3). From the XRD pattern, the peaks at 36.2°, 47.5° and 56.6° were considered to be slightly weaker and broader and then indexed as (101), (102), and (110), respectively, thereby representing the formation of low-crystalline materials. The result above was achieve probably because some Fe\(^{3+}\) was incorporated into the ZnO lattice, thereby causing mild lattice deformations. The reduction of crystallite size might be induced by an inner strain in the crystalline lattice, thereby leading to the peak widening of FZHx when less Fe\(^{3+}\) was incorporated into the ZnO lattice (ZFx represents Zn\(_{1-x}\)Fe\(_x\)O) to form αF and ZFx heterojunctions. The findings above demonstrated that the augmentation of lattice strains within ZFx might result from the synergistic effect of heterostructure construction and lattice distortion attributed to the replacement of host ions by other cations [24]. The structure distortion caused the nucleation rate to decrease, thereby reducing the crystallite size. Moreover, FZHx showed a shift to a higher angle because the radius of Fe\(^{3+}\) (0.64 Å) [25] was smaller than that of Zn\(^{2+}\) (0.74 Å) [26]. Besides, the distance between crystal decreased, and the samples of the in situ doping of Fe\(^{3+}\) into the ZnO lattice and synthesis of FZHx were found to be feasible. Fig. 3 presents the SEM images of αF and FZH3. αF presents regular particles, consistent with a tablet-like morphology with a thickness of ~10–15 nm and diameter of ~60–100 nm (Fig. 3a). The samples of FZH3 showed almost multangular particles, with the average sizes ~< 125 nm. Moreover, the number of edges decreased as the doping concentration of Fe\(^{3+}\) increased and the amount of αF increased. Considerable tablet-like αF was tightly inserted on the surfaces of ZFx, which indicated that the heterojunctions of αF and ZFx were obtained in the one-step hydrothermal process. This scaly structure was considered
to achieve a larger specific surface area and more active sites. The particle size tended to decrease with value of Fe augmentation, which was consistent with the foregoing XRD analysis. The sample of FZH3 was a spheroid (Fig. 3d). As indicated by the EDX spectra in Fig. S1, FZH3 sample was composed of Zn, O and Fe, and all the elements were evenly distributed in FZH3. To further observe the specific particle elemental distribution, a specific particle was analyzed on the EDX, which exhibited a ellipsoid structure. FZH3 achieved a high-concentration of Zn, O and Fe elements in this particle (Fig. 4a–c). As indicated by Fig. S2 and Table 1, the ratio of elements was consistent with synthetic raw.

Table 1
The different element ratio of FZH3.

| Element | Peak Area | Weight% | Weight% Sigma | Atomic% |
|---------|-----------|---------|---------------|---------|
| O K     | 2713      | 22.37   | 0.69          | 53.65   |
| Fe K    | 1464      | 7.81    | 0.40          | 5.36    |
| Zn K    | 10,692    | 69.82   | 0.73          | 40.99   |
| Totals  |           | 100.00  |               |         |

Fig. 3. SEM images of αF and FZHx.

Fig. 4. Energy disperse X-ray (EDX) elemental maps of a single FZH3 (a) SEM image, (b) Zn mapping, (c) O mapping, (d) Fe mapping.
materials (FZH3). The first peripheral core achieved slightly lower concentrations of Fe and O than the core. The change of the concentration of ions, including a sharp drop in the reaction of Zn, Fe, and O, had a radical effect to reduce the elemental density in the first peripheral core. Next, the second core periphery contained slightly higher concentrations of Zn, O, and Fe than the first one. The element distribution of Fe and Zn in the second core periphery was greater than that of the first one due to the increase in the concentration of OH.

Notably, the elements of core periphery turned out to be thinner gradually due to a gradual decrease in the concentration of Zn and Fe in the cyclical process. The FZHx ellipsoidal structure above might be correlated with solubility product rules and precipitation conversion. The specific computational process of solubility product rules could be compared with the ion product (Q) and solubility product constant (Ksp). Fig. 4d presents the formation of FZHx composite material. According to the literature, the solubility product constants of Zn(OH)2 and Fe(OH)3 were determined as 6.8 × 10^{-17} [27] and 2.8 × 10^{-39} [28], respectively.

\[
\text{Zn}^{2+}(aq) + 2\text{OH}^-(aq) \rightarrow \text{Zn(OH)}_2(s) 
\]

\[
Q(\text{Zn(OH)}_2) = \left\{ c(\text{Zn}^{2+}) \right\} \times \left\{ c(\text{OH}^-) \right\}^2 > K_{\text{sp}}(\text{Zn(OH)}_2) 
\]

\[
\text{Fe}^{3+}(aq) + 3\text{OH}^-(aq) \rightarrow \text{Fe(OH)}_3(s) 
\]

\[
Q(\text{Fe(OH)}_3) = \left\{ c(\text{Fe}^{3+}) \right\} \times \left\{ c(\text{OH}^-) \right\}^3 > K_{\text{sp}}(\text{Fe(OH)}_3) 
\]

Given the EDX spectra in Fig. 4a, high-concentrations of Zn, O and Fe in the core were explained by Eqs. (3-6).

\[
3\text{Zn(OH)}_2(s) + 2\text{Fe}^{3+}(aq) \rightarrow 2\text{Fe(OH)}_3(s) + 3\text{Zn}^{2+}(aq) 
\]

\[
Q_2(\text{Zn(OH)}_2) = \left\{ c(\text{Zn}^{2+}) \right\} \times \left\{ c(\text{OH}^-) \right\}^2 \geq K_{\text{sp}}(\text{Zn(OH)}_2) 
\]

\[
Q_3(\text{Fe(OH)}_3) = \left\{ c(\text{Fe}^{3+}) \right\} \times \left\{ c(\text{OH}^-) \right\}^3 \geq K_{\text{sp}}(\text{Fe(OH)}_3) 
\]

\[
K = \left\{ c(\text{Zn}^{2+}) \right\}^3 \times \left\{ c(\text{Fe}^{3+}) \right\}^2 \times \left\{ c(\text{OH}^-) \right\}^5 > 10^{27} 
\]

According to the EDX spectra in Fig. 4b, the first core periphery containing slightly lower concentrations of Fe and O than the core were expressed by Eqs. (8-9) and (7,10). When the.

Fe(OH)3 could produce precipitation other than Zn(OH)2. In addition, the K was excessive large, which revealed that Zn(OH)2 could be converted into Fe(OH)3. After recycling, FZHx were prepared. Lastly, the tablet-like αF was tightly embedded on the surfaces of ZFx due to Eq. (10).

The morphological characteristics exhibited by FZH3 were characterized with bright-field TEM, high-resolution TEM (HRTEM), and selected area electron diffraction (SAED) and dark-field TEM. According to Fig. 5a, the sample of FZH3 exhibited an almost ellipsoidal structure, in which the long axis was ~50-250 nm and the short axis was ~35–90 nm. The HRTEM image indicated that FZH3 was highly crystallized (Fig. 5b). Furthermore, the lattice spacings of d = 0.260, 0.281 and 0.248 nm belonged to the (002), (100), and (101) crystal faces.

Fig. 5. (a) Transmission electron microscopy (TEM) image of FZH3, (b) high-resolution TEM (HRTEM) image of FZH3, (c) selected area electron diffraction (SAED) pattern of FZH3, and (d) dark field image of FZH3.
According to Fig. 6, the surface composition and valence band (VB) of FZHx and ZnO were characterized through X-ray photoelectron spectroscopy (XPS) analyses. The total spectrum of FZHx showed the characteristic peaks of Zn, O, and Fe, which further proved that Fe was successfully inserted into the lattice of ZnO (ZFx), and that the heterojunction of FZHx was successfully constructed. The binding energies of Zn 2p, O 1s, Fe 2p, and C 1s were 1021.3, 529.9, 710.7 and 284.4 eV, respectively, which were comparable with existing studies of α-Fe2O3/ZnO [29]. At the same time, we have provided survey XPS and high resolution Fe 2p scan of ZnO. No difficult to find, the sample of ZnO is not found significant Fe peak. Notably, the C1s peak (284.4 eV) could be explained by the product’s residual carbon and XPS instrument’s adventitious hydrocarbon [30]. The high-resolution XPS spectrum of Fe 2p peaks indicated the binding energies of Fe 2p3/2 and Fe 2p1/2 at 711.5 and 724.1 eV, respectively (Fig. 6c). The high-resolution XPS spectrum of O 1s indicated the presence and chemical states of O, which was consistent with the lattice oxygen of FZH3 in Fig. 6d. According to Fig. 6e, two peaks corresponding with the Zn 2p3/2 and Zn 2p1/2 spin–orbital splitting photoelectrons of FZH3 were identified at the binding energies of 1044.2 and 1021.3 eV, respectively. Accordingly, the peaks of Fe 2p in Fig. 6c were correlated with the bonded iron and iron (e.g., Fe-O-Zn or Fe-Zn-O). Moreover, Fig. 6b presents the XPS valence band (VB) spectrum of FZH3. The VB was estimated as 2.15 eV from the image, and the value of VB demonstrated a major difference in αF (2.48 eV) and ZnO (2.89 eV). The phenomenon above might be because of the red-shift as a result of the maximum energy relative to the band. The bandgap variation was correlated with the iron impurities of ZnO and heterojunction.

3.2. Photocatalytic performance

Since the FZHx photocatalysts were synthesized through the hydrothermal process, whether the photocatalysts exhibited better photocatalyst properties was also investigated. Ribavirin, Chloroquine Phosphate and Arbidol were adopted to represent antiviral pollution agents in water to assess the photocatalytic activity of αF and series of FZHx. The overall antiviral pollution agents in water were self-degraded by < 1% before the simulated sunlight irradiation.

According to Fig. 7a and c, the adsorption of Ribavirin pollutant was lower than 25% in the dark under external (or without) magnetic field exposure. However, the adsorption capacity of samples (in the magnetic field) was significantly better than that of another group (in the absence of the magnetic field). This result was achieved because Lorentz force could facilitate the adsorption performance in external magnetic fields. Furthermore, FZHx disposed by an external magnetic field achieved the highest photocatalytic activity during the photocatalytic degradation. The optimal degradation rate of αF and FZHx at the highest concentration (50 mL 30 mg L−1 Ribavirin) was 46% after ~50 min in a magnetic field, which was significantly better than in the absence of a magnetic field. According to Fig. 7c, the degradation of Ribavirin when treated with αF and FZHx in a magnetic field fitted a pseudo-first-order kinetics model. The linear relationship of ln(Ct/C0) versus time was determined by ln(Ct/C0) = kt. Furthermore, its degradation constants (k) reached 0.0078 (αF), 0.0125 (FZH1), 0.0178 (FZH2), and 0.0188 (FZH3) min−1 (Fig. 8d), respectively, which confirmed that the photocatalytic properties of Ribavirin in a magnetic field were 1.5 times that in the absence of a magnetic field. According to the TOC results, it is can be seen that the TC are mineralized into carbon dioxide and water (Fig. S3). To reveal the degradation of other antiviral pollution agents, the highest concentrations of Chloroquine Phosphate (50 mL 10 mg L−1) and Arbidol (50 mL 30 mg L−1) were examined under the exposure of an external (or
without) magnetic field (Fig. S4 and Fig. S5). It was obvious that the degradation results of Chloroquine Phosphate and Arbidol were consistent with the removal of Ribavirin. According to Table 2, the photocatalytic degradation of all antiviral pollution agents exhibited advantageous performance in the magnetic field. In particular, the degradation of Arbidol was the most significant. Truism, a product of more free radicals, was critical to the photocatalytic degradation. It could be estimated that the production of free radicals increased by 30% in an external magnetic field. According to the Table 3, our design is better than that of the previous products [42,43]. On the one hand, the negative reluctance effect of αF and FZHx was regarded as a vital factor to determine the catalytic performance. And the error bars of photocatalytic degradation for antiviral agent have been shown in the Fig. S6. From the picture, we could find that the samples (αF and FZHx) of are relatively stable. On the other hand, the photocatalyst of FZH3 was regarded as relatively stable according to Fig. S7a and Fig. S7b. The Fig. S8 is shown that the standard deviation of FZH3 photocatalytic cyclic experiment for Chloroquine Phosphate is no more than 0.05. Therefore, the data of cyclic degradation generally tended to be stable.
3.3. Photoelectric properties

To further evaluate the light absorption properties, the UV–vis adsorption spectra and band gaps of αFe2O3 and FZHx were obtained, and the samples were scanned to show the wavelengths in the 800–200 nm range. According to the UV–vis DRS spectra (Fig. 8a), αFe was clear in the visible region, which was consistent with several studies. In addition, the absorbance of FZHx was prominently extended into the visible region, which was consistent with several studies. The absorbance of FZHx was prominently extended into the visible region, which was consistent with several studies. According to Fig. 8a, the calculated band gap energies of the samples were scanned to show the wavelengths in the 800–200 nm range. According to the UV–vis DRS spectra, the absorption coefficients were calculated to be 6.0%. This work provided in the presence and absence of a magnetic field [33].

The transient photocurrent response is found as a typical and valid photon frequency; α is the absorption coefficient; Eg represents the band gap energy. According to Fig. 8b, the calculated band gap energies included: 2.38 eV (αFe), 2.94 eV (FZH1), 2.87 eV (FZH2) and 2.75 eV (FZH3).

According to Eq. (11), the absorption coefficient of the samples was scanned to show the wavelengths in the 800–200 nm range. According to the UV–vis DRS spectra, the absorption coefficient of ZF2 could shift to the VB of αFe, thereby restraining the recombination of electrons and holes (ZF2); αFe, belonging to ferromagnetic semiconductor, showed a typical spintronic phenomenon, which revealed that the resistance could be reduced under a magnetic field (negative MR effect) [34]. To extensively discuss the effect of photoelectric properties under magnetic conditions, the sample was characterized by chronocoulometry and electrochemical impedance spectroscopy (EIS). A similar result was obtained through the photoelectrochemical impedance spectroscopy (EIS) experiment in the dark (Fig. 9b). The phenomenon above was explained by the following factors: 1) the structural defects caused Fe+3 to merge with ZF2, which acted as the trapping centers for photogenerated carriers and contributed to reconcile carrier separation [32]; 2) the interfacial interactions between αFe and ZF2, belonging to ferromagnetic semiconductor, showed a typical spintronic phenomenon, which revealed that the resistance could be reduced under a magnetic field (negative MR effect) [34]. To extensively discuss the effect of photoelectric properties under magnetic conditions, the sample was characterized by chronocoulometry and electrochemical impedance spectroscopy (EIS). As expected, photocurrent responses were provided in the presence and absence of a magnetic field, peaking at 0.75 and 0.55 μA cm−2, respectively, for FZH3 (Fig. 9c). EIS indicated that the sample of FZH3 in the magnetic field conditions had a smaller arc radius in the Nyquist plot than without magnetic field (Fig. 9d).

Table 3

| Content        | Illumination time | Reaction mass (degradation material, concentration, and photocatalytic dose) | Degradation rate | Reference |
|----------------|-------------------|--------------------------------------------------------------------------------|------------------|-----------|
| αFe2O3/Zn1−xFe2O4, x= 6.0% | 50 min            | Chloroquine Phosphate (50 mL; 10 mg mL−1)                                          | 61%              | This work |
| O-g-C3N4/HTCC  | 120 min           | HAadV2; 10 mg mL−1 (50 mL);                                                     | 65%              | [41]      |
| SnO2NPs@ZIF-8  | 120 min           | MTT; 5 mg mL−1 (50 mL);                                                         | 43%              | [42]      |
| N:Cu:TiO2      | 60 min            | VOOC; 10 mg mL−1 (50 mL)                                                        | 33%              | [43]      |

Fig. 9. Photoelectrochemical properties: (a) Photocurrent responses of FZHx, (b) electrochemical impedance spectra of FZHx, (c) photocurrent responses of FZH3 under magnetic field or without magnetic field, (d) electrochemical impedance spectra of FZH3 under magnetic field or without magnetic field.
result demonstrated that the separation efficiency of photogenerated carriers was improved, which was due to the lowest impedance of charge transfer. Thus, the separation efficiency of photogenerated electron-hole pairs obviously increased on FZH3 due to negative reluctance effect and heterojunction. The result above was consistent with the photocatalytic degradation of antiviral pollution agents under magnetic conditions.

In general, the higher recombination rates of photo-induced electrons and holes were adverse to photocatalytic performance. However, this study was different from the previous theory. The separation capability of photogenic charge carriers was assessed by the photoluminescence (PL) under (or without) a magnetic field. All samples (FZHx) showed similar and asymmetrical emission peaks at approximately 604 nm (Fig. 10a). Furthermore, the emission intensity of FZHx clearly decreased as the value of Fe decreased. High recombination rates of photogenerated electrons and holes revealed that the samples had high PL intensities. However, photo-induced electrons of Zn$_{1-x}$Fe$_x$O (ZFx) might be captured by the CB of αF, which demonstrated that the recombination of photo-induced electrons (e$^-$) and holes (h$^+$) (ZFx) could be effectively inhibited. In other words, the conduction bands of ZFx and αF consisted of the new band gap that effectively stopped the recombination of photogenic charge carriers of FZH3, which was assessed with and without magnetic field exposure to determine emission intensity (Fig. 10b). The emission intensity of the same sample was clearly higher under magnetic conditions than that without magnetic conditions. The sample of αF have higher PL density under magnetic field (Fig. 10c). According to Fig. 10d, a higher emission intensity in the magnetic field revealed that more photo-induced electrons (e$^-$) (the CB of ZFx) could be transferred to the CB of αF. Accordingly, the separation efficiency of photogenerated electron-hole pairs (the CB and VB of ZFx) obviously increased, thereby inhibiting the recombination of the sample in the magnetic field. In addition, the emission intensity of αF was higher with magnetic field than without it. This study inferred that when the external magnetic field was applied at the beginning (i.e., instantaneous magnetic field), the photogenerated carriers shifted due to the Lorentz force on αF (Hall effect was generated later than the Lorentz force), thereby increasing the transitory carrier recombination rate.

### 3.4. Magnetic property

To determine the high photocatalytic efficiency for the degradation of antiviral pollution agents in the magnetic field, the photocatalysts of FZHx were investigated (Fig. 11). A typical saturation magnetization (M-H curve) with high coercivity of αF was identified and saturated under a magnetic field of 20 KOe. It was found that the ferromagnetic αF had lower residual magnetization [35–37]. In addition, the ferromagnetic M-H curves of FZHx were not identified in the picture, suggesting that the samples of ZFx were non-ferromagnetic semiconductor materials. However, the photocatalysts were saturated with an external magnetic field. The saturation magnetizations (slope) of FZHx were

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**Fig. 10.** PL spectra of FZHx (a) without magnetic field, and (b) under magnetic field, (c) PL spectra of αF without magnetic field and under magnetic field. (d) The process of electron transfer.

**Fig. 11.** Magnetization curves of FZHx.
augmented as the Fe value increased. Moreover, M-H curves presented some bending in the illustrations, indicating the possibility of a slightly negative MR with saturation magnetization augmentation. However, the saturation magnetization of photocatalysts was lower than that of pure αFe since the Fe value was excessively lower than pure αFe.

### 3.5. Photocatalytic mechanism

To analyze the photocatalytic mechanism in depth, the free radical capture of FZH3 was used in the photocatalytic degradation for aqueous Arbidol (30 mg L⁻¹, catalyst dose = 0.1 g, pH = 7.0) in the visible light. On the whole, the high selectivity of free radical can be adopted to assess photocatalytic processes. AgNO₃, p-Benzoquinone, 2-Propanol and (NH₄)₂C₂O₄ are common capture agents since they are capable of capturing the free radicals of photogenerated electrons (e⁻), *O₂, *OH and photogenerated holes (h⁺), respectively [38]. According to Fig. 12, the degradation rates of FZH3 using different capture agents were AgNO₃ (74.9%), p-Benzoquinone (32.4%), 2-Propanol (22.2%), (NH₄)₂C₂O₄ (27.0%), respectively. In addition, the mechanism can be acquired by ESR and terephthalic acid photoluminescence analyses [39–41]. According to the Fig. S9, the obtained ESR and TA-PL results were also in good agreement with the outcomes of radical trapping tests, which strongly authenticated the production of *OH and O₂⁻ radicals during the photocatalytic process. The free radicals of *OH *O₂ and h⁺ were the main active species in the free radical capture experiment. Thus, e⁻ and *O₂ were found as the free radicals capable of degrading aqueous Arbidol, which was obviously weaker than the degradation abilities of e⁻.

Given the above mentioned results, the possible photocatalytic mechanism was proposed (Fig. 13). FZH3 could produce more photogenerated carriers in a magnetic field (Eq. 12). (↑ represents augmentation, ↓ represents reduction)

**Undermagnetic – field :** ZFHx + h⁺ → h₁₈↑ + e₁cb↑ (12)

**Without magnetic field :** ZFhx + h⁺ → h₁₈↓ + e₁cb↓ (13)

The intensities of free radicals were augmented under ten fixed permanent magnets (20 mT), thereby leading to a 30.0% improvement in antiviral pollution agents according to the photocatalytic degradation. This was mainly because the spin-related behaviors of ferromagnetic αFe (Negative MR effect), FZHx and Fe³⁺-incorporated ZnO were pivotal factors for improving carrier separation efficiency, expediting carrier transmission and facilitating free radical formation. The relevant reaction of free radicals is presented below: The holes (h⁺) of ZFhx were easily trapped at lower Fe³⁺ and converted into Fe⁴⁺, and considerable hydroxyl radicals (*OH) were oxidized H₂O/OH⁻ concentrations by holes (h⁺). The photo-induced electrons of ZFhx could be trapped by O₂ and Fe³⁺, which converted many hydroxyl radicals (*O₂) and Fe⁴⁺.

Indeed, some side effects might be exerted in the process above, including *HO₂ (Eq. 19), H₂O₂ (Eq. 20) and *OH (Eq. 21). Ultimately, the remaining and few photon-generated carriers were recombined, and more energy was released.

\[
\text{FZH}x - h₁₈↑ + OH⁻ → OH↑
\]

\[
\text{FZH}x - h₁₈↑ + H₂O → OH↑ (14)
\]

\[
\text{Fe}e⁺ + FZHx - h₁₈↑ → Fe⁺³
\]

\[
\text{Fe}e⁺ + OH⁻ → Fe⁺³ + OH↑ (15)
\]

\[
\text{FZH}x - e₁cb↑ + O₂ → O₂↑ (16)
\]

\[
\text{O}_2↑ + H⁺ + HO₂⁻ → H₂O₂↑ (17)
\]

\[
\text{HO}_2⁻↑ + H⁺ + FZHx - e₁cb↑ → H₂O₂↑ (18)
\]

\[
\text{FZH}x - e₁cb↑ + FZHx - h₁₈↑ → Energy↑ (20)
\]

The ferromagnetic materials (αFe) is regulated by the magnetic field due to negative MR effect. Ferromagnetic αFe include many magnetic domains. However, these magnetic domains are aligned in a disparate direction to maintain a lower magnetostatic energy without the magnetic field. And many magnetic domains of αFe can be arranged in order under magnetic field. In other word, the photoinduced charge carrier of ferromagnetic photocatalysts are contributed to their selective accumulation on the interface of FZHx under magnetic fields, which is due to ferromagnetic alignment of the active material leads to spin oriented electrons. On the other hand, the photo-induced electrons of ZFhx could transfer to the CB of αFe and reduction of the recombination rate according to PL analysis. (CB and VB of ZFhx). Of course, many host Zn ions are replaced by Fe³⁺, and finally participate in free radical reaction. In conclusion, the separation efficiency of photogenerated electron-hole pairs clearly increase, inhibiting the recombination rate of the sample under the external magnetic field and further improving the quantity of free radicals. Therefore, this dynamic cycle of degrading antiviral pollution agents is proposed.

### 4. Conclusion

In summary, the samples of FZHx were triumphantly fabricated by the one-step hydrothermal process. Magnetic-field-enhanced degradation of antiviral pollution agents on FZHx were demonstrated. Under magnetic fields, the first-order kinetics model exhibits that photocatalytic degradation efficiencies of antiviral pollution agent (Ribavirin, Chloroquine Phosphate, and Arbidol) are increased by 42.4% 45.4% and 15.0%, respectively. The quantities of free radicals (*OH and *O₂⁻) derived from FZHx are significantly improved (by 30.0%). In-depth researches show that the synergistic effects of ferromagnetic α-Fe₂O₃ (Negative MR effect), FZHx and Fe³⁺-incorporated ZnO are pivotal factors for improving carrier separation and transmission efficiency. Finally, the photocatalytic performance is significantly improved under magnetic field. This study provides a new method to handle with the increased antiviral pollution agent due to the COVID-19 pandemic.

**CRediT authorship contribution statement**

Ruishi Xie: Experimental design and writing guide. Hongsheng
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.jece.2021.106990.

References

[1] J. Williams, L. Namazova-Baranova, M. Weber, M. Vural, M. Mestrovic, A. Carrasco-Sant, J. Breda, N. Berdzuli, M. Petroillo-Mantovani, The importance of continuing breastfeeding during coronavirus disease-2019: in support of the world health organization statement on breastfeeding during the pandemic, J. Pediatr. 223 (2020) 234–236.

[2] N. Fatima, K.S. Karimov, T.A. Qasuria, M.A. Ibrahim, A novel and stable way for energy harvesting from Bi2Te3Se alloy based semitransparent photothermoelectric module, J. Alloy. Compd. 849 (2020), 156702.

[3] F. Güneș, A. Aykaç, M. Erol, G. Erdem, H. Hano, B. Uzunbayır, M. Şen, A. Erdem, Synthesis of hierarchical hetero-composite of graphene foam/α-Fe2O3 nanowires and its application on glucose biosensors, J. Alloy. Compd. (2021), 162688.

[4] S. Ahmed, F.S.A. Khan, N.M. Mubarak, M. Khalid, Y.H. Tan, S.A. Mazzei, R.R. Karr, E.C. Abdullah, Emerging pollutants and their removal using visible-light responsive photocatalysis-A comprehensive review, J. Environ. Eng. 8 (2020), 104416.

[5] M.A.U. Oloa, J.F. Bueno, A.X.M. Perez, Sampling and surface properties of semiconductors correlated to photocatalysis and photoelectrochemistry applied to organic pollutants - a review, J. Environ. Eng. 9 (2021), 106480.

[6] H.T. Xu, Z. Hao, W.H. Feng, T. Wang, Y. Li, Mechanism of photodegradation of organic pollutants in seawater by TiO2-based photocatalysts and improvement in their performance, ACS Omega 6 (2021) 30698–30707.

[7] A. Popa, D. Toloman, M. Stefan, A. Petran, S. Macavei, S. Ulinici, M. Stan, L. Barbu-Tudoran, M.V.O. Pana, Hybrid PVDF-P(L-DOPA)-ZnO membranes for dyes and antibiotics removal through simultaneous action of adsorption and photocatalysis processes, J. Environ. Eng. 9 (2021), 106812.

[8] Y.D. Wu, N. Luo, R.S. Xie, Roldike Cadmium-incorporated zinc tungstate nanoarchitecture fabricated by a facile and template-free strategy as a photocatalyst for the effective degradation of organic pollutants in sewage, ACS Omega 5 (2020) 24318–24328.

[9] M.L. Tong, D.R. Sun, R.R. Zhang, H. Liu, R.F. Chen, Preparation of Si–α-Fe2O3/GDS composites with enhanced visible-light photocatalytic activity for p-nitrophenol degradation, J. Alloy. Compd. 862 (2021), 158271.

[10] Z.P. Li, H.B. Cheng, Y.F. Li, W. Zhang, Y. Yu, H2O2 treated GDS with enhanced activity and improved stability by a weak negative bias for CO2 photocatalytic reduction, ACS Sustain. Chem. Eng. 7 (2019) 4325–4334.

[11] M. Barroso, A.J. Cowan, S.R. Pendlebury, M. Gratzel, D.R. Khug, J.R. Durrant, The role of cobalt phosphate in enhancing the photocatalytic activity of α–Fe2O3 toward water oxidation, J. Am. Chem. Soc. 133 (2011) 14868–14871.

[12] F. Achouri, M. Corbel, A. Aboulaich, L. Balan, A. Ghrabi, M.B. Said, R. Schneider, Aqueous synthesis and enhanced photocatalytic activity of ZnO/Fe2O3 heterostructures, J. Phys. Chem. Solids 75 (2014) 1081–1087.

[13] Z.Y. Liu, S. Lu, J.G. Wu, T. Fang, R. Cai, A. Wei, Preparation and photocatalytic activity of ZnO/Fe2O3 nanotube composites, Mater. Sci. Eng. B 194 (2015) 9–13.

[14] F.S. Hashim, A.F. Alkaim, S.M. Mahdi, A.H.O. Alkhayatt, Photocatalytic degradation of GRL dye from aqueous solutions in the presence of ZnO/Fe2O3 nanocomposites, Compos. Commun 16 (2019) 111–116.

[15] Y. Li, K.L. Liu, J.N. Zhang, J.D. Yang, Y.C. Huang, Y.X. Tong, Engineering the band-edge of Fe2O3/ZnO nanolamates via separate dual cation incorporation for efficient photocatalytic performance, Ind. Eng. Chem. Res. 59 (2020) 18865–18872.

[16] H. Tang, D. Zhang, G.G. Tang, X.R. Jia, W.L. Lia, C.S. Li, X.F. Yang, Hydrothermal synthesis and visible-light photocatalytic activity of α–Fe2O3/TiO2 composite hollow microspheres, Ceram. Int. 39 (2013) 8633–8640.

[17] R. Rajendran, S. Vignesh, V. Raj, B. Palanivel, A.M. Ali, M.A. Sayed, M. Shkir, Designing of TiO2/α–Fe2O3 coupled g-C3N4 magnetic heterostructure composite for efficient Z-scheme photo-degradation process under visible light exposures, J. Alloy. Compd. 894 (2022), 162498.
G.L. Xu, M.L. Du, J.B. Zhang, T. Li, Y.P. Guan, C. Guo, Facile fabrication of magnetically recyclable FeO\textsubscript{4}/BiVO\textsubscript{4}/Cu\textsubscript{5} heterojunction photocatalyst for boosting simultaneous Cr(VI) reduction and methylene blue degradation under visible light, J. Alloy. Compd. 895 (2022), 162631.

J. Li, Q. Pei, R.Y. Wang, Y. Zhou, Z.M. Zhang, Q.Q. Cao, D.H. Wang, W.B. Mi, Y. Wi Du, Enhanced photocatalytic performance through magnetic field boosting carrier transport, ACS Nano 12 (2018) 3531–3539.

Y. Wang, S.L. Wang, Y.B. Wu, Z.N. Wang, H.H. Zhang, Z.S. Cao, J. He, W. Li, Z. C. Yang, L.G. Zheng, D.Q. Peng, P. Pan, J.L. Bi, H.Y. Li, J.S. Zhao, K.L. Zhang, A α-Fe\textsubscript{2}O\textsubscript{3}-rGO magnetic photocatalyst: enhanced photocatalytic performance regulated by magnetic field, J. Alloy. Compd. 851 (2020), 156733.

A.M. Huizar-Félix, C. Aguilar-Flores, A.M. Cruz, J.M. Barandiarán, S. Sepúlveda-Guzman, R. Cruz-Silva, Removal of tetracycline pollutants by adsorption and magnetic separation using reduced graphene oxide decorated with α-FeO\textsubscript{4} nanoparticles, Nanomaterials 9 (2019), https://doi.org/10.3390/nano9030313.

Z. Huang, J. Chen, Y. Jia, H. Liu, C. Xia, H. Liu, Selective hydrogenolysis of xylitol to ethylene glycol and propylene glycol over copper catalysts, Appl. Catal. B-Environ. 147 (2014) 377–386.

K.V. Bineesh, D.K. Kim, D.W. Park, Synthesis and characterization of zirconium-doped mesoporous nano-crystalline TiO\textsubscript{2}, Nanoscale 2 (2010) 1222–1228.

J.A. Toledo, M.A. Valenzuela, F. Bosch, H. Armendariz, A. Montoya, N. Nava, A. Vázquez, Effect of Al\textsuperscript{3+} introduction into hydrothermally prepared ZnFeO\textsubscript{4}, Appl. Catal. A-Gen. 198 (2000) 235–246.

P.K. Siwach, P. Srivastava, J. Singh, H.K. Singh, O.N. Srivastava, Broad temperature range low field magnetoresistance in La\textsubscript{0.5}Ca\textsubscript{0.5}MnO\textsubscript{3}–nano-ZnO Composites, J. Alloy. Compd. 481 (2009) 17–21.

P. Dominik, M. Kaupenjohann, Reduction of Fe(III) (Hydr)oxides with known thermodynamic stability by geobacter metallireducens, Geomicrobiol. J. 21 (2004) 287–295.

G.L. Chen, L.Y. Yang, J. Chen, T. Miki, S.W. Li, H. Bai, T. Nagasaka, Competitive mechanism and influencing factors for the simultaneous removal of Cr(III) and Zn (II) in acidic aqueous solutions using steel slag: batch and column experiments, J. Clean. Prod. 230 (2019) 69–79.

J. Zhang, X.H. Liu, L.W. Wang, T.L. Yang, X.Z. Guo, S.H. Wu, S.R. Wang, S. M. Zhang, Synthesis and gas sensing properties of α-Fe\textsubscript{2}O\textsubscript{3}@ZnO core–shell nanospindles, Nanotechnology 22 (2011), 185501.

Y. Pang, X. Zhou, E. Vovk, C. Guana, S. Li, A. van Bavel, Y. Yang, Understanding lanthanum oxide surface structure by DFT simulation of oxygen \textsuperscript{18}O-calibrated binding energy in XPS after in situ treatment, Appl. Surf. Sci. 548 (2021), 149214.

S.J. Song, K. Wu, H.D. Wu, J. Guo, L.F. Zhang, Multi-sheeted ZnO decorated with nitrogen and phosphorus Co-doped carbon quantum dots: synthesis and enhanced photodegradation activity of Methylene Blue in aqueous solutions, RSC Adv. 9 (2019) 7362–7374.

D. Sarkar, K.S. Palival, S. Ganguli, A.E. Praveen, D. Saha, V. Mahalingam, Engineering of oxygen vacancy as defect sites in silicates for removal of diverse organic pollutants and enhanced aromatic alcohol oxidation, J. Environ. Eng. 9 (2021), 105134.

Y.J. He, H.L. Lv, X.Y. Tang, Q.W. Song, Y.M. Zhang, C. Han, T. Guo, X.N. He, Y. M. Zhang, Y.M. Zhang, Ohmic contacts simultaneously formed on n-type and p-type 4H-SiC at low temperature, J. Alloy. Compd. 805 (2019) 999–1003.

S.J. Song, K. Wu, H.D. Wu, J. Guo, L.F. Zhang, Multi-sheeted ZnO decorated with nitrogen and phosphorus Co-doped carbon quantum dots: synthesis and enhanced photodegradation activity of Methylene Blue in aqueous solutions, RSC Adv. 9 (2019) 7362–7374.

D.H. Wang, Enhanced photocatalytic performance through magnetic field boosting simultaneous Cr(VI) reduction and methylene blue degradation under visible light, J. Alloy. Compd. 895 (2022), 162631.

J. Zhang, X.H. Liu, L.W. Wang, T.L. Yang, X.Z. Guo, S.H. Wu, S.R. Wang, S. M. Zhang, Synthesis and gas sensing properties of α-Fe\textsubscript{2}O\textsubscript{3}@ZnO core–shell nanospindles, Nanotechnology 22 (2011), 185501.