A facile strategy to fabricate polyaniline-ferrite (PANI-MFe₃O₄ₓ, M = Cu, Y) nanocomposites with differing ferrite content via an in situ oxidative polymerization method has been reported. X-ray diffraction, scanning electron microscopy and ultraviolet-visible diffuse reflectance spectroscopy were employed to study the phase structure, morphology and optical properties of the samples. The photocatalytic activity of as-prepared photocatalysts is evaluated by the degradation of rhodamine B in aqueous solution under visible-light (420 nm < λ < 800 nm) irradiation. The results show that polyaniline-ferrite nanocomposites exhibit higher photocatalytic activity and stability than both the naked ferrite and pure PANI. Among these as-prepared photocatalysts, PANI-CuFe₂O₄ composites with a PANI-to-ferrite ratio of 1:1 possess the highest degradation rate. Its apparent rate constant is 0.081 min⁻¹, which is 3.71 times as much as that of pristine PANI (0.021 min⁻¹). The presence of synergetic effect between PANI and ferrites is believed to play a vital role in affecting the photoactivity.

Key-words : PANI, Ferrite, Photocatalysis

1. Introduction

Nowadays, increasing environmental pollution and the shortage of clean water have become compelling problems threatening the development of human society.¹ It is estimated that about 10–15% of organic dyes mainly from industrial waste are directly discharged into rivers.² For this reason, tremendous efforts have been dedicated to water treatment research and substantial progress.³

Semiconductor photocatalysis, a promising “green” technology,⁴ has been widely applied in purifying air, solar water splitting, and eliminating the organic dye due to its strong photocatalytic activity and environmental friendliness.⁵–⁸ However, most of the semiconductor nanomaterials still have several problems, such as low photocatalytic activity, complex operations for recycling, and low stability. Some semiconductors require high-energy ultraviolet light (UV) radiation for photocatalytic activation due to their wide energy band gap.⁹ It is well-known that UV light accounts for only a small fraction (5%) of the solar energy compared with visible light (45%). Therefore, it is indispensable and highly desirable to develop an efficient visible-light-responsive photocatalyst to treat organic dyes. Enormous efforts have been devoted to develop a series of new visible-light responsive organic and inorganic photocatalysts, such as polyaniline (PANI)-graphene,¹⁰ PANI-TiO₂,¹¹,¹² PANI-ZnO,¹³ PANI-CdO,¹⁴ PANI-CoFe₂O₄,¹⁵,¹⁶ and so on.

Magnetic ferrites with general formula MFe₃O₄ₓ have been a major subject of intensive research due to their potential use in catalysis, lithium ion batteries,¹⁷,¹⁸ photocatalytic hydrogen production,¹⁹ photocatalytic degradation²⁰ and biotechnology.²¹ There are several strategies for synthesizing the magnetic ferrites, such as co-precipitation,²² hydrothermal method,²³ sol–gel,²⁴ micro-emulsions,²⁵ solid state reaction method,²⁶ combustion method and high-energy ball milling.²⁷ The structural and magnetic properties of ferrites are strongly influenced by their microstructures and composition, which are sensitive to the synthesis method.²⁸ Recently, our group has reported that single-crystalline YFeO₃ particles with the perovskite structure can be fabricated through a facile salt-assisted solution combustion synthesis.²⁹

Conducting polymer PANI has received extensively investigated owing to its narrow band gap (2.8 eV), high absorption capacity in the visible light range and high mobility of charge carriers. In addition, PANI not only is an electron donor but also is an excellent hole acceptor. Very recently,²⁰ we have found that there exists a synergistic effect between semiconductor photocatalyst and PANI, and PANI can increase the separation efficiency of photogenerated electron–hole pairs, resulting in enhanced photocatalytic activity.

In this work, we provide a simple and feasible strategy to synthesize the magnetically recyclable polyaniline-ferrite (PANI-MFe₃O₄ₓ, M = Cu, Y) photocatalysts via in situ oxidative polymerization. The photocatalytic activity of polyaniline-ferrites was highly enhanced after PANI addition, compared to both the pristine PANI and naked ferrite.
2. Experimental section

2.1 Preparation of photocatalysts

All the reagents used in our experiments were of analytical purity and were used without further purification. We employed salt-assisted solution combustion syntheses (SSCS) method, which reported in our previous work, to prepare ferrite nanoparticles using alanine as a fuel and corresponding metal nitrates as oxidants.\(^{29}\)

The polyaniline-ferrite hybrids were prepared by in situ oxidative polymerization method. The typical preparation of PANI/ferrite photocatalyst was as follows: CuFe\(_2\)O\(_4\) nanoparticles (0.50 g), and ammonium peroxydisulfate (1.25 g) were dispersed in 100 mL of 1 mol/L HCl aqueous solution under ultrasonic vibrations for 30 min to obtain a uniform suspension. Then, aniline (0.50 mL) was added into this mixture dropwise under vigorously stirring in an ice-water bath, after which the resulting mixture was allowed to polymerize under stirring for 6 h in an ice-water bath. Finally, the CuFe\(_2\)O\(_4\)-PANI hybrid was filtered out, washed with large amount of deionized water, and then dried at 60 °C. For comparison, pure PANI was prepared without the addition of ferrite.

2.2 Characterization

The X-ray power diffraction of the products was recorded on a PANalytical X’Pert Pro X-ray diffractometer with Cu-K\(\alpha\) radiation (\(\lambda = 0.154178\) nm). The product morphology was analyzed by field emission scanning electron microscopy (SEM) (JEOL JSMT300, operated at 10 kV). UV–vis diffuse reflectance spectra of the samples were obtained on an UV–vis spectrophotometer (Cary 5000). Fourier transform infrared (FT-IR) spectra of the polymers in KBr pellets were recorded on a Nicolet Avatar 670 FT-IR spectrometer (Nicolet Corp., USA).

2.3 Tests of photocatalytic activity

The photocatalytic degradation of rhodamine B (RhB) was performed in quartz tubes under visible-light irradiation in the presence of different photocatalysts. The visible-light source was a 175 W metal halide lamp with a cut-off filter (\(\lambda > 400\) nm). The catalyst (0.10 g) was suspended in 100 mL of RhB solution (10 mg·L\(^{-1}\)). Prior to irradiation, the suspensions were magnetically stirred in the dark for 30 min in order to reach adsorption–desorption equilibrium between the catalyst and RhB. After equilibrium, the mixture was continuously stirred under visible-light irradiation and 0.10 mL of 30% H\(_2\)O\(_2\) was added. At given time intervals, 3 mL aliquots were sampled and centrifuged to remove the catalyst. The degraded solutions were analyzed using UV–visible spectrophotometer, and the absorption peak at 553 nm was monitored.

3. Results and discussion

3.1 X-ray diffraction (XRD)

Figure 1 shows the XRD spectra of ferrites, PANI and PANI-ferrite composites. For PANI, there is a broad diffraction peak centered at 2\(\theta = 25.3^\circ\) corresponding to (101) can be observed, which can be put down to the periodicity parallel and perpendicular to the polymer chains. In the case of naked copper and yttrium ferrite, all the characteristic diffraction peaks could well be indexed to spinel structure CuFe\(_2\)O\(_4\) (JCPDS:34-0425) and perovskite YFeO\(_3\) (JCPDS: 39-1489), respectively. No peaks of any other phases or impurities are observed, suggesting the formation of pure ferrite compound. The PANI-ferrite composite displays the characteristic peaks of ferrite, but the intensity of peaks significantly decreases. For PANI-CuFe\(_2\)O\(_4\) nanocomposites [Fig. 1(a)], the diffraction peak intensity centered at 35.2° corresponds to the (311) plane of ferrite weaken greatly due to PANI addition. For PANI-YFeO\(_3\) nanocomposites [Fig. 1(b)], the diffraction peak intensity centered at 33.1° corresponds to the (121) plane of ferrite weaken greatly due to PANI addition. There is no diffraction peak of PANI is observed for all PANI-based composites, implying that PANI is amorphous in the composites.\(^{30}\)

3.2 Infrared spectra

Figure 2 shows the FT-IR spectra of PANI, copper and yttrium ferrites, and PANI-ferrite nanocomposites. The bands in the region 500–650 cm\(^{-1}\) are attributed to pure
ferrite intrinsic vibration of the tetrahedral sites in absence of any organic. For polyaniline, two peaks of 1486 and 1577 cm\(^{-1}\) are put down to C=\(\equiv\)C stretching of benzenoid and quinoid ring structure. Bands at 1248 and 1303 cm\(^{-1}\) are designated as C-N stretching of the benzenoid ring, while the peak of 3250–3540 cm\(^{-1}\) is ascribed to N-H stretching mode. The peaks at 1041–1097 cm\(^{-1}\) corresponds to C-H bending mode. For PANI-ferrite nanocomposites (Fig. 2), similar characteristic bands as PANI are observed.

3.3 Morphology

Representative SEM images of PANI, CuFe\(_2\)O\(_4\), YFeO\(_3\), PANI-CuFe\(_2\)O\(_4\) and PANI-YFeO\(_3\) are shown in Fig. 3. It is obvious that the PANI samples consist of irregular particles with the diameter in the range of 300–500 nm which are heavily agglomerated. The ferrite particles fabricated by SSCS method are irregular in shape and sizes. Figures 3(b) and 3(c) exhibit the typical morphology of ferrite particles (CuFe\(_2\)O\(_4\) and YFeO\(_3\)) obtained in the SSCS route, foamy agglomerated particles with a wide distribution and presence of large voids in its structure.\(^{29}\)

Figures 3(d) and 3(e) show that the PANI-CuFe\(_2\)O\(_4\) and PANI-YFeO\(_3\) nanocomposite still retain the morphology of the pristine PANI, on which ferrite nanoparticles disperses uniformly into the matrix of PANI.

3.4 Optical absorption properties

The PANI and ferrite composite PANI was analyzed by diffuse UV–visible reflectance spectroscopy to investigate their optical properties. Figure 4 shows the band edge absorption spectra of the pristine PANI and PANI–ferrite nanocomposites. The band-gap of the nanocomposites was calculated by using the equation of 
\[
\alpha h\nu = A (h\nu - E_g)^n/2,
\]
Where \(\alpha\) is the absorption coefficient, \(h\) is the Planck constant, \(\nu\) is the frequency of light, \(E_g\) is the band-gap, \(A\) is a constant and \(n\) depends on whether the transition is direct \((n = 1)\) or indirect \((n = 4)\). By plugging into the formula, the band gap energy of PANI and PANI-ferrite composite can be estimated from a plot of \([F(R)E]\)^{1/2} versus the photon energy \((h\nu)\). The estimated band gap energies of PANI homopolymer, PANI-ferrite composite
were approximately 2.23 and 2.04 eV, respectively (See in the inset of Fig. 4).

3.5 Photocatalytic activity and stability

RhB is chosen as the representative dye pollutant to evaluate the photocatalytic performance of as-prepared samples. The photodegradation process was carried out under visible-light irradiation \((\lambda > 400 \text{ nm})\). Figure 5 show the photoactivity curves and the apparent reaction kinetic curves of the samples for the degradation of RhB.

As can be seen from Figs. 5(a) and 5(b), after 100 min, only 34.2 and 36.1% RhB are degraded by the naked CuFe\(_2\)O\(_4\) and YFeO\(_3\), respectively. It is obvious that the PANI–ferrite nanocomposites with a PANI-to-ferrite ratio of 1:1 exhibits a higher photocatalytic activity than the naked ferrites and the pristine PANI. With the addition of PANI, the photocatalytic activities of the catalysts are dramatically enhanced [Figs. 5(a) and 5(b)]. Among the polyaniline-ferrite photocatalysts with different ferrite contents, both PANI/CuFe\(_2\)O\(_4\) and PANI/YFeO\(_3\) with a PANI-to-ferrite ratio of 1:1 exhibit the highest photocatalytic activity for the degradation of RhB. It is well-known that photocatalytic oxidation of organic pollutants follows Langmuir–Hinshelwood kinetics. This kind of reaction can be described by pseudo-first-order kinetics.\(^{31}\) The corresponding kinetic constants \((k)\) are calculated and displayed in Figs. 5(c) and 5(d). The apparent rate constant of the PANI-CuFe\(_2\)O\(_4\) (1:1) and PANI-YFeO\(_3\) (1:1) is 0.081 and 0.048 min\(^{-1}\), respectively, which is 3.71 times and 2.27 times as much as that of pristine PANI (0.021 min\(^{-1}\)). The presence of synergic effect between PANI and ferrites is believed to play a crucial role in affecting the photoreactivity.

The stability of photocatalyst is a very important characteristic with regard to practical application. The reusability and stability of polyaniline-ferrites was evaluated by using cyclic experiments. After each photodegradation cycle, catalyst powders were collected by magnet and reused in

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**Fig. 4.** Diffuse UV–visible spectra of PANI and nanocomposites of PANI-CuFe\(_2\)O\(_4\) and PANI-YFeO\(_3\).

**Fig. 5.** Photodegradation of RhB over (a) PANI, CuFe\(_2\)O\(_4\) and PANI-CuFe\(_2\)O\(_4\), (b) PANI, YFeO\(_3\) and PANI-YFeO\(_3\); (c) and (d) Rate constant of the PANI, PANI-CuFe\(_2\)O\(_4\), and PANI-YFeO\(_3\) for RhB photodegradation.
the next cycle. As shown in Fig. 6(a), after three times run of degradation reaction, the PANI-CuFe₂O₄ (1/1) still exhibits excellent photocatalytic performance and stability, and remains a decolorization ratio of 96% for the photodegradation of RhB under visible light. However, for PANI-YFeO₃ photocatalysts, there is an obvious decrease in photocatalytic activity and only 68% of RhB was degraded after three cycles. Moreover, owing to the excellent magnetic property of copper ferrite, PANI-CuFe₂O₄ can be easily separated from the heterogeneous solution reaction system by an external magnet after photocatalysis [Fig. 6(b)].

3.6 Photocatalysis mechanism

Electrochemical impedance spectroscopy (EIS) is a powerful analysis technique to characterize the electrical conductivity of the catalyst and understand the synergistic effect between PANI and ferrite. The smaller arc diameter in Nyquist plots implies a lower resistance of the interfacial charge transfer in the electrode–electrolyte interface region on the surface of electrode. As shown in Fig. 7, for the pure PANI and the naked ferrite, both of them show a pronounced arc at higher frequencies in the EIS plane. The radius becomes smaller when PANI was coupled with CuFe₂O₄ and YFeO₃. Both the PANI-CuFe₂O₄ (1/1) and the PANI-YFeO₃ (1/1) electrodes show much smaller arc radius than pure ferrite electrode, which means a more effective separation of photogenerated electron–hole pairs and faster transfer of interfacial photogenerated charge. It is obvious that the PANI-CuFe₂O₄ has the smallest radius.

It is vitally important to identify the main active oxidant in the photocatalytic reaction process for better understanding the mechanism. It is well-known that the active oxidants generated in the photocatalytic process can usually be measured through trapping by triethanolamine (TEOA) (hole scavenger) and isopropanol (IPA) (hydroxyl radical scavenger). Figure 8 displays the trapping experiment of active species during the photocatalytic degradation of RhB over PANI-CuFe₂O₄ and PANI-YFeO₃ under visible light irradiation. It can be seen that the photodegradation rate was obviously restrained after the injection of TEOA and IPA, which suggests that both holes (h⁺) and hydroxyl radicals (·OH) are the main active species in this system.

The general photocatalysis mechanism is that the electrons of the photocatalyst material excite from the valence band (VB) to the conduction band (CB) and leave positive holes in the VB, resulting in the electron–hole pair eᵥCB.
/hVB+ generation. On the basis of the experimental results, a possible mechanism for the PANI-ferrite photocatalytic enhancement is proposed as follows and illustrated in Fig. 9.

Under visible light irradiation both PANI and ferrite undergo charge separation, electrons (e⁻) in the VB of photocatalysts can be excited to their CB, causing the generation of h⁺ in the VB simultaneously. It is known that PANI homopolymer is a conducting polymer. The ferrite can act as a sink for the photogenerated electrons, and the PANI could act as an acceptor for the photogenerated holes in the composite photocatalysts. For the PANI-ferrite composite, ferrite and PANI closely combine together and form interfaces. The excited electrons in \( \pi^* \)-orbital of PANI can readily inject into CB of ferrite. Simultaneously, the photogenerated holes in VB of ferrite move to the \( \pi \)-orbital of PANI. PANI offer an electron to the CB of ferrite and itself accept a hole from VB of ferrite, leading to a restraining of the recombination of the electron–hole pair and finally promoting the migration efficiency of photogenerated electron–hole on the interface. Then, the electrons can react with the dissolved oxygen to produce superoxide anion radicals (O₂⁻•), while the holes react with the hydroxide ions to form •OH. Finally, the active species (holes and hydroxyl radicals) oxidize the dye molecules.

4. Conclusions

The magnetically recyclable polyaniline-ferrite (PANI-MFeₓO₃ₓ, M = Cu, Y) photocatalysts have been prepared via an in situ oxidative polymerization method. The as-prepared PANI-ferrite composites show much higher photocatalytic activities for the degradation of RhB than the naked ferrite due to the matched band structure of two components, more effective charge transportation and separations. Among all as-prepared photocatalysts, PANI-CuFe₂O₄ composites with a PANI-to-ferrite ratio of 1:1 possess the highest degradation rate. Its apparent rate constant is 0.081 min⁻¹ and is 3.71 times as much as that of pristine PANI (0.021 min⁻¹). The trapping experiments show that h⁺ and •OH radicals are the main reactive species in the photodegradation of RhB. Furthermore, the composites could be easily separated and recycled by a magnet. After three times run of degradation reaction, the PANI-CuFe₂O₄ (1/1) still exhibits excellent photocatalytic performance and stability, and remains a decolorization ratio of 96% for the photodegradation of RhB under visible light. The greatly enhancement in photocatalytic performances can be attributed to the synergic effect between polyaniline and ferrite, which can lead to efficient charge separation.

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