Fabrication of magnetic ZnO/ZnFe₂O₄/diatomite composites: improved photocatalytic efficiency under visible light irradiation

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ABSTRACT

The magnetic recoverable ZnO/ZnFe₂O₄/diatomite (ZZFDT) composite was synthesized by hydrothermal-precipitation method. The structure, optical properties and magnetic properties of the composites were characterized by different analytical instruments. ZZFDT-1 is composed of cubic spinel, hexagonal wurtzite, tetrahedron structure. SEM and TEM showed that ZnO and ZnFe₂O₄ particles were loaded onto the surface of diatomite, and the particle size was uniform. In addition, ZZFDT-1 is a typical mesoporous material with a specific surface area of 65.3 m²/g and pore size of about 12 nm. The response range of ZZFDT-1 is extended to visible light, and the band gap is 1.5 eV. Moreover, the M–H hysteric curves of ZZFDT-1 exhibited superparamagnetic properties. The photocatalytic activity of different samples was evaluated by the conversion rate of oxytetracycline (OTC) under visible light. ZZFDT-1 has the best photocatalytic activity and the conversion is up to 95%. Because of its magnetic nature, it can be easily separated from the solution. The results showed that the ZZFDT composite has good photocatalytic activity under visible light. After being reused six times, it still has good stability.

1 Introduction

In recent years, antibiotics have been widely produced and used in medicine, food processing, live-stock breeding, aquaculture and other fields. But the antibiotic itself is difficult to be degraded, the residual antibiotic will enter the water body, will cause considerable harm to the human and the ecological environment [1,2]. Thus, we need to find an effective and green way to deal with it. Photocatalysis

technology has attracted much attention because it can effectively degrade antibiotics to small molecules without secondary pollution [3–6]. ZnO has attracted much attention because of its low cost, non-toxicity and high quantum efficiency. Because ZnO has a band gap of 3.2 eV, it can only absorb ultraviolet light. However, ultraviolet light only accounts for 3–5% of solar energy, and the insufficient utilization of solar energy seriously hinders the practical application of ZnO [7–11].

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Many scholars have proposed many methods to modify ZnO. The most typical method is to combine with other narrow band gap semiconductors to form a heterostructure. The energy band potential of the narrow band gap semiconductor matches the energy band potential of ZnO, and a uniform FERMI energy level is formed between the two semiconductors, this leads to the generation of an internal electronic field and the diffusion of electrons at the conduction and valence band positions. This charge transfer effectively impedes the recombination rate of photogenerated electron-hole pairs and improves the optical quantum efficiency such as in ZnO/Bi₂O₃ [12], MoO₃/ZnO [13], Ag₂O/ZnO [14], ZnO/AgI [15].

Magnetic nanomaterials are widely used in biomedicine, sensors, catalysts, optics and other fields [16–19] because of their excellent biocompatibility, adaptability, physical chemistry stability, excellent magnetic properties [20]. Yang et al. [21] prepared ZnFe₂O₄ hollow spheres by one-step hydrothermal method using carbon plate as a template. The results showed that the response range of ZnFe₂O₄ Hollow Sphere Sensor to ethylene glycol is 35.5 ~ 100 ppm. The ZnFe₂O₄ hollow ball Sensor still has a good gas response during the measurement within eight weeks, showing long-term stability. Patade et al. [22] prepared superparamagnetic MnFe₂O₄ nanoparticles (NPS) were synthesized by the co-precipitation method. Under the condition of 4 kA/m amplitude and 280 kHz frequency, the induction heating of MnFe₂O₄ magnetic NPS was studied. The results showed that 0.4 g/mL MnFe₂O₄ magnetic NPS could reach the thermotherapy temperature (42 °C) within 260 s, proving that the material can be used as a heating agent for magnetic heat treatment. However, magnetic nanoparticles in solution is easy aggregation and toxicity. To solve these problems, Kharat et al. [23] coated CoFe₂O₄ particles with Surfactant (oleic acid), which has anti-inflammatory and complementary anticancerous effects, improved the stability of the nanoparticles, and reduced the accumulation. CoFe₂O₄ nanoparticles coated with 1 mg/mL oleic acid have great potential for magnetic fluid hyperthermia through biocompatibility research and ongoing clinical trials. Somvanshi et al. [24] prepared ZnFe₂O₄ nanoparticles by combustion synthesis method and their surface were functionalized by silica and carboxyl-modified polyvinyl alcohol. They proposed a novel approach to extract COVID-19 virus RNA using surface-functionalized

ZnFe₂O₄. The method is simple and can reduce the diagnostic time.

In the family of magnetic nanomaterials, spinel ferrite nanomaterials are characterized by their high electrical resistivity, high saturation magnetization, low eddy current, good physical chemistry properties, and low cost [25,26], which is widely used in memories storage, a drug targeted delivery, magnetic hyperthermia, magnetic resonance imaging, photocatalysis and other fields [27–30]. The general formula of Spinel ferrite material is MFe₂O₄, where M is Co²⁺, Ni²⁺, Mn²⁺, Zn²⁺ and other divalent metal ions, which are in tetrahedral position, while trivalent Fe ions are in octahedral place. Many ferrite semiconductors also exhibit good photocatalytic activity under visible light. ZnFe₂O₄ (ZF) is a p-type semiconductor photocatalyst, which can be used as an alternative material because of its relatively small band gap (about 1.8 eV), non-toxic, stable photochemical properties and low cost [31–35]. In recent years, ZF has been reported to photodegrade pollutants [36]. In addition, because of its magnetic properties, it can be recovered from solution by an external magnet, which makes it have great potential in practical application. The formation of ZnO/ZF heterojunction can inhibit the recombination of photogenerated electron-hole pairs and improve photocatalytic performance [37–41]. M. Kuang et al. [37] prepared octahedral-like ZnO/ZnFe₂O₄ heterojunction photocatalyst by solvothermal method. The photocatalytic activity of different samples was evaluated by degradation of Methylene blue. The results showed that ZnO/ZnFe₂O₄ photocatalyst has the best photocatalytic degradation efficiency compared with ZnO and ZnFe₂O₄. Under 120 min of UV-Vis (350 ≤ λ ≤ 780 nm) and 140 min of visible light (λ ≥ 420 nm) irradiation, the degradation efficiency of optimal photocatalyst (ZF3) is 91.2% and 82.7%, respectively. Because ZnFe₂O₄ can absorb visible light, ZnO/ZnFe₂O₄ can form heterojunction, hindering the recombination of photoelectron electron-hole pairs and improving its photocatalytic activity. Wang et al. [42] prepared magnetic photocatalyst ZnFe₂O₄/Bi⁰-Bi₂MoO₆ with Z-scheme heterojunction by solvothermal-liquid phase reduction method. Under visible light irradiation, ZnFe₂O₄/Bi⁰-Bi₂MoO₆ composite exhibited better photocatalytic activity than pure Bi₂MoO₆, ZnFe₂O₄ and Bi⁰-Bi₂MoO₆ for the degradation of tetracycline hydrochloride. In the meantime, the ternary catalyst also has an excellent

photocatalytic activity for norfloxacin and levofloxacin hydrochloride. In addition, $\text{ZnFe}_2\text{O}_4/\text{Bi}^0\text{-Bi}_2\text{MoO}_6$ can be separated from the solution by an external magnet. Besides, $\text{ZnFe}_2\text{O}_4/\text{Bi}^0\text{-Bi}_2\text{MoO}_6$ was steadily reused several times. Manzoor et al. [43] reported $\text{ZnFe}_2\text{O}_4/\text{Bi}^0\text{-Bi}_2\text{MoO}_6$ heterojunction photocatalyst can be used for photocatalytic reduction of CO_2 to methanol. Under visible light irradiation, when the coupling ratio of $\text{ZnFe}_2\text{O}_4/\text{TiO}_2$ is 1:1 and the calcination temperature is 900 °C, the maximum methanol yield (141.22 $\mu\text{mol/gcat h}$) is obtained.

Now, there is been another research interest on the immobilization of photocatalyst particles onto various substrates. Compared with activated carbon and Graphene, diatomite (DT) is a mineral-rich natural material, which has the advantages of graded porous structure, excellent adsorption capacity, high chemical stability and low price [44–47]. Diatomite-based photocatalysis composite materials often have excellent photocatalytic activity, which is attributed to the diatomite can effectively improve the contact probability between catalysts and pollutants, leading to the increase of degradation rate such as in $\text{F-TiO}_2/\text{DT}$ [48].

ZnFe_2O_4 and ZnO can form n–n homotype heterojunction, which hinders the recombination of photogenerated electron–hole pairs and improves the utilization ratio of carriers. Because ZnFe_2O_4 can absorb visible light, the response range of $\text{ZnO}/\text{ZnFe}_2\text{O}_4$ can be extended to the visible light region. Diatomite as a carrier of $\text{ZnO}/\text{ZnFe}_2\text{O}_4$ can improve the contact probability between the photocatalyst and antibiotics because of its excellent adsorption property. In addition, ZZFDT is magnetic and easy to recycle. In a word, the $\text{ZnO}/\text{ZnFe}_2\text{O}_4/\text{diatomite}$ composite has a good synergistic effect. Moreover, $\text{ZnO}/\text{ZnFe}_2\text{O}_4/\text{diatomite}$ ternary composites have not been reported and have high research value.

This research aims to prepare $\text{ZnO}/\text{ZnFe}_2\text{O}_4/\text{diatomite}$ (ZZFDT) composites by a hydrothermal-precipitation method. The structure, morphology and optical properties of ZZFDT were analyzed. The photocatalytic activity of ZZFDT was evaluated by the degradation of oxytetracycline (OTC) under visible light, and the mechanism of photocatalytic degradation of OTC was proposed.

2 Experimental

2.1 Materials

$\text{C}_4\text{H}_6\text{O}_4\text{Zn}\cdot 2\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$, NaOH and $(\text{C}_6\text{H}_9\text{NO})_n$ (PVP) were purchased from Sinopharm Group Chemical Reagent Co., Ltd and are all analytical grade. The crude diatomite was purchased from Yuan-Tong Mineral Co., Ltd (Jilin Province, PRC), and pretreated by pickling [49]. Deionized water was homemade.

2.2 Preparation of photocatalysts

$\text{ZnFe}_2\text{O}_4/\text{diatomite}$ (ZFDT) was synthesized by the hydrothermal method. The pretreated diatomite (0.7 g) was mixed with 20 mL deionized water, and $\text{C}_4\text{H}_6\text{O}_4\text{Zn}\cdot 2\text{H}_2\text{O}$ (0.66 g), $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ (2.424 g), PVP (0.1 g) were added to the above mixture, which was kept under constant stirring. The NaOH solution was added into the mixed solution to pH 11 and stirred for 30 min. Then, the hybrid solution was transferred to a 100 mL reactor and heated at 180 °C for 24 h. After the autoclave was cooled to room temperature, the solid product in the reaction solution was collected by a magnet and washed three times with water and ethanol. The solid product was dried at 80 °C for 6 h and calcined at 500 °C for two h to afford ZFDT. Pure ZF was prepared by the above method without adding diatomite.

ZZFDT was described synthesized by precipitation method. ZFDT (0.5 g) and $\text{C}_4\text{H}_6\text{O}_4\text{Zn}\cdot 2\text{H}_2\text{O}$ (0.68 g) were added into absolute ethanol (20 mL), and the mixture was kept under constant stirring. After 0.5 h, NaOH (0.25 g) was added dropwise into the mixture. The mixed solution was then kept in a water bath at 80 °C for two h, during which 5 mL deionized water was added twice. The solid product in the reaction solution was collected by a magnet and washed three times with water and ethanol. The solid product was dried at 120 °C for 6 h to afford ZZFDT (ZZFDT-1) composite. Adjusting to the mass ratios of ZnO , ZF, and DT, the obtained products were defined as ZZFDT-2 (1:1:1), ZZFDT-2 (1:1:2), ZZFDT-3 (1:1:3), ZZFDT-4 (1:2:1), ZZFDT-5 (1:3:1), ZZFDT-6 (2:1:1), and ZZFDT-7 (3:1:1). For comparison, ZnO , $\text{ZnO}/\text{diatomite}$ (ZDT) and $\text{ZnO}/\text{ZnFe}_2\text{O}_4$ (ZZF) were prepared by the above methods.

Figure 1 shows the schematic illustration of the synthesis process of ZZFDT. The chemical reactions involved in the synthesized of ZZFDT:

2.3 Characterization

The Crystal Structure of the sample was determined by a Bruker 8-Advance X-ray diffractometer at $2\theta = 10^\circ$ to 80° under the following conditions: Cu Ka = 0.15406 nm, 40 kV, 40 mA, $5^\circ/\text{min}$. The absorption peaks in the wavenumber range of $400\text{--}4000\text{ cm}^{-1}$ were measured by FT-IR spectrometer (NICOLETIS5). The XPS spectra of the samples were measured by X-ray photoelectron spectroscopy (TFSK-250XI) at the vacuum of 5×10^{-10} Pa. The charge correction is carried out with C 1s = 284.8 eV as the energy standard. The UV-Vis DRS of the samples were measured by ultraviolet-visible Spectrometer (UV-2500, Shimadzu, Japan), with Barium Sulfate as reference. The morphology of the samples was tested by FE-SEM (MX2600FE, U.K.) and TEM (JEM2100F, Japan). The DLS and zeta potential of the samples were measured, and the particle size and potential were obtained. The specific surface area and pore size distribution of the samples were measured using a particular surface area and pore size analyzer (V-SorbX800) at 77 K. The magnetic properties of the

samples were analyzed by VSM (EV-9 Hitachi, Japan).

2.4 Photocatalytic evaluation

The photocatalytic activity of the composite was evaluated by degrading OTC solution (10 mg/L) under visible light irradiation (300 W Xenon lamp). The mixture of 10 mg/L OTC solution (100 mL) and 0.1 g catalyst sample was stirred in darkness for 30 min to establish adsorption-desorption equilibrium between OTC molecule and photocatalyst. After the illumination was turned on, 3 mL of the suspension was removed at regular intervals. The absorbance of the sample was determined by a UV-Vis spectrophotometer (SPECORD S600, Germany) at 362 nm. Combined with the standard curve of OTC solution, the concentration variation of different samples was studied. The OTC conversion rate is calculated by the following formula:

$$\text{Conversion rate (\%)} = \frac{C_0 - C}{C_0} \times 100 \quad (6)$$

where C_0 is the initial concentration of OTC solution, C is the concentration of OTC solution after a reaction period.

3 Results and discussion

3.1 Characterization of materials

3.1.1 XRD

Figure 2a shows the XRD patterns of prepared ZnO, ZF, DT and ZZFDT-1 (mass ratio of ZnO: ZF: DT = 1:1:1). The Standard Spectrum of ZnO, ZF and SiO_2 were also provided for comparison. All peaks of the XRD pattern of ZZFDT-1 in Fig. 2a were indexed using Bragg's law. The characteristic diffraction peaks at $2\theta = 30.2^\circ, 35.6^\circ, 43.3^\circ, 53.7^\circ, 57.3^\circ$ and 62.9° was indexed according to "Bragg's X-ray diffraction" law and matched with the standard diffraction data PDF data card sheet No. 73-1963. The indexed results showed that these peaks correspond to the (220), (311), (400), (422), (511) and (440) crystal planes of cubic spinel-type ZF, respectively [50]; the characteristic diffraction peaks at $2\theta = 31.7^\circ, 34.4^\circ, 36.3^\circ, 47.5^\circ, 56.5^\circ, 62.8^\circ, 67.9^\circ$ and 69.0° were indexed according to "Bragg's X-ray diffraction" law and matched with the standard diffraction data PDF data

Fig. 1 The schematic illustration of the synthesis process of ZZFDT

Fig. 2 **a** XRD patterns of ZnO, ZF, DT, and ZZFDT-1. **b** The magnified region in (220) crystal plane of ZF and ZZFDT-1

card sheet No. 89-1397. The indexed results showed that these peaks correspond to the (100), (002), (101), (102), (110), (103), (112) and (201) crystal planes of hexagonal-wurtzite structure ZnO, respectively [51]. In addition, the diffraction peaks appearing at $2\theta = 21.89^\circ, 35.9^\circ$ were indexed according to “Bragg’s X-ray diffraction” law and matched with the standard diffraction data PDF data card sheet No. 76-0973. The indexed results showed that these peaks correspond to the diffraction peaks of crystal quartz SiO_2 [52], indicating the existence of crystal quartz in DT. The main component of DT is amorphous silicon dioxide, which XRD cannot detect. ZZFDT-1 contains diffraction peaks of pure ZnO, ZF, and DT, proving that the ZZFDT ternary composite has been successfully synthesized.

As can be seen from the illustration in Fig. 2b, the diffraction peak of ZZFDT-1 on the (220) crystal plane is shifted to the left compared with pure ZF, this may be due to the formation of Si–O–Zn, Si–O–Fe bonds (FT-IR can be demonstrated) by the hybridization between DT and ZF, ZnO, resulting in lattice distortion. Figure 3a is the XRD pattern of ZZFDT with different mass ratios. With the increase of the content of one component in ZZFDT, the intensity of its diffraction peak increases gradually, without changing the crystal structure of any component. The diffraction peaks in ZZFDT with different mass ratios widen slightly and the intensity decreases, which indicates that the hybridization between DT and ZF, ZnO impedes the growth of crystal particles [53].

The crystallite size of the ZF in pure ZF and various composite ratios ZZFDT was calculated using the Debye–Scherrer formula [54]:

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (7)$$

where D is the crystallite size (nm), K is the constant (0.9), λ is X-ray wavelength (1.541 nm), θ is diffraction angle, β is half-peak width of XRD diffraction peak. The average crystallite size of the prepared ZF was 18 ~ 24 nm. The lattice constant can be calculated from the following formula [55]:

$$a = d * (h^2 + k^2 + l^2)^{1/2} \quad (8)$$

where d is the interplanar spacing and $(h \ k \ l)$ is the Miller exponent of the plane. With the increase of DT, the constant lattice decreases from 8.600 to 8.545 Å, and the crystallite size decreases from 21 to 18 nm, because of the interaction between ZF and DT resulted in the formation of new chemical bonds. The X-ray density of ZF was determined by molecular weight and unit cell volume and was calculated using the following formula [56]:

$$d_x = \frac{8M}{N_A a^3} \quad (9)$$

where N_A is the Avogadro number and a is a lattice parameter. The values of the lattice parameter are listed in Table 1.

To verify the crystallite size of ZF in ZZFDT-1 which was calculated by Debye–Scherrer formula, it was recalculated by the Williamson–Hall (W–H) method [36]. The Williamson–Hall (W–H) method is

Fig. 3 **a** XRD pattern of ZZFDT components. **b** Williamson-Hall plot of ZF in ZZFDT-1

Table 1 Structural parameter values of ZF

Sample	<i>a</i> (Å)	<i>V</i> (Å ³)	<i>D</i> (nm)	<i>d_x</i> (gm/cm ³)
ZF	8.423	597.6	24	5.557
ZZFDT-1	8.600	636.1	21	5.220
ZZFDT-2	8.563	627.9	19	5.289
ZZFDT-3	8.545	623.9	18	5.322
ZZFDT-4	8.572	629.9	22	5.272
ZZFDT-5	8.584	632.5	23	5.250
ZZFDT-6	8.452	603.8	21	5.500
ZZFDT-7	8.491	612.2	22	5.424

an elegant method used to define the crystallite size and the microstrain from the reflection broadening. The strain has a direct effect on the physical broadening of the XRD spectrum, and the broadening peak of the strain is:

$$\varepsilon = \frac{\beta_x}{4 \tan \theta} \quad (10)$$

Equation (11) is given by Eq. (7):

$$\beta = \frac{1}{\cos \theta} \times \frac{K\lambda}{D} \quad (11)$$

Equation (12) can be obtained by combining Eqs. (10) and (11):

$$\beta \cos \theta = \frac{K\lambda}{D} + 4\varepsilon \sin \theta \quad (12)$$

where *D* and ε are the crystal size value and microstrain value, respectively. For prepared ZZFDT-1, a plot is drawn with $4\sin\theta$ as x-axis and $\beta\cos\theta$ as y-axis,

as shown in Fig. 3b. The crystallite size is calculated by the y-axis intercept of linear fitting, and the strain ε is estimated by the slope of the fitting.

$$D = \frac{K\lambda}{y} \quad (13)$$

The crystallite size of ZF in ZZFDT-1 calculated by Eq. (13) is 20 nm, which is a little different from 21 nm calculated by the Debye Scheler formula.

3.1.2 FE-SEM and TEM

To further study the morphology and microstructure, SEM of ZZFDT-1 were also observed. Figure 4a shows that diatomite has a disc-like appearance and is rich in the pore structure. The smaller pieces around the disk come from skeletons of different shapes, cylindrical, elliptical, or fragmented^[57]. This structure makes diatomite have some adsorption ability, which provides a good condition for the loading of photocatalytic materials and the occurrence of photocatalytic reaction. Figure 4b illustrates the coagulation and deposition of ZnO and ZF particles on the pore edge and surface of the diatom disk. The interaction between ZnO and ZF at the interface can enhance the charge transfer ability and thus improve the photodegradation efficiency. Figure 4c and d are TEM diagrams of ZZFDT-1 with different magnification. It can be seen that ZnO and ZF are loaded on DT surfaces with uniform sizes. Figure 4e shows the particle size distribution obtained by fitting the TEM diagram with the Gaussian function. The crystallite size of ZF in ZZFDT-1 is about 15 nm,

Fig. 4 FE-SEM images of **a** DT, **b** ZZFDT. **c**, **d** TEM image of ZZFDT-1 with different magnification. **e** particle distribution for ZF in ZZFDT-1

which is consistent with the average crystallite size of XRD analysis.

3.1.3 FT-IR

Figure 5 shows the FT-IR Spectra of ZnO, DT, ZF, ZZFDT. The characteristic absorption peak of about 3400 cm^{-1} is the stretching vibration peak of the O–H bond adsorbing water in the air, and the absorption peak of about 1600 cm^{-1} is the O–H bending vibration peak of the Silica hydroxyl group [58]. The

absorption peaks of 2920 cm^{-1} and 2850 cm^{-1} are the vibrational peaks of the organic impurity C–H [59]. Because the main component of diatomite is amorphous SiO_2 , the absorption peak of about 1100 cm^{-1} is the antisymmetric stretching vibration peak of Si–O–Si in Silica Tetrahedron, and the absorption peak is very strong. The absorption peak about 800 cm^{-1} is the symmetrical stretching peak of Amorphous SiO_2 , and the bending peak about 450 cm^{-1} is the bending peak of O–Si–O [60]. It can be seen from the lines of ZZFDT that the characteristic absorption peaks of

Fig. 5 The FT-IR spectra of ZnO, DT, ZF, and ZZFDT-1

about 550 cm^{-1} and 450 cm^{-1} are the stretching vibration peaks of the octahedral Fe–O bond and the tetrahedral Zn–O bond in ZF, respectively [61]. Compared with pure ZnO, ZF, and DT, the strength of the absorption peaks of about 1100 cm^{-1} and 1600 cm^{-1} decreased. New absorption peaks of about 860 cm^{-1} and 930 cm^{-1} appeared, which were the antisymmetric stretching peaks of Si–O–Fe [62] and Si–O–Zn [63], the results show that ZnO, ZF, and diatomite are chemically bonded during the synthesis process, which is consistent with the XRD results.

3.1.4 XPS

The composition and combination state of elements in the ZZFDT-1 composite was analyzed by XPS spectra. Figure 6a shows the survey spectrum of the ZZFDT, including the Zn, Fe, O, Si, and C elements. Among these, carbon element comes from the carbon contaminant of the XPS analytical instrument. Figure 6b is the spectrum of Zn 2p, and two peaks are located at 1021.1 eV and 1044.1 eV, belonging to Zn $2p_{3/2}$ and Zn $2p_{1/2}$, indicating the existence of Zn as Zn²⁺ [64]. Figure 6c shows the spectrum of Fe 2p, two peaks are located at 710.9 and 724.3 eV, corresponding to Fe $2p_{3/2}$ and Fe $2p_{1/2}$, indicating the existence of Fe as Fe²⁺ [65]. Figure 6d is the XPS spectrum of O 1s. Three characteristic peaks can be obtained by software processing. The peaks at 527.4 eV is attributed to O in the silanol group on the surface of the sample. The peak at 530.6 eV is attributed to O in the Lattice [66], and the peak at 532.2 eV is attributed to

Si–O–Fe and Si–O–Zn [67,68]. These bonds can be used as electron transport channels to enhance the charge transfer ability and thus improve the efficiency of photocatalysis.

3.1.5 BET and BJH

Figure 7 shows the N₂ adsorption–desorption isotherms and pore size distribution curves of ZnO and ZZFDT-1. As shown in Fig. 7a, the N₂ adsorption–desorption isotherms of ZZFDT-1 exhibit the classical type IV curves according to the International Union of Pure and Applied Chemistry (IUPAC) classification. With the increase of the relative pressure, the adsorption amount of N₂ increases slowly, which indicates that the interaction between the adsorbate and the adsorbent is weak. Subsequently, near the saturation pressure, the adsorbate molecules congregate at the most favorable active sites on the surface of macropores of diatomite, leading to the adsorption amount of N₂ increasing significantly. The curve-shaped hysteresis loop belongs to the H3 type, related to the capillary condensation with slit-like pores in the material. Because as the capillaries condense, they merge to form narrow slit-like pores. ZZFDT-1 is a typical mesoporous material [69]. Compared with ZnO, the adsorption volume of ZZFDT-1 on nitrogen increased slightly in the wide range of P/P₀ relative pressure. The specific surface area of ZZFDT-1 is more significant than that of ZnO. This is due to the introduction of a special skeleton DT, so that ZnO and ZF are loaded to the surface, playing a certain role in dispersion. The addition of DT can inhibit the growth of ZnO and ZF particles, resulting in smaller grains, which can also improve the surface condition. ZZFDT-1 has a high specific surface area, which is helpful to adsorb pollutants and increase the reaction site, thus improving the photocatalytic activity [70].

The surface pore size distribution was investigated using the BJH method, and the results are shown in Fig. 7b. The average pore diameters of ZZFDT-1 and ZnO are 11.94 nm and 32.52 nm. The total pore volume ($0.25\text{ cm}^3/\text{g}$) of ZZFDT-1 is much larger than that of ZnO. The mesoporous volume of ZZFDT-1 is more significant than that of ZnO, which may be related to the morphology of diatomite (confirmed by SEM).

Fig. 6 XPS spectra of the ZZFDT-1 composite: **a** full scan survey of ZZFDT-1, **b** Zn 2p, **c** Fe 2p, **d** O 1s

Fig. 7 **a** The BET isotherms and **b** pore size distribution curves of ZnO and ZZFDT-1

3.1.6 Dynamic light scattering (DLS) and zeta potential

The particle size distribution of the sample was studied by dynamic light scattering (DLS) [71]. Figure 8a shows the cumulative crystallite size curve of ZnO, ZZFDT-1. The particle sizes of 90% ZnO and 90% ZZFDT-1 are smaller than 43.57 nm and 29.49 nm, respectively. Because ZnO is insoluble and agglomerative easily in colloidal suspension, its particle size is larger. The decrease of ZZFDT-1 hydrodynamic diameter may be related to the reduction of the crystallite size of ZF. The reduction of particle size of ZZFDT-1 shows that the degree of particle aggregation is reduced, which means that the addition of DT improved the stability of ZZFDT-1. To understand the stability of ZZFDT-1 in the fluid medium, zeta potential was also measured. Figure 8b shows the zeta potential of ZnO and ZZFDT-1 as a function of PH. If the zeta potential of the particle is higher than ± 30 mV, the electrostatic stability of the particle is better [72]. Zeta potentials of ZnO and ZZFDT-1 were ± 35 mV and ± 48 mV, which were significantly higher than ± 30 mV. The isoelectric point (Ip) of ZnO and ZZFDT-1 are 5.8 and 6.8, respectively. The isoelectric point of ZZFDT-1 is higher than that of ZnO, which indicates that the composite has higher colloidal stability.

3.1.7 UV-Vis DRS

Figure 9a displays the UV-Vis DRS of the ZnO and ZZFDT-1 photocatalysts. The absorption edge of ZnO is about 400 nm, and there is only weak absorption in

the visible region. Compared with ZnO, the absorption edge of the ZZFDT-1 composite exhibits a red shift, which indicates that the light response range of the composite can be widened by introducing a third component ZF. Figure 9c shows the UV-Vis DRS of different mass ratios of ZZFDT. ZZFDT-1 exhibits superior visible light absorption. Figure 9b and d show that the band gap of ZnO, ZZFDT-1, ZZFDT-2, ZZFDT-3, ZZFDT-4, ZZFDT-5, ZZFDT-6 and ZZFDT-7 are estimated to be 3.17, 1.5, 1.68, 1.85, 1.8, 1.85, 1.72, 1.71 eV, respectively, based on the Kubelka-Munk function. It is reported that the band gap of ZF is about 1.8 eV [73], and that of the ZZFDT composite is less than 1.8 eV, which indicates that ZF and ZnO have a good synergistic effect, which can reduce the band gap and improve the quantum efficiency of the composite [74].

3.1.8 VSM

The magnetic properties of ZFDT and ZZFDT-1 were measured using VSM, as shown in Fig. 10a. The magnetic hysteresis loops of ZFDT and ZZFDT-1 were observed at room temperature. The saturation magnetization (M) of ZFDT (3.12 emu/g) is greater than ZZFDT-1 (1.82 emu/g). This may be due to the addition of ZnO, which reduces the ferromagnetism of the composite. The ternary ZZFDT-1 composite can be effectively separated from the OTC solution by an external magnet, although its magnetism is reduced compared with ZFDT (Fig. 10b).

Fig. 8 a The cumulative crystallite size curve of ZnO, ZZFDT-1. b Zeta potential of ZnO and ZZFDT-1 as a function of PH

Fig. 9 **a** UV-Vis DRS of ZnO and ZZFDT-1. **b** Plots of $[F(R)h\nu]^2$ versus photo energy ($h\nu$) of ZnO and ZZFDT-1. **c** UV-Vis DRS of ZZFDT with different mass ratios. **d** Plots of $[F(R)h\nu]^2$ versus photo energy ($h\nu$) of ZZFDT with varying ratios of mass

Fig. 10 **a** VSM plots of ZFDT and ZZFDT-1. **b** The suspension of ZZFDT-1 and OTC solution before and after applied with an external magnet

3.2 Photocatalytic properties

Figure 11a is the photocatalytic degradation curve of the OTC solution by DT, ZnO, ZF, ZDT, ZFDT, ZZF, ZZFDT-1, without catalyst. To study the adsorbability of different samples, the whole apparatus was operated in darkness for 30 min before illumination. As can be seen from the diagram, ZZFDT-1 has the strongest adsorption capacity, which can be attributed to its large specific surface area. In addition, the adsorption-desorption equilibrium of all samples can be established within 30 min because the solution concentration hardly changes between 15 and 30 min of dark adsorption. In the absence of catalyst and no light, the concentration of OTC did not change, indicating that the photocatalytic reaction did not take place. The photocatalysis activity of ZZF is higher than that of ZnO and ZF, which means that

Fig. 11 **a** Photocatalytic degradation curves of different samples to OTC. **b** The conversion rate of different samples to OTC. **c** The conversion rate of varying mass ratios ZZFDT. **d** Kinetic curves of

different samples. **e** The conversion efficiency of different samples to OTC

ZnO and ZF interact with each other and can inhibit the recombination of photogenerated electron–hole pairs, leading to the enhancement of photoactivity. The photocatalytic activity of ZDT and ZFDT is higher than that of ZnO and ZF, because of the adsorption capacity of DT. DT can adsorb OTC molecules near catalyst particles, thus improving the contact rate between catalyst particles and OTC, accelerating the photocatalytic rate [75]. As shown in Fig. 11b and c, the conversion rate of ZZFD-1 to OTC is 95%, which is 4.13, 1.90, 1.40, 1.38, 1.36, and 1.27 times higher than that of DT, ZnO, ZF, ZDT, ZFDT and ZZF, respectively. Compared with ZZFD-2, ZZFD-3, ZZFD-4, ZZFD-5, ZZFD-6 and ZZFD-7, the conversion of OTC is increased by 21%, 12%, 15%, 13%, 1% and 4%, respectively. When the doping amount of ZnO or ZF exceeds a certain limit, the excess components may become the composite center of photocarriers, thus reducing the photoactivity of the composite. Conversion efficiency refers to how many grams of OTC can be converted per gram of catalyst/per hour. It can be seen from Fig. 11e that ZZFD-1 has the highest conversion efficiency (4.75 mg/g/h) for OTC, indicating that there is synergy among the three components.

To prove the photocatalytic activity of the ZZFD composite, the total organic carbon (TOC) of the OTC solution was analyzed. 10 mg/L OTC solution (100 mL) TOC is 13.12 mg/L. After two hours of photocatalytic reaction, the remaining TOC was 1.72 mg/L, indicating mineralization in the course of OTC degradation.

By applying the first-order model of dynamics to acquire reaction rate constant:

$$\ln\left(\frac{C}{C_t}\right) = kt \quad (14)$$

where C_t represents the concentration of OTC solution after 30 min in darkness, when the adsorption–desorption equilibrium has been established; k represents the reaction rate constant; Because the concentration of OTC is unchanged after 105 min, so t is 30–105 min). The fitted kinetic plots are shown in Fig. 11d, and the rate constants are indicated in Table 2.

Table 2 Kinetic data of OTC photodegradation using different catalysts

Catalyst	k ($10^{-3}/\text{min}$)	R^2
DT	1.91	0.9945
ZnO	7.04	0.9977
ZF	6.48	0.9990
ZDT	8.96	0.9985
ZFDT	3.51	0.9997
ZZF	7.29	0.9986
ZZFD-1	9.81	0.9954

3.3 Recyclability and metal leaching studies

Figure 12 is the reusability test results of ZZFD-1. After completing the experiment of photocatalytic degradation of OTC, the catalyst samples were collected by an external magnet and washed three times with deionized water and ethanol. Then, it was dried at 80 °C for the next degradation test. After five repeated tests, ZZFD-1 kept the removal rate of OTC at 90%, which meant that ZZFD-1 had good stability and repeatability in the photodegradation process. The results of metal leaching experiments are shown in Table 3. Assuming that the added ZZFD-1 (0.1 g) is completely dissolved in 100 mL OTC solution, the total amounts of Zn^{2+} and Fe^{3+} in the solution are 360 and 160 $\mu\text{g/mL}$. The leaching amounts of Zn^{2+} and Fe^{3+} are 8.527 and 3.386 $\mu\text{g/mL}$ after being used six times, which shows that ZZFD-1 has good stability.

3.4 Photocatalytic reaction mechanism

It is well known that hole (h^+), superoxide ions ($\cdot\text{O}_2^-$), hydroxyl radicals ($\cdot\text{OH}$) and other active compounds play a significant role in photocatalytic activity. To verify which kind of active substance is dominant in the photocatalysis reaction, the photocatalysis degradation experiment with an active group trapping agent was designed. The additives are benzoquinone (BQ), ethylenediamine tetraacetic acid disodium salt (EDTA) and isopropyl alcohol (IPA), which are scavengers of superoxide radical ($\cdot\text{O}_2^-$), hole (h^+) and hydroxyl radical ($\cdot\text{OH}$), respectively. As shown in Fig. 13, IPA showed the highest inhibitory effect, which meant that $\cdot\text{OH}$ was

Fig. 12 The reusability test results of ZZFDT-1

Table 3 The results of metal leaching experiments of Zn^{2+} and Fe^{3+}

Ion species	Total amount ($\mu\text{g/mL}$)	6st use ($\mu\text{g/mL}$)
Zn^{2+}	360	8.527
Fe^{3+}	160	3.386

Fig. 13 Photocatalytic activity of ZZFDT-1 under the different scavengers

the most effective active species during photodegradation.

Mott–Schottky (MS) was used to study the flat band potential of the semiconductor materials, as shown in Fig. 14. The linear portion of the curve extends to the potential axis, and the value of the

intersection point is the flat-band potential. The slope of the linear portion of all the curves in Fig. 14 is positive, which indicates that ZnO, ZF, ZZFDT are n-type semiconductors. The slope of the linear part of the MS curve can be used to calculate the carrier density. The formula is as follows:

$$\frac{d(C^{-2})}{dV} = \frac{2}{N\epsilon\epsilon_0e_0} \quad (15)$$

where N is the carrier density, C is the capacitance, e_0 is the electron charge (1.602×10^{-19} C), ϵ_0 is the dielectric constant of the vacuum (8.854×10^{-12} F/m), ϵ is the dielectric constant of the sample and V is the applied potential. The results showed that the carrier densities of ZnO and ZZFDT-1 are 9.22×10^{18} and 4.35×10^{19} , respectively.

The DC resistivity of ZnO and ZZFDT-1 was 2.65×10^6 and 1.27×10^6 Ω cm. When there are defects or structural vacancies in the Lattice, oxygen ions are diffused. The Diffusion Coefficient of oxygen vacancy is calculated using formula (16):

$$D = \frac{\sigma k_B T}{Ne^2} \quad (16)$$

where σ is the reciprocal of the resistivity, k_B is the Ludwig Boltzmann constant, T is the temperature, D is the diffusion coefficient, N is the number of atoms/ cm^3 , e is the electronic charge. At 298 K, the diffusion coefficients of ZnO and ZZFDT-1 are 2.90×10^{-8} and 6.05×10^{-8} cm^2/s . The diffusion Coefficient of ZZFDT-1 is larger than ZnO, which indicates that more oxygen vacancies are diffused in ZZFDT-1.

Fig. 14 Mott–Schottky curves of **a** ZnO, **b** ZF and **c** ZZFD-1

As shown from Fig. 14, the flat band potential of ZnO, ZF, ZZFD-1 is -0.69 , -0.36 and -0.90 V vs Ag/AgCl. For n-type semiconductors, the flat band potential is 0.1 or 0.2 eV positive than the conduction band potential. So the conduction potential (E_{CB}) of ZnO, ZF is about -0.89 , -0.56 eV. The value of the valence band (E_{VB}) is calculated using the following formula:

$$E_{VB} = E_{CB} + E_g \quad (17)$$

As can be seen from the illustration in Fig. 14b, the band gap of ZF is 1.67 eV, so the E_{VB} potential of ZnO, ZF is 2.28, 1.11 eV. Moreover, we know that the work function of ZnO is about 5.20 eV [76] and that of ZF is about 5.38 eV [77]. ZF has a more excellent function than ZnO, so ZF has a lower Fermi level than ZnO. To achieve a uniform Fermi level for both semiconductor materials, the electrons in the ZnO

conduction band are transferred to the conduction band of ZF until the whole system reaches a uniform Fermi level. This will cause the overall fermi level of the ZZFD-1 to move to a more negative potential, thus forming a new flat band potential and staggered n–n heterostructure. Compared with ZnO, the flat band potential of ZZFD-1 shifted negatively to -0.90 eV.

In summary, the mechanism of OTC degradation by ZZFD-1 composite is proposed, as shown in Fig. 15. The carrier DT adsorbs the OTC molecule to the surface of ZZFD-1. The electrons in the valence band are excited to transition into the conduction band (CB) after ZnO absorbs UV light, leaving holes in the valence band (VB). In addition, because ZF has a narrow band gap, it absorbs visible light to create electrons (on the CB) and holes (on the VB). Since the newly formed CB potential in ZZFD-1 is higher than that of ZnO, and ZnO has a lower VB potential than

Fig. 15 Mechanism of OTC degradation by ZZFD-1

ZF, the electrons from ZF On CB are transferred to ZF's CB, and the holes from ZnO on VB are transferred to ZF's VB [78]. Similarly, the holes on the VB of ZnO could migrate to the VB of ZF. This migration can promote the separation of photogenerated electron-hole pairs and hinder recombination, which means that more charge carriers react with O_2 or H_2O to produce more $\cdot O_2^-$ or $\cdot OH$, resulting in higher photodegradation efficiency. The degradation process of ZZFD-1 to OTC is as follows [79,80]:

4 Conclusion

In summary, this work presented a novel magnetic ternary ZZFD-1 composite with visible light activated by the hydrothermal-precipitation method. XRD, FT-IR, FE-SEM, TEM and XPS analysis showed that the ZZFD-1 ternary composite was successfully prepared. The crystallite size of ZF in ZZFD-1 calculated from Debye Scherrer and the W-H method are nearly the same and exhibit nanocrystalline nature. The magnetic properties of ZZFD-1 show that it has superparamagnetic nature. The photocatalytic activity of different samples was studied by degrading OTC solution under visible light. All the results showed that ZZFD-1 has good photocatalytic activity and reusability. Because of its high activity, low cost and convenient recycling, it is a promising wastewater treatment material.

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