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Preparation and photocatalytic properties of magnetic g-C₃N₄/MnZnFe₂O₄ composite

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Abstract: By self-assembly method, the new g-C₃N₄ was mixed with MnZnFe₂O₄. The samples were characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and so on. The photocatalytic performance of g-C₃N₄ doped MnZnFe₂O₄ composite photocatalyst was studied. The photocatalytic activity of Rhodamine B was investigated by using hydrogen peroxide as oxidant. It was found that the doping mass ratio (3:2) of g-C₃N₄ doped MnZnFe₂O₄ showed higher activity and better photocatalytic effect than single component MnZnFe₂O₄ or g-C₃N₄. The activity and stability of g-C₃N₄ and MnZnFe₂O₄ composite were significantly improved because of the heterojunction formation produced by compositing g-C₃N₄ with MnZnFe₂O₄. The g-C₃N₄ doped MnZnFe₂O₄ composite has a good application prospect for the decomposition of environmental pollutants.

1. Introduction

At present, in the wastewater treatment process, many manufacturers use different kinds of catalysts, which can decompose organic pollutants and show good catalytic performance. The recovery of catalyst is easy to cause the second pollution of water pollution management, thus the research of recovering catalyst effectively and easily has become the key of wastewater treatment at present. When the manganese zinc ferrite is stimulated by light, photoelectrons and holes are produced. Photogenerated electron interacts with trace O₂ in wastewater solution to generate superoxide anion $\cdot\text{O}_2^-$, while the hole interacts with H₂O molecule to generate $\cdot\text{OH}$ free radicals. The generated $\cdot\text{O}_2^-$ and $\cdot\text{OH}$ can react directly with organic molecules in the discard solution adsorbed on the surface of MnZn ferrite to mineralize the pollutants^[1]. As the complex of oxides, MnZnFe₂O₄ has good magnetic properties, gas sensitivity, sensing and catalytic properties. Combined with magnetic properties and catalytic properties, manganese zinc ferrite as catalyst has obvious advantages in the treatment of organic wastewater. Ferrite spinel is a new heterogeneous Fenton reagent that avoids disadvantages of conventional Fenton reagents, such as sludge generation and recycling^[2].

g-C₃N₄ has a unique electronic band structure, good thermal stability and chemical stability. Semiconductor photocatalyst technology can convert solar energy into chemical energy. There are wide application prospects in dye degradation. In recent years, the research on g-C₃N₄ and ferrite spinel at home and abroad, and the change of photocatalytic performance and magnetic separation recycling performance of g-C₃N₄ and ferrite spinel composite. The photocatalytic activity of g-C₃N₄ was improved by doping g-C₃N₄ with different materials^[3,4]. The heterostructure of g-C₃N₄ has a good effect on the degradation of various pollutants, such as $\alpha\text{-Fe}_2\text{O}_3/\text{g-C}_3\text{N}_4$ ^[5], $\text{CeO}_2/\text{g-C}_3\text{N}_4$ ^[6], $\text{Ag/g-C}_3\text{N}_4$



C_3N_4 ^[7], $TiO_2/g-C_3N_4$ ^[8] and $BiVO_4/g-C_3N_4$ ^[9], showing the excellent photocatalytic performance of $g-C_3N_4$. There are few research reports of $g-C_3N_4/MnZnFe_2O_4$ Magnetic Separable circulating photocatalyst material. This paper reports the preparation and properties of $g-C_3N_4/MnZnFe_2O_4$ (MZF) photocatalyst materials.

2. Experimental

2.1. Materials

Manganese sulfate ($MnSO_4 \cdot H_2O$), Zinc sulfate heptahydrate ($ZnSO_4 \cdot 7H_2O$), Ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), Methanol, Melamine, Citric acid, Sodium hydroxide ($NaOH$) were provided by Sinopharm Chemical Reagent, China.

2.2 Synthesis of $g-C_3N_4$

The 5.00 g $C_3H_6N_6$ is taken into a crucible of ceramic with lid, put in a horse furnace, heating up to $550^\circ C$ at a temperature of $2^\circ C/min$, calcined 4h, cooled and ground, to obtain yellow powder $g-C_3N_4$ ^[10].

2.3 Synthesis of $MnZnFe_2O_4$

With $MnSO_4 \cdot H_2O$, $ZnSO_4 \cdot 7H_2O$ and $FeCl_3 \cdot 6H_2O$ as the basic reagents, the synthetic raw material solution was prepared according to the molar ratio of MnO , ZnO and Fe_2O_3 of 3:2:5, and was injected into the reactor. NH_4HCO_3 , which was 1.5 times of the molar amount of metal ions in the synthetic raw material, was selected as the precipitant, and was slowly injected into the reactor under condition of $50^\circ C$ water bath. The feeding time was controlled to be 30 min. And then was fully stirred for 20min. After adjusting the pH value to 7.1 with 0.5mol/L $NaOH$ solution, the system was stirred constantly for 40 min. After the reaction was finished, the samples were naturally aged at room temperature for 12 h, filtered and washed, and then dried at $100^\circ C$ to obtain manganese zinc ferrite precursor. The precursor was calcined in a muffle furnace. MZF was obtained by calcining at $1150^\circ C$ for 3.0 h^[11].

2.4 Synthesis of $g-C_3N_4/MnZnFe_2O_4$

The self-assembly method is adopted^[12]. A certain amount of $g-C_3N_4$ is usually added into the beaker of methanol solution for ultrasonic dispersion. MZF was dissolved in the mixed solution of citric acid, water and ethanol, and ultrasonic dispersed into suspension. The mixture of MZF suspension and $g-C_3N_4$ suspension, ultrasonic dispersion for 30min, mixing at room temperature for 2h. Then refluxing at $90^\circ C$ for 3 hours, stop heating, continue mixing until it is cooled to room temperature. After the reaction, the product was filtered and washed repeatedly with deionized water and absolute ethanol. Finally, $g-C_3N_4/MZF$ composites were prepared by drying at $60^\circ C$ for 12 hours. According to this method, $g-C_3N_4/MZF$ catalysts in different mass ratios (1:1, 2:1, 3:1 and 3:2) of $g-C_3N_4/MZF$ were prepared and thus named as $g-C_3N_4/MZF$ (1:1), $g-C_3N_4/MZF$ (2:1), $g-C_3N_4/MZF$ (3:1), and $g-C_3N_4/MZF$ (3:2), respectively.

3. Results and discussion

3.1 Structural analysis

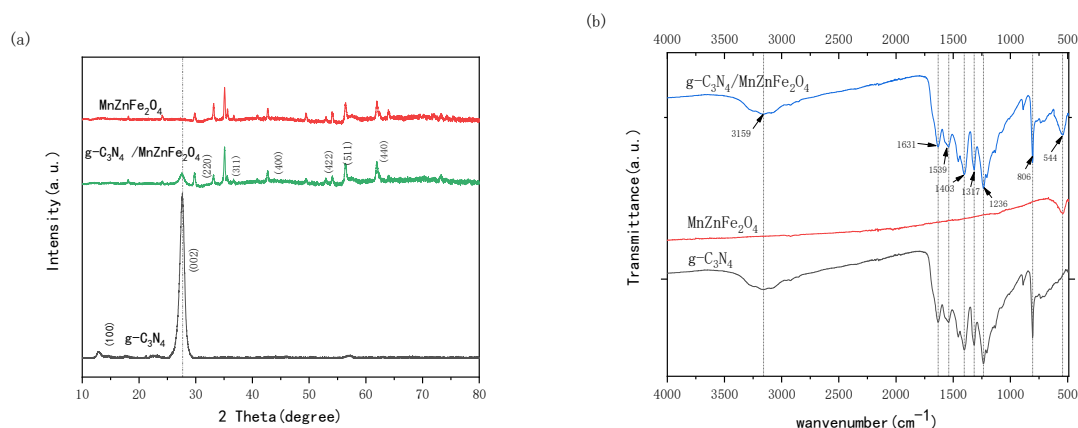


Fig.1 (a) XRD spectrum of each substance; (b) FTIR spectrum of each substance

Fig. 1 (a) shows the XRD spectrum of MZF, $\text{g-C}_3\text{N}_4$ / MZF, and $\text{g-C}_3\text{N}_4$. The diffraction peaks of MZF appear at 30.5° , 35.0° , 43.1° , 53.5° , 57.1° , and 62.6° , respectively corresponding to (220), (311), (400), (422), (511) and (440) crystal planes. The diffraction peak of MZF agrees well with the standard diffraction peak of the standard cards (JCPDS74-2401)^[11]. Although the difference of XRD pattern is not large, the XRD peak of MZF material is clearly broadened and its grain size is smaller. As can be seen from figure 1 (a), $\text{g-C}_3\text{N}_4$ has a weak diffraction peak at 13.3° , can be indexed as (100) diffraction surface (JCPDS87-1526)^[13]. And formed in a 3-s-triazine structural unit constituting a plane corresponding to the (100) crystal plane of $\text{g-C}_3\text{N}_4$. And a strong diffraction peak appears at 27.6° , which is caused by the stacking of aromatic layers. The crystal phase of MZF in $\text{g-C}_3\text{N}_4$ / MZF composite has no change. And the diffraction peak (002) of $\text{g-C}_3\text{N}_4$ exists in the XRD spectrum of $\text{g-C}_3\text{N}_4$ / MZF. However, the diffraction peak (100) of $\text{g-C}_3\text{N}_4$ has not been observed, which means some defects was caused in $\text{g-C}_3\text{N}_4$ by MZF, meanwhile the periodic structure is destroyed

Fig. 1 (b) is a FTIR spectrum diagram of $\text{g-C}_3\text{N}_4$ / $\text{MnZnFe}_2\text{O}_4$, $\text{MnZnFe}_2\text{O}_4$ and $\text{g-C}_3\text{N}_4$. The peak located at 3159 cm^{-1} is the stretching vibration peak of the N-H bond. The absorption peaks located at 1631 cm^{-1} correspond to the stretching vibration and bending vibration of O-H bonds, respectively^[6]. The absorption peak of 544 cm^{-1} in pure $\text{MnZnFe}_2\text{O}_4$ ^[11] corresponds to the symmetric tensile vibration peak of the medium Fe-O band. The primary absorption peaks in pure $\text{g-C}_3\text{N}_4$ are sequentially located at 1236, 1317, 1403 and 1539, corresponding to typical stretching vibrations of the carbon nitrogen hexagonal ring. The absorption peak at 806 cm^{-1} corresponds to the bending vibration of s-triazine ring system. All the characteristic absorption peaks of $\text{g-C}_3\text{N}_4$ and $\text{MnZnFe}_2\text{O}_4$ were observed in the composite photocatalyst $\text{g-C}_3\text{N}_4$ / $\text{MnZnFe}_2\text{O}_4$, indicating that $\text{g-C}_3\text{N}_4$ and $\text{MnZnFe}_2\text{O}_4$ coexist in the composite photocatalyst, which is consistent with the XRD results.

3.2. Morphology and microstructure analysis

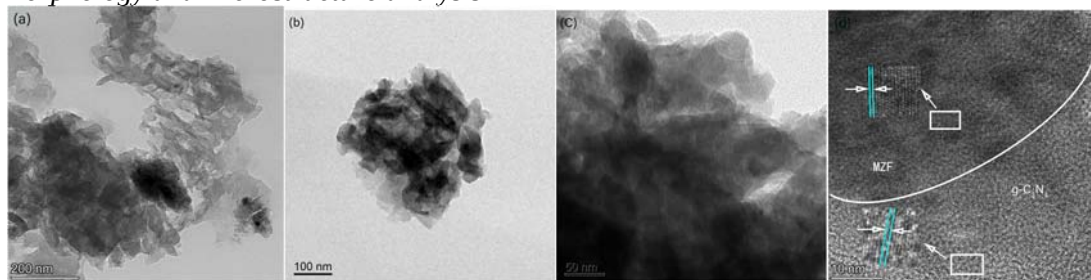


Fig.2. FESEM image of (a) bare $\text{g-C}_3\text{N}_4$; (b), (c) and (d) HRTEM images with $\text{g-C}_3\text{N}_4$ / MZF(3:2) hybrid.

By FESEM and TEM (Figs. 2(a) and 2(b)), g-C₃N₄ has a graphene like layered structure. MZF is the dark part, and g-C₃N₄ is the bright part. It can be clearly observed that g-C₃N₄ is well crossed with each other (Fig. 2(c)). Meanwhile the junction of MZF and g-C₃N₄ is smooth, which further verifies the formation of MZF and g-C₃N₄ heterojunction. In Fig. 2(d), MZF is surrounded by g-C₃N₄, with MZF core and g-C₃N₄ as shell, which further verifies the g-C₃N₄ / MZF heterojunction. The plane of the two - atom lattice stripe corresponding to the (311) plane of the MZF, and the (002) plane of g-C₃N₄, are consistent with the results of XRD. Before the TEM observation, the complex was found to have a strong interaction with the g-C₃N₄ / MZF even after the long term ultrasonic treatment, and the g-C₃N₄ / MZF heterojunction was structurally heterogeneous, not the physical mixture of the two separated phases. This tight coupling facilitates charge transfer between g-C₃N₄ and MZF, facilitates separation of photogenerated electron-hole pairs and improves photocatalytic performance.

3.3. Catalytic Evaluation

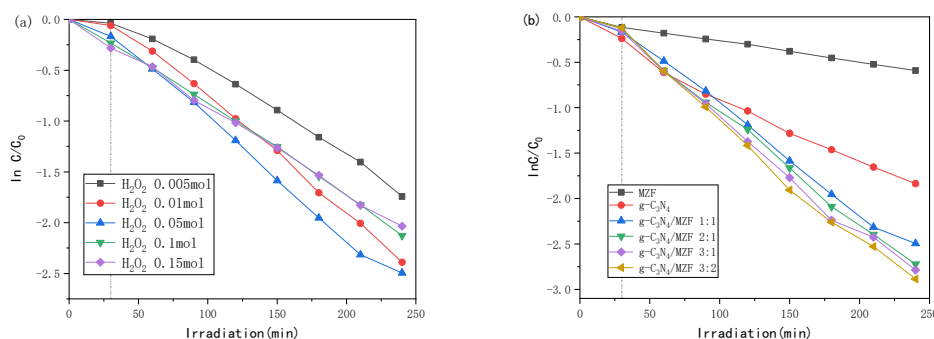
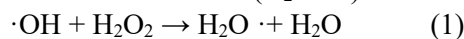


Fig 3. Kinetics of Rh B degradation over H₂O₂ concentration (a) and the different photocatalysts (b). Insets: degradation rate constant k . (Reaction conditions: [Rh B] = 10 mg/L, [catalyst] = 0.5 g/L, T = 25 °C).

The degree of degradation of Rh B solution was evaluated by the photocatalytic activity of the composite, the reaction was carried out by a photoreaction instrumentation and simulated solar light (with a 300 W xenon lamp source) as a visible light source. It is said that a 0.05 g catalyst is added to 100.00 mL concentration of 10 mg.L⁻¹ Rh B solution, and the solution suspended in the dark is stirred 30 minutes to achieve the adsorption-desorption is balanced. A small sample (5ml) of this floating solution is taken every half hour and centrifuged at a rotational speed of 6000rpm / min, then the upper cleaning solution is taken. The absorbance was measured at 554 nm by UV-VIS spectrophotometer^[14]. In (0-30 min) is stirred in a dark condition, and the sample reaches Rh B and adsorption - desorption equilibrium. It can be seen from Figure 3 (b) that the degradation effect of MZF catalyst on Rh B dye is poor under dark conditions (0-30 min) and visible light irradiation (30-240 min). Pure g-C₃N₄ exhibits high photocatalytic activity because of its equal band gap and unique electronic structure. However, the g-C₃N₄ / MZF composite catalyst had obvious degradation effect on Rh B under the irradiation of H₂O₂ and visible light, showing a high catalytic effect, and the degradation rate reached 95.1%. This is due to the effective heterojunction of g-C₃N₄ / MZF complex.

In order to better explain the reaction of degradation of Rh B, the experimental data were fitted by pseudo first-order model, which accorded with the first-order kinetic equation. The rate constant (k) is obtained from the data in the following formula: $\ln(C/C_0) = kt$, where k is the apparent first-order rate constant (min⁻¹), t is the illumination time (min), C_0 is the initial concentration of the solution, and C is the concentration at the reaction time t under light. The results showed that the photodegradation of Rh B by $\ln(C/C_0)$ was a first-order kinetic reaction. The best doping ratio of the composite was determined by the photocatalytic activity^[11]. The degradation rate of g-C₃N₄ / MZF(3:2) complex was the highest ($k = 0.028 \text{ min}^{-1}$). The experimental results show that the concentration of H₂O₂ is an important factor affecting the degradation efficiency of Rh B. Fig. 3(a) shows that the degradation

rate constant of RhB increases significantly in the range of 0.005 to 0.50M. However, further increasing the initial concentration of H_2O_2 to 0.1 M can reduce the degradation rate constant. This phenomenon can be explained by the inhibition of hydrogen peroxide. The increase of H_2O_2 concentration can promote the scavenging of $\cdot\text{OH}$ radicals (see equation 1) and the subsequent formation of new radicals ($\text{H}_2\text{O} \cdot$). The oxidation potential is much lower than that of $\cdot\text{OH}$ ^[14].



3.4. Reaction Mechanism.

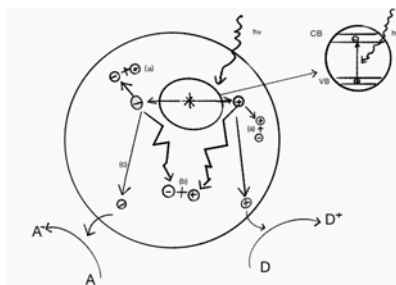


Fig.4 Mechanism diagram of photocatalytic reaction

As shown in the figure 4, the process (a) in the figure is that photogenerated electrons and holes migrate to the surface of semiconductor materials for recombination; The process (b) is the recombination of photogenerated electrons and holes in semiconductor materials. The remaining uncomposite electrons and holes participate in the reactions of (c) and (d), the photocatalysis reaction occurred on the surface of semiconductor materials. Under visible light irradiation, MZF and $\text{g-C}_3\text{N}_4$ are excited, and photogenerated holes and electrons are in valence band (VB) and conduction band (CB), respectively. The photogenerated electrons in MZF and $\text{g-C}_3\text{N}_4$ migrate to each other, which can effectively improve the separation of photogenerated electron hole pairs and greatly reduce the possibility of photogenerated electron recombination. The separated photogenerated electron and holes react with surface adsorbed substances to produce strong oxidants $\cdot\text{OH}$, and $\cdot\text{OH}$ decomposes organic matters in the waste water efficiently. The recombination of $\text{g-C}_3\text{N}_4$ and MZF can form heterojunction structure, which leads to the improvement of photodegradation efficiency^[15,16].

4. CONCLUSIONS

Magnetic recoverable $\text{g-C}_3\text{N}_4$ and $\text{MnZnFe}_2\text{O}_4$ composites were prepared by self-assembly method and used for photodegradation of Rhodamine B aqueous solution. The prepared sample $\text{g-C}_3\text{N}_4/\text{MZF}$ has good photo Fenton activity and magnetism, and is easy to be separated. Under the same conditions, compared with the simple mixture of $\text{g-C}_3\text{N}_4$ and $\text{MnZnFe}_2\text{O}_4$, the activity of $\text{g-C}_3\text{N}_4/\text{MZF}$ composite photocatalyst is improved, the recombination probability of photogenerated electrons and holes is reduced, and the visible light absorption of the catalyst is enhanced.

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