Synthesis of polypyrrole-modified Fe₃O₄/SiO₂/TiO₂ nanocomposite microspheres and their photocatalytic activity

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Abstract

A polypyrrole-modified Fe₃O₄/SiO₂/TiO₂ composite material was successfully synthesized on the FST surface by in situ polymerization of pyrrole. Structural, morphological and magnetic response of Fe₃O₄/SiO₂/TiO₂/PPy(FST/PPy) were characterized by transmission electron microscopy, scanning electron microscopy, X-ray diffraction pattern, Fourier transform infrared spectroscopy and energy-dispersive X-ray spectroscopy, etc. Through SEM images, the crystal sizes of the prepared FST/PPy nanoparticles were determined to be about 110 nm. The catalytic activity of FST/PPy was evaluated by the degree of decomposition of rhodamine B under ultraviolet and visible light, respectively. FST/PPy had the photocatalytic activity under the action of the light: the degradation rate of rhodamine B reached 92.8% and 63.5% after 3 h of UV and Vis light irradiation, respectively. Especially, compared with FST, the degradation rate has shown obvious improvement under the action of Vis light. Furthermore, FST/PPy photocatalyst could be easily recycled using a magnet.

1. Introduction

Photocatalysis technique in wastewater treatment is considered as the most effective method thanks to its high effectiveness, simple operation, no secondary pollution and low cost [1–3]. In particular, the development of better photocatalysts with excellent visible (Vis) light response is a research area that is drawing attention from researchers due to its wide application range such as environmental purification, hydrogen production and energy storage, etc [4–6]. Among numerous photocatalysts, TiO₂ is one of the materials which have been widely used in the wastewater treatment because of its excellent photocatalytic activity, low manufacturing cost, and high chemical stability [7]. However, TiO₂ can be used by absorbing only the ultraviolet (UV) region of the solar spectrum, due to its wide band gap (3.20 eV) [8]. In addition, the high percentage of electron–hole recombination of TiO₂ is another important factor hindering the catalytic activity [9]. Therefore, some composite materials about TiO₂ with Vis light response have been extensively studied in recent years to extend band gap and enhance the charge transfer ability [10]. For example, Zhao et al synthesized a BiOBr-TiO₂-graphene composite by combining BiOBr and graphene with TiO₂, and studied its Vis light response [11]. Xiao tong Sun et al synthesized TiO₂@polydopamine photocatalyst material using self-assembly method and confirmed the range of its light utilization through decomposition experiments on rhodamine B under Vis light [12]. Xiubing Huang et al synthesized a Fe₃O₄/SiO₂/TiO₂ (FST)- polyaniline composite material with a core–shell structure and studied its catalytic performance and recycling ability under Vis light [13]. Clearly, the composite materials about TiO₂ exhibited enhanced Vis light utilization and improved catalytic activity.

Conductive polymers are widely used in catalysts, charge storage and optoelectronic devices thanks to their excellent electronic and optical properties such as high electron mobility, high photon absorption ability,
excellent stability and material diversity under Vis light [14, 15]. Amidst many conductive polymers, Polypyrrole (PPy) has superior Vis light absorption capacity, high mobility of electric charge and eco-friendliness [16]. PPy is also widely used in preparation of nanocomposite materials, because of its high conductivity, favorable physicochemical properties and easy manufacturing [17]. Moreover, like most conductive polymers, PPy is a p-type semiconductor that works as good hole transporter and efficient electron donor in the synthesis of nanocomposites, and a good material for the sensitization of TiO2 [18].

Catalysts with magnetic response characteristics can be easily separated from the mixture using a magnetic material and recycled [19]. Rashid et al synthesized a nanocomposite material with magnetic response characteristics by inserting a silicon layer between Fe3O4 core and TiO2 [20].

If a nanocomposite material with magnetic response characteristics is synthesized by combining PPy, which is widely used as a conductive polymer material with TiO2, it will be possible to enhance the performance and the efficiency of the catalyst. As far as the authors are aware, little or no research has been done in this regard. Based on above discussion and analysis, the preparation of FST/PPy catalyst with magnetic response characteristics and its catalytic performance under Vis light were studied in this paper. The characterization of the prepared FST/PPy was performed by SEM, TEM, FT-IR and XRD. The photocatalytic activity of FST/PPy was evaluated by measuring the degradation of rhodamine B (RhB) under irradiation of Vis light and UV light. Finally, through the separation and reuse of FST/PPy from the mixture, its stability and recycling were confirmed.

2. Experiment

2.1. Materials
Ferric chloride (FeCl3 · 6H2O, AR), ferrous sulfate (FeSO4 · 7H2O, AR), tetraethyl orthosilicate (TEOS, AR), tetrabutyl titanate (TBT, AR), weak nitric acid (HNO3, AR) were purchased from Shanghai Chemical Reagent Co., Ltd (Shanghai, China). Pyrrole (98%), Sodium dodecyl benzene sulfonate (C18H29NaSO3, 95%), Rhodamine B (RhB), ethyl alcohol (C2H5OH, 95%) and aqueous ammonia (28 wt %) were supplied by Jiangtian Chemical Technology Co., Ltd (Tianjin, China). All chemical reagents were directly used without further purification.

2.2. Synthesis of nano-Fe3O4
In a 200 ml beaker, a mixture of 2.78 g of FeSO4, 4.73 g of FeCl3 and 100 ml of deionized water was ultrasonically dispersed for 30 min and then placed into a 500 ml three-necked round bottom flask equipped with two needles (an inlet needle and an exit needle) pierced through a rubber septum, a dropping funnel and a mechanical stirrer. At this time, the two needles (the exit needle and the inlet needle) were connected with and a mineral oil bubbler and a compressed nitrogen tank, respectively. After replacing the air in the flask with nitrogen, the flask was heated to 65 °C. Then, using the dropping funnel, 30 ml of aqueous ammonia (28 wt%) was added drop by drop to the flask with mechanical stirring. After stirring this content at 85 °C for 40 min, the reaction was stopped. After placing the sufficiently cooled reaction mixture in a 500 ml beaker, the black solid powder was separated from the mixture by the external magnetic material. Finally, the prepared Fe3O4 solid powder was washed with ethyl alcohol and deionized water 5 times to disappear the ammonia smell and then dried in a vacuum at 50 °C for 8 h [21].

2.3. Preparation of nano-Fe3O4/SiO2
The mixture of 0.2 g of Fe3O4 and 50 ml of ethyl alcohol was put into a 500 ml two-necked round bottom flask equipped with a dropping funnel and a mechanical stirrer. 5 ml of aqueous ammonia (28 wt%) and 20 ml of deionized water were added drop by drop to the flask using the dropping funnel with vigorous stirring. After adding 2 ml of tetraethyl orthosilicate (TEOS) through the dropping funnel, the contents of the flask was stirred at room temperature for 10 h. The solid material separated by an external magnet was washed with deionized water and ethyl alcohol 5 times and dried in a vacuum at 50 °C for 12 h [22].

2.4. Synthesis of core–shell Fe3O4/SiO2/TiO2 (FST)
The mixture of 0.5 g of Fe3O4/SiO2, 120 ml of ethyl alcohol, 100 ml of deionized water and 2 ml of aqueous ammonia(28 wt%) was dispersed under the ultrasound for 30 min. It was put into a 500 ml three-necked round bottom flask equipped with a dropping funnel, a mechanical stirrer and a reflux condenser. After adding 7 ml of TBT dropwise to the flask through the dropping funnel, the contents were mechanically stirred at 45 °C for 24 h. After placing the mixture into a 500 ml beaker, the solid powder was separated by the magnet. Finally, FST was washed with deionized water and ethyl alcohol and then kept in a vacuum at 60 °C for 10 h [23].
2.5. Preparation of FST/PPy
First, 0.2 g of FST and 0.8 g of FeCl₃·6H₂O were added to 100 ml of deionized water in a 200 ml beaker. Then, the mixture was mechanically stirred at room temperature for 30 min to accumulate Fe³⁺ ions on the surface of the nanocomposite FST. 10 ml of C₁₈H₂₉NaSO₃ solution (3 wt%) was added into the beaker to catalyze the polymerization of pyrrole. After putting quantitative pyrrole monomer into the beaker, the content was mechanically stirred at 5 °C for 10 h to maintain the polymerization process. The separated FST/PPy was washed with deionized water and ethyl alcohol and dried in a vacuum at 60 °C for 10 h to obtain a brown powder. In this experiment, different volumes of pyrrole were used to prepare FST/PPy. The obtained material were referred to as FST/PPy(x), where x is the volumes (ml) of added pyrrole.

2.6. Characterization
X-ray diffraction (XRD) patterns were recorded by Rigaku D/max-2500/PC, Japan with Cu-Kα radiation. Scanning electron microscope (SEM) images and energy-dispersive x-ray (EDX) spectra were recorded using a Hitachi S4800 microscope (Japan). FT-IR analysis of the samples was recorded by KBr pellets from 500 to 4000 cm⁻¹ with a resolution of 2 cm⁻¹ on the FTIR spectrometer (NICOLET-3809, USA). TEM images were obtained by JEM-2100F electron microscope (Japan) operated at 200 kV. N₂ adsorption/desorption isotherms were measured using a Micromeritics ASAP 2020 Analyzer (USA).

2.7. Photocatalytic degradation of RhB
The photocatalytic performances of FST and FST/PPy were tested by the degree of degradation of RhB under the irradiation of Vis light and UV light, respectively. As the UV irradiation source, a 300 W Xenon lamp (PLS-SXE300) with a cut-off filter (320 nm < λ < 780 nm) was used. The degree of RhB degradation was investigated with a Shimadzu UV-2600 spectrophotometer (Japan). After putting 0.05 g of FST, FST/PPy(1), FST/PPy(3), FST/PPy(5) into four 200 ml beakers containing 100 ml, 20 mg l⁻¹ RhB solution, respectively, the content was magnetically stirred in the dark for 30 min to allow RhB and catalyst to reach absorption/decomposition.
Results and discussions

3.1. Characterization of samples

Figure 1 showed the TEM images of Fe3O4, Fe3O4/SiO2, FST, FST/PPy(1), FST/PPy(3) and FST/PPy(5). In figure 1(A), Fe3O4 had a monodisperse structure with a distribution of about 100 nm. The silicon layer was densely formed around Fe3O4 core with a thickness of about 15 nm (figure 1(B)). Also, TiO2 layer with a thickness of about 40 nm was coated on the surface of Fe3O4/SiO2; its structure was very rough and porous (figure 1(C)). From the TEM images of FST/PPy(1), FST/PPy(3) and FST/PPy(5) shown in figures 1(D)–(F), it can be seen that PPy was formed on the FST surface with a thickness of about 15 nm, 25 nm and 33 nm.

The morphologic structure of the prepared Fe3O4, Fe3O4/SiO2, FST, FST/PPy(1), FST/PPy(3) and FST/PPy(5) was evaluated by SEM (figure 2). Fe3O4, Fe3O4/SiO2 and FST had a spherical structure with an average diameter of 40 nm, 55 nm and 90 nm (figures 2(A)–(C)). FST/PPy(1), FST/PPy(3) and FST/PPy(5) also exhibited spherical structures with average diameters of about 100 nm, 110 nm, and 120 nm, respectively (figures 2(D)–(F)). From the SEM images, it can be recognized that the size of the spheres increased due to the coating layer.

XRD patterns of the Fe3O4, Fe3O4/SiO2, FST and FST/PPy were presented in figure 3. The detection peaks at (220), (311), (400), (511) and (440) shown in figure 3(A) completely agree with the standard XRD spectral data of Fe3O4 [24]. The XRD patterns of Fe3O4/SiO2 (figure 3(B)) showed the same diffraction peak of Fe3O4, which means that the crystalline nature of Fe3O4 was still retained after silica coating. The XRD of FST confirmed that a series of diffraction peaks at positions 25.32°, 27.52° and 48.00° with lines (101), (004) and (200) was in accord with the recorded data of TiO2 (JCPDS 04-0477) (figure 3(C)). All the characteristic peaks of FST/PPy were almost the same as FST, except that the peak strength was slightly decreased (figure 3(D)). Adding the PPy layer caused the decrease in intensity of three previous parts and the increase in the crystal size of nanocomposites.

From the XRD patterns, the size of the prepared nanomaterials can be calculated using Scherrer formula. The size of nanomaterials calculated using Scherrer formula is as follows: Fe3O4 (41.3 nm) < Fe3O4/SiO2 (53.6 nm) < FST (93.2 nm) < FST/PPy(1) (104.3 nm) < FST/PPy(3) (109.3 nm) < FST/PPy(5) (120.3 nm). The result of the XRD patterns was consistent with the SEM and TEM results.
The existence of C, Fe, Si, Ti and O elements was confirmed through the EDX analysis of FST/PPy (figure 4). From the very weak peak of nitrogen in the EDX analysis, it is clear that PPy was less grafted to the surface of FST [25].
FT-IR of Fe₃O₄, Fe₃O₄/SiO₂, FST, FST/PPy(1), FST/PPy(3) and FST/PPy(5) was represented in figure 5. A strong peak following the Fe-O stretching vibration at about 588 cm⁻¹ and a peak related to OH detected at 3422 cm⁻¹ can be found in figure 5(A), which are completely consistent with those presented in the previous literature [26]. In figure 5(B), the peaks related to the Si-O-Si bond in SiO₂ were located in about 1085 cm⁻¹, indicating SiO₂ layer was covered on Fe₃O₄ [27]. A broad absorption peak between 400 cm⁻¹ and 800 cm⁻¹ in figure 5(C) was related to the Ti-O-Ti bond. This is clear evidence that TiO₂ layer was correctly formed on the Fe₃O₄/SiO₂ [28]. The peaks at 1196 cm⁻¹, 1568 cm⁻¹ and 964 cm⁻¹ (figures 5(D)–(F)) related with the C–N, C=C and C–H bond revealed that FST/PPy was correctly prepared [29].
The surface area and porous structure of the catalysts are quantified by nitrogen adsorption-desorption process. As shown in figure 6, all isotherms with a H3-type hysteresis loop indicated that both FST/PPy(5) and FST had mesopores with a diameter of 5–20 nm [30]. The relative size of surface area was calculated by the Brunauer-Emmett-Teller (BET) [31]. Table 1 showed the BET surface of the prepared samples.

Table 1. BET surface and pore volume of photocatalysts.

| Photocatalyst     | BET surface | Pore volume |
|------------------|-------------|-------------|
| FST              | 168.6 m² g⁻¹| 0.3973 cm³ g⁻¹|
| FST/PPy(5)       | 80.8 m² g⁻¹ | 0.453 cm³ g⁻¹ |

The magnetic properties of Fe₃O₄, Fe₃O₄/SiO₂, FST and FST/PPy(5) were evaluated by a Magnetic Property Measurement System (MPMS XL-7). The magnetization saturation values (Ms) of the prepared samples were shown in table 2. All magnetic catalysts revealed superparamagnetic response without the coercivity at 300 K (figure 7). The magnetic characteristics may be attributed to Fe₃O₄ which acts as superparamagnet.

Although the Ms value of FST/PPy(5) is about half that of pure Fe₃O₄, it is sufficient for separation and purification using an external magnet. Under the action of an external magnetic field, FST/PPy(5) was separated from the solution in the form of aggregates within 30 s. When the magnetic field was removed and the beaker was shaken, the aggregates were uniformly dispersed. It showed that the composite microspheres have excellent magnetic responsivity and redispersibility.
3.2. Photocatalytic activity of samples

The catalytic degradation of FST/PPy was estimated by monitoring the degree of RhB degradation under the irradiation of Vis light and UV light (figure 8). The degradation of RhB was quantified indirectly through the variation of the intensity of the absorption peak at 550 nm of the RhB solution using a standard curve concerning its concentration [32]. In the case of FST, the peak position of RhB was maintained at 550 nm under UV light irradiation and the absorption peak was still remained after 180 min (figure 8(A)). Under the action of UV light, when using FST/PPy(5) as a photocatalyst, the position of adsorption peak maintained at 550 nm for 3 h and then the absorption peak almost disappeared after 180 min (figure 8(B)). That is, the catalytic efficiency of FST was not high than FST/PPy(5). Even under Vis light, FST/PPy(5) revealed clearer catalytic performance than FST. The catalytic performance of FST under Vis light was significantly reduced than under UV light (figure 8(C)). In the case of FST/PPy(5), a small peak than FST appeared at 550 nm under Vis light (figure 8(D)). It is clear that FST/PPy has higher photodegradation performance than FST.

The change of C/C0 with time under light irradiation was represented in figure 9. The adsorption/desorption equilibrium state between the samples and RhB was reached for 30 min in the dark (figure 9(A)). Also, the decomposition efficiency of FST/PPy(5) is almost 92.8% after 150 min under UV light, which is the highest among the catalysts. Meanwhile, the degradation efficiency of the others was as follows: FST/PPy(3) (82.5%) > FST/PPy(1) (72.3%) > FST > (65.8%) > Fe3O4/SiO2 (9.5%). The first order degradation kinetics curves in figure 9(B) showed that the decomposition rate of FST/PPy(5) is 3 times higher than that of FST under UV light. The catalytic performance of FST/PPy(5) was obviously higher than other catalysts under Vis light (figure 9(C)). Under the irradiation of Vis light, the photoexcited electrons of PPy are transferred to conduction band (CB) of TiO2, which has a similar energy level to that of the PPy. These exited electrons also react with singlet oxygen (1O2) and dissolved oxygen molecules to give superoxide radical anions (O2−). The holes formed by moving from valance band (VB) of TiO2 to HOMO of PPy and the superoxide radical anions (O2−) can decompose organic materials. The degradation efficiency of catalysts under the action of Vis light was as follows: FST/PPy(5) (74.8%) > FST/PPy(3) (68.4%) > FST/PPy(1) (60.2%) > FST (25.8%) > Fe3O4/SiO2 (7.5%). The first order degradation kinetics curves in figure 9(D) showed that the decomposition rate of FST/PPy(5) is 5 times higher than that of FST under Vis light. The photocatalytic activity of FST/PPy did not change significantly even after five cycles (figure 10): the catalyst has high stability and excellent reusability.

When the FST/PPy catalyst absorbs the Vis light, the excited electrons are transferred from HOMO of PPy to LUMO of TiO2 with a similar energy level. These electrons react with oxygen molecules dissolved in water to form superoxide radical anions (O2−). The

Figure 7. Magnetic hysteresis loops of the catalysts (300 K).

Table 2. Magnetization saturation values (M_s) of catalysts.

| No | Catalyst       | Magnetization saturation values (M_s) |
|----|----------------|---------------------------------------|
| 1  | Fe3O4          | 75.7 emu g⁻¹                          |
| 2  | Fe3O4/SiO2     | 65.5 emu g⁻¹                          |
| 3  | FST            | 47.5 emu g⁻¹                          |
| 4  | FST/PPy(5)     | 40.3 emu g⁻¹                          |

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Figure 8. Absorption spectra of RhB with (A) FST under UV light, (B) FST/PPy(5) under UV light, (C) FST under Vis light and (D) FST/PPy(5) under Vis light.

Figure 9. RhB degradation activity of the catalysts (A) under UV light irradiation and (C) under Vis light irradiation; kinetic curves of photocatalysts (B) under UV light irradiation (D) under Vis light irradiation.

Figure 10. Cycling runs degradation of FST/PPy(5).
superoxide radical anions \((O_2^{-})\) and the hole formed by electron transfer from LUMO of PPy to CB of TiO\(_2\) play a role in decomposing RhB (scheme 1).

4. Conclusion

The FST/PPy photocatalyst was successfully synthesized and characterized through \(\textit{in situ}\) polymerization of pyrrole. FST/PPy showed higher catalytic activity in RhB degradation than FST with the core–shell structure under Vis light, which means that FST/PPy has the wide range of light utilization. In addition, FST/PPy can be easily separated and recycled using magnetic material after the reaction, which shows that this nanocomposite has high stability and recyclability. Therefore, this approach provides a new opportunity for the preparation of TiO\(_2\)-based photocatalyst for wastewater treatment using Vis light.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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