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Influence of mass ratio and calcination temperature on the physical and photoelectrochemical properties of ZnFe-layered double oxide/cobalt oxide heterojunction semiconductor for dye degradation applications

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Abstract

A visible light-active photoelectrocatalyst, ZnFe-layered double oxide (LDO)/cobalt(II,III) oxide (Co₃O₄) composites were obtained by calcining the Co loaded ZnFe-layered double hydroxide (LDH) prepared by a hydrothermal and microwave hydrothermal method. The morphological studies revealed that the ZnFe-LDO/Co₃O₄ composites exhibited a flower-like structure comprising Co₃O₄ nanowires and ZnFe-LDO nanosheets. Further, when the mass ratio of Co(NO₃)₂·6H₂O/LDH was 1:1.8 and the calcination temperature was 550 °C, the ZnFe-LDO/Co₃O₄ composite exhibited 93.3% degradation efficiency for methylene blue (MB) at the applied voltage of 1.0 V under visible light after 3 h. Furthermore, the Mott-Schottky model experiments showed that the formation of a p-n heterojunction between ZnFe-LDO and Co₃O₄ could effectively inhibit the recombination of electrons and holes in the photoelectrocatalytic process. Meanwhile, free radical scavenging experiments showed that the active radicals of •OH played an important role in the degradation of MB. Therefore, the photoelectrocatalytic effect of ZnFe-LDO/Co₃O₄ provides a simple and effective strategy for the removal of organic pollutants.

Keywords: ZnFe-LDO/Co₃O₄, Photoelectrocatalytic, p-n heterojunction, Methylene blue.

1. Introduction

With the progress of science and technology and the rapid development of the economy, human beings' living standards have been greatly improved (Chen et al., 2021; Gao et al., 2022; Hou et al., 2022; Jing et al., 2022b; Pan et al. 2022; Shao et al., 2022; Su et al. 2021; Su et al. 2022; Xie et al. 2022; Yu et al. 2022; Zhao et al. 2022a; Zhao et al. 2022b; Zhao et al., 2022c). Thus, energy shortage and environmental pollution have become important problems that human beings must face (Ahmadi et al., 2021; Ma et al., 2014; Ouyang et al., 2022; Shi et al., 2017; Si et al., 2022; Yin et al., 2021; Zhang et al. 2022). Methylene blue (MB) is one of the typical organic pollutants in wastewater treatment. As a reactive cationic dye, it has a high loss rate in industrial production, and the generated wastewater can easily cause water pollution (Zhao, Ge et al., 2019; Jing et al., 2022a). Although the treatment of organic dyes in industrial wastewater has attracted much attention, it is still important for researchers to remove them efficiently (Kim, Durand, André, & Carteret, 2017; S. Ma, Zhan, Jia, & Zhou, 2015; Sun et al. 2022;).

At present, the removal of dye from wastewater includes physical adsorption, biodegradation, catalysis, etc(Bhatti et al., 2020). Owing to the merits of simple operation, wide source of adsorption materials, low price, and reusability, the adsorption method has attracted extensive research interest and has been widely adopted for practical application (Guo et al. 2021; Li, He et al 2021; Sun, Qu, et al. 2021; Wang, Xie, et al. 2020; Wang, Yuan et al 2022). However, the adsorption method could not degrade the pollutants, and the pollutant removal efficiency is limited by the adsorption capacity. The biodegradation method uses microorganisms to treat organic pollutants, which is safe, convenient, non-toxic, and does not produce secondary pollution, but the method suffers from high energy costs. In recent years, photocatalysis and photoelectrocatalytic have become important technologies for the degradation of organic dye in wastewater. As an emerging, green and environmentally friendly catalytic technology, it is widely used due to its low cost and high efficiency (Li, Yan, & Zhu, 2021; Zhao, Ge et al., 2019).

In recent years, semiconductor photocatalysis has shown great potential in degrading organic pollutants in wastewater (He et al., 2020; Wu et al., 2018; Zhu et al., 2009). In the photocatalytic

process, the photogenerated electrons and holes react with the reactants on the surface of the photocatalyst to achieve the purpose of degrading pollutants (Lei et al., 2019; Li et al., 2017). However, the recombination of photogenerated electrons and holes and the recovery and reuse of photocatalyst are often important problems for researchers (Chen & Lin, 2014; Schneider et al., 2014; Wang, Shi, Lin, & Zhu, 2011). Photoelectrocatalysis has gradually become a hot topic, in which the photocatalytic and electrocatalytic processes synergistically offer the advantages of high efficiency and environmental protection (Garcia-Segura & Brillas, 2017; Georgieva et al., 2012; Zhang, Chen, & Bahnemann, 2009). For example, Chatchai et al.(Chatchai, Nosaka, & Nosaka, 2013) synthesized WO₃/BiVO₄ photo-anode by the electrodeposition technique, and demonstrated that the composite material showed a high performance for MB degradation under the photoelectrocatalytic process. Li et al (Li, Zhang et al., 2019) prepared graphene oxide and TiO₂ using the hydrothermal method, the photoelectrocatalytic process exhibited the synergistic effect, in which the degradation rate of MB by photoelectrocatalytic treatment was higher than the summary of photocatalytic and electrocatalysis treatment.

Among various reported materials, layered double hydroxides (LDHs) have attracted wide attention in recent years due to their tunable chemical composition and multifunctional properties as catalysts and catalyst support (Karami et al., 2021; Mendoza-Damian, Tzompantzi, Mantilla, Barrera, & Lartundo-Rojas, 2013; Rashki et al., 2021). Layered materials are classified according to their different uses, including thermoelectric materials, supercapacitors and amphoteric metals (Abdulhusain, Alshamsi, & Salavati-Niasari, 2021; Fan, Li, Evans, & Duan, 2014; Huang et al., 2013). Furthermore, the calcination of LDH materials at different temperatures results in layered double oxides (LDO) nanocomposites with thermal stability and high surface area (Uddin et al., 2012; Yang et al., 2017), which can promote the transfer of photoelectrons under visible light conditions to the catalyst surface and enhance photocatalytic degradation. It is reported that constructing a heterostructure between two semiconductor materials can increase the separation rate of photoexcited electrons and holes and inhibit their recombination. According to the conductivity type of the heterojunction, the heterojunction can be divided into inversion

heterojunction (p-n) and homotype heterojunction (n-n, p-p) (Lee, Hwang, & Chung, 2015). It is thus desirable to couple LDO with another semiconductor with a narrower band gap to achieve absorption of visible light. It is reported that Co₃O₄ is a p-type semiconductor with a narrow band gap and has been widely used as an electrocatalyst for water oxidation applications(Xi et al., 2012; Yang, Cheng, & Cheng, 2019). Therefore, fabrication of LDO/Co₃O₄ can utilize the wide-range light absorption of narrow-band gap semiconductors and the rapid separation of light-induced carriers induced by the built-in electric field, thereby inhibiting the recombination of electrons and holes and improving its photocatalytic activity(Cerron-Calle, Aranda-Aguirre, Luyo, Garcia-Segura, & Alarcon, 2019; Li, Salvador, & Rohrer, 2014; Liao et al., 2021; Liu, Yin et al., 2020). However, the preparation of ZnFe-LDO/Co₃O₄ composites with excellent photoelectrocatalytic performance has rarely been reported.

In this work, by using urea as a homogeneous precipitant, Co loaded ZnFe-LDH was prepared via hydrothermal and microwave hydrothermal methods, and then calcined under air atmosphere to obtain ZnFe-LDO/Co₃O₄ heterojunction, which was coated on nickel foam to make a photoelectrode, and the photoelectrocatalytic properties of the samples were detected by performing degradation experiments of MB in aqueous solution under visible light irradiation and 0.7 V applied voltage. The microwave hydrothermal method shortens the reaction time and avoids caking during the reaction. Due to the p-n heterojunction between ZnFe-LDO and Co₃O₄ and the applying a bias voltage, ZnFe-LDO/Co₃O₄ enhanced the separation of photogenerated electrons and holes, and thereby improved the photoelectrocatalytic degradation of MB in wastewater. Furthermore, the degradation mechanism of the composite catalyst was further investigated by Mott-Schottky and radical capture experiments.

2. Experimental

2.1 Catalyst preparation

2.1.1. Preparation of ZnFe-LDH precursors

The ZnFe-LDH precursor was synthesized by the microwave hydrothermal method. The specific preparation method was as follows. First of all, 2.38 g of Zn(NO₃)₂·6H₂O, 1.62 g of

Fe(NO₃)₃·9H₂O and 3.5 g of urea were dissolved in 40 mL of deionized water. Then the mixture was refluxed at a temperature of 90 °C for 4 h to obtain ZnFe-LDH precursor solution. After cooling the mixture to room temperature, 4 ml of precursor solution and 60 mL of deionized water were poured into a teflon reactor and then heated at 150 °C for 2 h in the microwave hydrothermal parallel synthesizer (XH-800S, Beijing XiangHu Science and Technology Development Co., Ltd, China). Upon completion of the reaction, the resulted red-brown precipitate was centrifuged and washed with deionized water until its pH reaches 7, and then dried in an oven at 70 °C for 12 h.

2.1.2. Preparation of ZnFe-LDO/Co₃O₄

The ZF-LDO/Co₃O₄ was obtained by using a mixed solvothermal strategy (Wang et al., 2014). In a typical process, the Co(NO₃)₂·6H₂O(0.44 g) and urea(0.36 g) were dissolved in a 40 mL mixed solvent of deionized water and ethanol (V_{deionized water}: V_{ethanol} = 1: 1) to form a pink solution. The mass of the LDH was fixed to 1.5 g, then added to a different volume (20 mL, 25 mL, 30 mL, 40 mL) of pink solution, the mass ratio of Co(NO₃)₂·6H₂O/LDH could be obtained as 1:1.5, 1:1.8, 1:2.2, 1:3.0, respectively. Then, the solution was poured into a teflon reactor and transferred to an oven at 90 °C for 8 h. After the reaction, the composite was centrifuged and washed several times with deionized water and dried at 60 °C. Further, to investigate the effect of calcination temperature, the prepared composites were calcined at 500 °C, 550 °C, 600 °C, and 650 °C in a muffle furnace for 2 h in air at a heating rate of 5 °C / min. These samples were denoted as ZnFe-LDO/Co₃O₄-n(M), where n=1, 2, 3, 4 represents the mass ratio of 1:1.5, 1:1.8, 1:2.2, 1:3.0, respectively, and M represents the calcination temperature. For example, the composite obtained by adding 1.5 g ZnFe-LDHs to a pink solution of 25 mL and calcined at a temperature of 550 °C was labeled as ZF-LDO/Co₃O₄-2(550).

2.2 Photoelectrocatalytic performance test

The PEC performance was investigated by using the electrochemical workstation (Autolab, Metrohm Co. Ltd.) in a three-electrode cell system with the light irradiation of a xenon lamp. 30 mg of catalyst was coated on nickel foam, the platinum (Pt) wire, calomel electrode, and 0.1 mol/L Na₂SO₄ solutions were used as the working electrode, counter electrode, reference electrode and

electrolyte, respectively. Firstly, the as-prepared ZF-LDO/Co₃O₄ photoelectrode was placed in 100 mL of 20 mg/L MB (Dissolved 20 mg of methylene blue trihydrate in a beaker with a small amount of distilled water, then poured it into a 1000 mL volumetric flask, rinsed the beaker with distilled water and poured it into the volumetric flask, finally added distilled water to dilute to the mark and shook well) and for 1 h in the dark to achieve adsorption/desorption equilibrium. During the reaction period, 3 mL of the reaction solution were taken every 30 min and centrifuged quickly for 3 min. The absorbance of the MB solution at a wavelength of 664 nm was measured by UV-vis (UV-9000, Metash, China) spectrophotometer to determine the concentration of MB in the solution.

3. Results and discussion

3.1 Influence of mass ratios of metal ions

Different mass ratios of metal ions influence the performance of the composite material. Hence, ZnFe-LDO/Co₃O₄ composites with different Co(NO₃)₂·6H₂O/LDH mass ratios are prepared under identical reaction conditions (calcination temperatures: 550 °C). Fig. 1A shows the X-ray diffraction (XRD) patterns of ZnFe-LDH, ZnFe-LDO and Co₃O₄. The diffraction peaks at $2\theta = 12.8^{\circ}$, 23.4°, 33.1°, and 35.5°, correspond to (003), (006), (009), and (015) crystal planes of LDH, displaying well crystallized hydrotalcite-like LDH materials(Tao, Liu, Cong, & Huang, 2018). For the ZnFe-LDO, the characteristic peaks of ZnFe-LDH disappeared and new diffraction peaks appeared. The diffraction peaks at 29.92°, 35.26°, 42.84° and 53.11° could be indexed to the (220), (311), (400) and (422) planes of ZnFe₂O₄ (JCPDS, no. 22-1012). The diffraction peaks at 31.77°, 34.42°, 36.25°, 47.54°, 56.60°, 62.86° and 69.10° could be indexed to the (100), (002), (101), (102), (110), (103) and (112) planes of the hexagonal wurtzite ZnO (JCPDS, no. 36-1451)(Di et al., 2017; Li, Yu et al., 2019). For Co₃O₄, the diffraction peaks at 19.1°, 31.3°, 36.9°, 44.7°, 59.4° and 65.4° correspond to the (111), (220), (311), (400), (511) and (440) planes of cubic Co₃O₄(JCPDS, no. 42-1467), respectively(Wang, Wan, Zhao, Yang, & Wang, 2019).



Fig. 1. XRD patterns of ZF-LDH, ZF-LDO and Co₃O₄ (A), XRD patterns (B), (C) and PEC performance for MB (D) of the ZF-LDO/Co₃O₄ with different mass ratios.

The XRD patterns of ZF-LDO/Co₃O₄ with different mass ratios are shown in Fig. 1B and the diffraction peaks between $29^{\circ}-39^{\circ}$ are shown in Fig. 1C. It is obvious that there are ZF-LDO and Co₃O₄ diffraction peaks in the ZF-LDO/Co₃O₄, which indicates that the formation ZF-LDO/Co₃O₄ composites. With the increase of Co(NO₃)₂·6H₂O/LDH mass ratio, the diffraction peak intensity of Co₃O₄ gradually increases, while the diffraction peak intensity of ZnO and ZnFe₂O₄ first increases and then weakens. When the mass ratio of Co(NO₃)₂·6H₂O/LDH is 1:1.8, the diffraction peak intensities of Co₃O₄, ZnO and ZnFe₂O₄ in the obtained samples are all high and narrow. The photoelectrocatalytic (PEC) activity with respect to mass ratio was shown in Fig 1D. After stirring for 1 h in the dark, MB reached the adsorption-desorption equilibrium on the photocatalyst to

eliminate the effect of photocatalyst adsorption, and the concentration after adsorption for 1 h was taken as the new initial concentration for photoelectrocatalysis. The PEC performance of ZF-LDO/Co₃O₄-2 initially increases and thereafter decreases with increasing the mass ratio of $Co(NO_3)_2 \cdot 6H_2O/LDH$. The removal rate of MB by ZF-LDO/Co₃O₄-2 is the highest (86.6%). At the same time, the PEC performances of ZF-LDO/Co₃O₄-2 are significantly better than that of ZF-LDO/Co₃O₄-1, ZF-LDO/Co₃O₄-3 and ZF-LDO/Co₃O₄-4. Therefore, the prepared sample with the mass ratio of 1:1.8, exhibits better crystallinity and PEC performance.



3.1 Influence of calcination temperature

Fig. 2. XRD patterns (A), (B) of (a) ZF-LDO/Co₃O₄-2(500), (b) ZF-LDO/Co₃O₄-2(550), (c) ZF-LDO/Co₃O₄-2(600), and (d) ZF-LDO/Co₃O₄-2(650).

The calcination temperature will affect the crystallinity and structure of the sample, therefore, the ZF-LDO/Co₃O₄-2 was calcined at different temperatures. Fig. 2A shows the XRD patterns of ZF-LDO/Co₃O₄-2 obtained at different calcination temperatures and Fig. 2B shows the diffraction peaks between 29°-39°. The results show that the intensity of the diffraction peaks of ZF-LDO/Co₃O₄-2 increases first and then decreases with the increase of calcination temperature. At 550 °C, the diffraction peak intensity of ZF-LDO/Co₃O₄-2 is stronger, indicating that the crystallinity of ZF-LDO/Co₃O₄-2(550) is higher.



Fig. 3. SEM images of ZF-LDO/Co₃O₄-2(500) (A, B), ZF-LDO/Co₃O₄-2(550) (C, D), ZF-LDO/Co₃O₄-2(600) (E, F), and ZF-LDO/Co₃O₄-2(650) (G, H).

The calcination temperature affects the morphology of the prepared samples. Fig. S1 and Fig. 3 show the SEM images of the as-obtained Co₃O₄, ZF-LDO and ZF-LDO/Co₃O₄-2 at different calcination temperatures. As shown in Figs. S1A and B, Co₃O₄ consists of a floral structure comprises of nanorods, and the ZF-LDO is made up of flower-like structures formed by the accumulation of porous sheets. Figs. 3A-H show the morphology of the composites synthesized at different calcination temperatures. It is observed that the Co₃O₄ nanorods are uniformly loaded on the surface of the ZF-LDO nanosheets. With the increase of calcination temperature, the composites become more agglomerated, thereby deteriorating the morphology of nanowires and nanosheets. Therefore, the ZF-LDO/Co₃O₄-2 calcinated at 550 °C has a better morphology with no agglomeration.

Furthermore, the influence of calcination temperatures on the specific surface area of the sample was explored. Fig. 4 shows the N₂ adsorption-desorption isotherms of ZF-LDO/Co₃O₄ obtained at different calcination temperatures. The adsorption-desorption isotherm curves of the as-prepared samples belong to the type IV isotherm according to the IUPAC classification(Sun et al., 2020; Zhao, Ge et al., 2019). The specific surface areas, pore diameter data and pore volume of all samples are given in Table 1. The pore-size distribution diagram reveals that the samples are mainly mesoporous. The pore diameter of ZF-LDO/Co₃O₄-2(550) (6.25 nm) is larger than other samples. It can be seen that ZF-LDO/Co₃O₄-2(550) has the largest specific surface area (19.37 m²/g) and pore volume (0.030 cm³/g) compared to other samples. On the basis of SEM and N₂ adsorption-desorption analysis, it is concluded that at calcination temperatures higher 550 °C, the morphology of ZF-LDO/Co₃O₄ becomes more agglomerated, which leads to the specific surface being reduced. Therefore, ZF-LDO/Co₃O₄-2(550) can provide more active sites, thereby supporting better photoelectrochemical performance.



Fig. 4. N_2 adsorption-desorption isotherms and pore size distribution curve of samples: ZF-LDO/Co₃O₄-2(500) (A), ZF-LDO/Co₃O₄-2(550) (B), ZF-LDO/Co₃O₄-2(600) (C), and ZF-LDO/Co₃O₄-2(650) (D).

 Table 1 Specific surface area, pore diameter date and pore volume of samples.

Samples	$S_{BET} \left(m^2 \left/g\right)$	Pore diameter (nm)	Pore volume (cm^3/g)
ZF-LDO/Co ₃ O ₄ -2(500)	16.03	5.47	0.022
ZF-LDO/Co ₃ O ₄ -2(550)	19.37	6.25	0.030
ZF-LDO/Co ₃ O ₄ -2(600)	14.02	5.48	0.019
ZF-LDO/Co ₃ O ₄ -2(650)	11.21	5.14	0.014

To examine the catalytic performance of the as-prepared catalysts, the PEC degradation of the MB by ZF-LDO/Co₃O₄-2 with different calcination temperatures at an applied voltage of 0.7 V is shown in Fig. 5. The PEC performance of ZF-LDO/Co₃O₄-2 increases with the increase of

the calcination temperature up to 550 °C and then decreases. The PEC performance of ZF-LDO/Co₃O₄-2(500), ZF-LDO/Co₃O₄-2(550), ZF-LDO/Co₃O₄-2(600), and ZF-LDO/Co₃O₄-2(650) is 83.6%, 86.6%, 79.6%, and 75.3%, respectively. From XRD, SEM and BET results, it can be concluded that the calcination temperature affects the crystal structure and specific surface area of the sample, which in turn affect the catalytic activity of the sample (Zhu et al., 2016). These results show that 550 °C is the optimum calcination temperature to obtain better crystallinity and higher PEC performance.



Fig. 5. PEC performance for MB of the ZF-LDO/Co₃O₄-2 with different calcination temperature.

3.3 Characterization of the products

The microstructure and morphology of the as-prepared ZF-LDO/Co₃O₄-2(550) is investigated further by the transmission electron microscopy (TEM). Fig. 6A depicts that the composite is composed of irregular nanoparticles with a particle size of about 50 nm. The lattice spacing (Fig. 6B) of 0.263, 0.292, and 0.238nm coincides with ZnO (002) (Liu, Shao et al., 2020), ZnFe₂O₄ (111) (Chen et al., 2016), and Co₃O₄ (220) (Pan et al., 2018b) planes, respectively, which is consistent with the XRD results. The corresponding elemental mapping and EDS spectra results of elements O, Fe, Zn, and Co for the ZF-LDO/Co₃O₄-2(550) are shown in Figs. 6C-H. It can be clearly observed that all the elements of O, Fe, Zn, and Co are uniformly distributed in ZF-



LDO/Co₃O₄-2(550), further proving the formation of the ZF-LDO/Co₃O₄-2(550) composite.

Fig. 6. Low magnification TEM images (A) and HRTEM images (B), SEM image (C), elemental mapping (D~G), and EDS measurement (H) of the plotted area of ZF-LDO/Co₃O₄-2(550).



Fig. 7. XPS spectra of ZF-LDO/Co₃O₄-2(550): survey spectrum (A) and high-resolution XPS spectra of Zn 2p (B), Fe 2p (C), Co 2p (D), and O 1s (E).

The chemical composition and elemental valence states of the as-prepared samples were investigated by XPS. The survey spectrum (Fig. 7A) shows the presence of Zn, Fe, Co and O, in ZF-LDO/Co₃O₄-2(550). Fig. 7B shows the binding energies correspond to Zn $2p_{1/2}$ and Zn $2p_{3/2}$ at

1045.4 eV and 1022.1 eV, respectively, indicating the characteristic of Zn^{2+} (Liu, Zhai, Hu, Yang, & Liu, 2017). The binding energies at 726.4 eV and 713.5 eV along with their shake-up satellite peak at 719.2 eV are assigned to Fe $2p_{1/2}$ and Fe $2p_{3/2}$ (Fig. 7C), respectively, which implies the oxidation state of Fe³⁺ (Hou et al., 2016). As depicted in Fig. 7D, the Co 2p fits with two spin doublets characteristic of Co³⁺, Co²⁺. The peaks at 782.7 eV (Co $2p_{3/2}$) and 797.3 eV (Co $2p_{1/2}$) are attributed to Co³⁺ species. Meanwhile, the peaks at 784.1 eV (Co $2p_{3/2}$) and 799.4eV (Co $2p_{1/2}$) are attributed to Co²⁺ species (Tiruneh et al., 2018). The high-resolution XPS spectrum of the O 1s (Fig. 7F) can be deconvoluted into three peaks at 530.6, 532.3, and 533.7 eV, which are related to the lattice oxygen, oxygen vacancy (V₀) and molecular water (H₂O) species, respectively(Sun et al., 2020). Due to the existence of V₀, the O₂ can be converted into •O₂⁻ more easily.

3.4 Optical and electrical properties

In order to detect the optical properties of the prepared samples, the UV–Vis diffuse reflectance of ZF-LDO, the visible light response range of ZF-LDO/Co₃O₄ extends from 650nm to 800nm, which can be attributed to the light absorption of Co₃O₄. At the same time, the light absorption intensity of the ZF-LDO/Co₃O₄-2(550) sample is higher than that of other composite samples. The band gap (E_g) of the as-prepared samples are calculated using equation (1) (Eq (1))(Yang et al., 2019):

$$\left(ahv\right)^{\frac{n}{2}} = k\left(hv - E_g\right) \tag{1}$$

where α , hv, K and E_g represent the absorption coefficient, photon energy, proportionality constant and band gap, and n is equal to 1 or 2 for an indirect or direct bandgap semiconductor respectively(Wang et al., 2020; Zhang, Han, Yu, Zou, & Dong, 2019). Because ZnFe-LDO and Co₃O₄ are direct bandgap semiconductors, the corresponding band gaps are shown in Fig. 8B. The band gaps of ZF-LDO/Co₃O₄-2 (500) (1.81eV), ZF-LDO/Co₃O₄-2(550) (1.79 eV), ZF-LDO/Co₃O₄-2(600) (1.86 eV) and ZF-LDO/Co₃O₄-2(650) (1.92 eV) composites are obviously smaller than that of pure ZF-LDO (2.15eV). This shows that the composite material has a strong ability to absorb visible light, which is beneficial to the degradation of MB under the irradiation of visible light.



Fig. 8. UV–vis diffuse reflectance spectra (A), the plotting of $(ahv)^2$ vs. *hv* based on the direct transition (B), PL spectra (C), Nyquist plots (D) and transient photocurrent spectra (E) of the samples.

The charge separation behaviour of the as-prepared catalyst is investigated by recording photoluminescence (PL) spectra, the transient photocurrent spectra and electrochemical impedance spectra (EIS) for the as-prepared composites. It is well known that the intensity of the

photoluminescence emission spectrum depends on the recombination of electron-hole pairs generated by light(Zhao et al., 2016). The catalytic performance of the sample will be higher for the samples with a lower electron-hole pair recombination rate. As shown in Fig. 8C, the ZF-LDO/Co₃O₄-2(550) composite has the lowest fluorescence intensity, indicating that it has better photogenerated electron-hole pair generation and charge transfer efficiency. As shown in Fig. 8D and E, compared with other composites, the ZF-LDO/Co₃O₄-2(550) has the smallest arc radius and the highest photocurrent density, indicating that the photoelectrode has the lowest charge transfer resistance and the fastest electron mobility in the sample, which is beneficial to its PEC performance.

3.5 Catalytic activities



Fig. 9. The PEC (1.0 V), PC and the EC (1.0 V) degradations of MB over the ZF-LDO/Co₃O₄-2(550) electrode (A), effect of bias voltage on MB removal over the ZF-LDO/Co₃O₄-2(550) under PEC (B), the PEC degradation kinetic curves of ZF-LDO/Co₃O₄-2(550) electrode at different

applied voltages (C).

In order to explore the catalytic performance of the obtained catalyst, PC, EC and PEC degradation of MB were carried out with ZF-LDO/Co₃O₄-2(550). From Fig. 9A, it can be observed that the PEC degradation rate reaches 93.3%, which is significantly higher than that of PC (53.7%) plus EC (29.0%), showing a photoelectric synergy. This is because the applied voltage forces the photogenerated electrons to move towards the opposite electrode, thus reducing the probability of recombination and thereby improving the catalytic efficiency (Li, Li, Zheng, Xian, & Jin, 2006).

The PEC degradation of MB by ZF-LDO/Co₃O₄-2(550) as function of applied bias voltage is shown in Fig. 9B. It clearly depicts that the rate of MB removal gradually increases with the increase in the applied voltage. When the applied voltage is 1.2V, the degradation rate of MB reaches 100% within 2.5h. To further clarify the PEC degradation process, the PEC degradation kinetics of MB is shown in Fig. 8C. The kinetic equation (Eq. (2)) is given below:

$$\ln(C_0 / C) = kt \tag{2}$$

where C_0 is the initial concentration of MB, *C* is the concentration of MB at time *t*, *t* represents the reaction time, and *k* is the apparent first-order rate constant. The kinetic constant (*k*) and correlation coefficient (R^2) are displayed in Table 2. It can be found that ZF-LDO/Co₃O₄-2(550) exhibited higher kinetic constant and superior photocatalytic activity at the applied voltage of 1.2 V. **Table 2.** The kinetic constant k and correlation coefficient (R^2) the photodegradation of MB by ZF-LDO/Co₃O₄-2(550) under different applied voltages.

Applied voltage	K (h ⁻¹)	\mathbb{R}^2	Efficiency ^a (%)
0.5V	0.53	0.9973	79.4
0.7V	0.66	0.9979	86.6
1V	0.86	0.9928	93.3
1.2V	1.07	0.9861	100

^aThe degradation efficiency of MB under solar-simulated light irradiation for 3h.



Fig. 10. Reusability of PEC degradation of MB by ZF-LDO/Co₃O₄ under different applied voltages.

The reusability of ZF-LDO/Co₃O₄-2(550) was tested for the degradation of MB under different applied voltages. As shown in Fig 10, under different applied voltages, the ZF-LDO/Co₃O₄-2(550) can be cycled three times or more, and maintain good PEC performance, showing that ZF-LDO/Co₃O₄-2(550) has a good reusability. Furthermore, as shown in Fig. S2, the results of XRD, FT-IR, and XPS for ZF-LDO/Co₃O₄-2(550) after photocatalytic reaction show the superior stability of the sample (the detailed explanation is seen in the Structural stability section of the Supporting Information). In summary, under 1.0V applied voltages, ZF-LDO/Co₃O₄-2(550) can also be conveniently reused with a stable performance in MB degradation.

Furthermore, comparisons of the catalytic efficiency of several composites toward the

degradation of MB are listed in Table 3. It shows that the ZF-LDO/Co₃O₄ composite reported in this study has a superior photoelectrocatalysis effect.

Catalysts	Dosage	Dye	Catalytic	References
	(mg)	concentration	efficiency	
ZnO/Co ₃ O ₄	3mg	MB 4.5mg/L	Photocatalytic	(Rakibuddin, &
		150mL	90% after 5h	Ananthakrishnan, 2015)
ZnFe ₂ O ₄ /ZnO	50mg	MB 20mg/L,	Photocatalytic	(Rameshbabu, Kumar,
		100 mL	96% after 6h	Karthigeyan, &
				Neppolian, 2016)
ZnFe ₂ O ₄ @ZnO	10mg	MB 20mg/L	Photocatalytic	(Nam, Nam, Choi,
		20mL	97% after 2h	Park, & Jung, 2017)
F doped TiO ₂	0.2g	MB 10mg/L	Photoelectrocatalytic	(Liu, Tian et al., 2017)
		60mL	97.8% after 4h	
ZF-LDO/Co ₃ O ₄	30mg	MB 20mg/L	Photoelectrocatalytic	This work
		100mL	100% after 2.5h	

Table 3. Comparison of catalytic performance of similar catalysts.

3.6 PEC degradation mechanism

The flat-band potential (V_{fb}) and photocarrier concentration of the as-prepared catalysts are characterized by Mott-Schottky model experiments, to clarify the energy band structure of ZF-LDO/Co₃O₄-2(550) heterojunction. As shown in Figs. 11A and 11B, ZF-LDO shows two positive slopes and Co₃O₄ shows a negative slope, indicating that ZF-LDO and Co₃O₄ are n and p-type semiconductors, respectively. The flat band potential of ZF-LDO is estimated to be -0.69 V (vs Hg/Hg₂Cl₂), and that of Co₃O₄ is 0.32 V (vs Hg/Hg₂Cl₂), respectively. As shown in Fig. 11C, an inverted "v-shape" is shown in the Mott-Schottky diagram of ZF-LDO/Co₃O₄-2(550), indicating that the p-n heterojunction is formed between ZF-LDO and Co₃O₄(Fanke, Jiangtian, Cushing, Mingjia, & Nianqiang, 2013; Li et al., 2012). At the same time, the conduction band (CB) of the n-type semiconductor is about 0.2 V lower than V_{fb} (V_{fb} – 0.2 V), and the valence band of the p-type semiconductor is about 0.2 V higher than V_{fb} (V_{fb} + 0.2V)(Zou, et al., 2019). Based on E_{NHE} = E_{SCE} + 0.241V, the CB potential for ZF-LDO and VB potential for Co₃O₄ are calculated to be - 0.65 V and 0.76 V (vs NHE). Therefore, according to E_{CB} = E_{VB} – E_g, E_g was obtained by UV-Vis analysis (Figs. 7A and 7B), therefore, it can be calculated that the VB energies of the as-prepared ZF-LDO and CB energies of Co₃O₄ are 1.50V and -0.69V (vs NHE). The CB and VB of Co₃O₄

are higher than those of ZF-LDO, which belongs to the type II heterojunction(Du, Liu, Shen, & Xu, 2017). Therefore, under the action of the energy band difference of the two semiconductors, the separation of electron holes and PEC performance are promoted.



Fig. 11. Mott-Schottky plots of ZF-LDO (A), Co₃O₄ (B), ZF-LDO/Co₃O₄ -2(550) (C).

Active free radicals (e.g. •OH, $\bullet O_2^-$, h^+) produced in the process of photoelectrodegradation play an important role in the degradation process. Free radical scavenging experiments are conducted to determine which free radicals caused MB degradation. 1 mM isopropyl alcohol (IPA), P-benzoquinone, and EDTA-2Na were used as the scavenger of $\bullet OH$, $\bullet O_2^-$ and h^+ , respectively. As shown in Fig. 12, it is obvious that the addition of these three scavengers leads to the reduction of MB degradation efficiency compared with the absence of scavengers. After adding pbenzoquinone, IPA and EDTA-2Na, the degradation efficiency of MB decreased from 87.34% to 72.55%, and 40.56% respectively. The result reveals that $\bullet OH$ plays a leading role in the degradation of MB, while h^+ and $\bullet O_2^-$ play a secondary role.



Fig. 12. Effect of different scavengers on PEC degradation of MB.



Fig. 13. Schematic diagram of the PEC mechanism for MB by ZF-LDO/Co₃O₄-2(550) electrode. According to the results of Mott-Schottky model experiments and free radical scavenging experiments, the PEC degradation mechanism of MB on ZF-LDO/Co₃O₄-2(550) is determined (Fig. 13) and equations (3) to (8). Under visible light irradiation, e⁻ is transferred from VB to the CB, producing electron-hole (e⁻ – h⁺) (Eq. (3) and (4)). Electrons are transferred from the CB of

Co₃O₄ to the CB of ZF-LDO. Since the VB of ZF-LDO is higher than that of Co₃O₄, holes in the VB of ZF-LDO are transferred to the VB of Co₃O₄. At the same time, a p-n heterojunction formed between ZF-LDO and Co₃O₄ effectively enhances the electron migration and charge separation efficiency (Eq. (5)). When a bias voltage is applied, it helps the photogenerated electrons to move quickly to the counter electrode and thereby reducing the recombination of photogenerated electrons and holes. In particular, the presence of V₀ (Fig. 6E) can enhance the absorption of visible light, improving the catalytic performance. Meanwhile, the photogenerated e⁻ and h⁺ would convert H₂O and O₂ to •OH and •O₂⁻ (Eqs (6) and (7)). MB is degraded into other products due to the oxidizing properties of these active species (•OH, h⁺, and •O₂⁻) (Eq (8)).

)

)

$$ZF-LDO+hv \rightarrow e^{-}+h^{+}$$
(3)

$$\operatorname{Co}_3\operatorname{O}_4^+ \operatorname{hv} \to \operatorname{e}^- + \operatorname{h}^+$$
 (4)

$$p-ZF-LDO+n-Co_3O_4 \rightarrow e^- + h^+$$
 (5)

$$h^{+} + H_2 O \rightarrow \cdot O H + H^{+}$$
 (6)

$$O_2 + e^- \rightarrow O_2^- \tag{7}$$

$$\begin{pmatrix} h^{+} \\ \cdot OH \\ \cdot O_{2}^{-} \end{pmatrix} + MB \rightarrow CO_{2} + H_{2}O + Other Products \qquad (8)$$

4. Conclusions

In summary, the ZF-LDO/Co₃O₄ composite photoelectrocatalyst was obtained by calcining the Co loaded ZF-LDH precursors prepared by hydrothermal and microwave hydrothermal methods. The physical and photoelectrocatalytic properties of the ZF-LDO/Co₃O₄ composite was tuned by varying the molar ratio between the Co and ZF-LDH as well as the calcination temperature. Meanwhile, increasing an applied voltage would also improve the photoelectrocatalytic performance of the ZF-LDO/Co₃O₄ composites. Moreover, the bandmatching and p-n heterojunction formed between ZF-LDO and Co₃O₄ effectively prevent the electron-hole recombination and improved the charge transport kinetics. When the mass ratio of Co(NO₃)₂·6H₂O /LDH was 1:1.8 and the calcination temperature was 550 °C, under the visiblelight irradiation and applied voltage of 1.0 V, the 20 mg/L ZF-LDO/Co₃O₄ degraded 93.3% of MB in 3h. Further, the ZF-LDO/Co₃O₄ photoelectrode can also be conveniently reused with a stable performance in MB degradation under 1.0 V applied voltages. Thus, this work provides a new strategy for improving the degradation of organic pollutants in simulated waste water, and has potential applications in photoelectrocatalytic degradation.

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