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Article

Preparation and characterization of ternary magnetic g-C₃N₄ composite photocatalysts for removal of tetracycline under visible light

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ABSTRACT

A stable PNIPAM/Fe₃O₄/g-C₃N₄ composite photocatalyst was designed and prepared by a thermal photoinitiation technology. The structure and properties of the materials were characterized and the composite photocatalyst was found to show good stability for tetracycline degradation. The sample not only retained the magnetic properties of Fe₃O₄, allowing it to be recycled, but its photocatalytic properties could also be changed by controlling the temperature of the reaction system. The degradation intermediate products of tetracycline were further investigated by MS. This work provides a new facile strategy for the development of intelligent and recyclable photocatalytic materials.

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1. Introduction

Tetracycline, an artificial synthetic drug, has been widely used in livestock farming and aquaculture for disease treatment. At the same time, pharmaceutical industrial wastewater discharged to nature has caused environmental problems. As one of the most environmentally friendly, low cost, and promising technologies, photocatalysis has been applied to the treatment of such wastewater.

Stimuli-responsive photocatalysts, namely “intelligent” photocatalysts, have received increasing interest in recent years [1]. Using thermo-responsive polymers to load semiconductors or combine them with noble metal particles to prepare “intelligent” photocatalysts can allow their photocatalytic activ-

ity to be switched on and off by adjusting the temperature of the surrounding environment below or above the lower critical solution temperature [2,3].

Poly *N*-isopropylacrylamide (PNIPAM) is one of the most common thermo-sensitive polymers [4]. PNIPAM molecular chains show hydrophilicity and become highly swollen at temperatures lower than the lower critical solution temperature (LCST, 32 °C), which arises from the hydrogen bonding interactions between the amide groups of PNIPAM and water molecules. Conversely, with increasing temperature, the PNIPAM molecular chains shrink rapidly as these hydrogen bonds are destroyed, resulting in hydrophobicity [5,6]. With the rapid development of temperature sensitive materials, many studies have been carried out to exploit the thermo-responsivity of

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PNIPAM, such as the investigation of Au-Pt/thermo-responsive copolymer microgels at the oil/water interface [7,8] and thermo-sensitive core/shell microgels with carbon cores [9], which have proved that PNIPAM exhibits effective intelligent control performance.

However, the application of the special properties of PNIPAM to the field of photocatalysis has rarely been reported [10–12]. Numerous semiconductor photocatalysts have been widely investigated for the removal of organic contaminants. Among these semiconductors, g-C₃N₄ has been systematically and deeply investigated owing to its stable chemical structure, nontoxicity, and low cost [13–15]. However, there are still many issues which have greatly limited the further development and application of g-C₃N₄ in the field of photocatalysis [16]. For example, g-C₃N₄ is not controllable, is difficult to recover from the solution for reuse [17], and has low visible-light efficiency [18]. To overcome the above-mentioned disadvantages, in this work we introduced PNIPAM and Fe₃O₄ to the surface of g-C₃N₄ using a simple and facile method.

Currently, Fe₃O₄ has been paid much attention owing to its unique physical chemical properties, and its use has spread into many areas, including drug delivery systems, biological medicine [19,20], sewage treatment [21], and even photocatalysis [22]. Particularly, great progress has been made in its application to photocatalysis. In previous studies, many researchers have coupled Fe₃O₄ with other semiconductors, producing WO₃/Fe₃O₄ [23], TiO₂/Fe₃O₄ [24], and even graphene-Fe₃O₄ [25]. These composite photocatalytic materials have shown ideal performance. For this reason, we also introduced magnetic Fe₃O₄ to the surface of g-C₃N₄. On one hand,

Fe₃O₄ can be considered to be a better conductor because its conductivity is about 1.9×10^6 S/m [26]. Therefore, Fe₃O₄ can rapidly transmit electrons and decrease the recombination rate of photogenerated electrons and holes, which significantly enhances photocatalytic activity. On the other hand, the favorable magnetic characteristics of Fe₃O₄ makes it easy to separate from a reaction system using an external magnet [27], which improves the recycling efficiency [28]. Therefore, as a conductive magnetic substance, Fe₃O₄ will not only enhance the recycling rate, but also the photocatalytic activity of the intelligent material.

With the above in mind, we report the design and fabrication of an intelligent recyclable photocatalyst in this paper. We introduced thermo-sensitive PNIPAM to the surface of Fe₃O₄/g-C₃N₄, the photocatalytic activity of which can be externally modulated as shown in Fig. 1. At temperatures lower than 32 °C, the thermo-sensitive polymer is swollen. At temperatures higher than 32 °C, the thermo-sensitive polymer dehydrates to the collapsed state owing to the breakdown of the delicate hydrophilic/hydrophobic balance in the spherical structure distances [29]. The findings reported here for the novel PNIPAM/Fe₃O₄/g-C₃N₄ composite are critical and necessary inputs in the development of photocatalytic degradation/purification processes from both academic and industrial points of view. We also expect that the modification of photocatalytic materials with thermo-sensitive materials will enable the intelligent removal of organic pollutants in waste water.

The fabricated intelligent composite PNIPAM/Fe₃O₄/g-C₃N₄ photocatalyst was characterized by a series of methods including X-ray diffraction (XRD), Fourier-transformed infrared spec-

Fig. 1. Schematic diagram of the synthesis of PNIPAM/Fe₃O₄/g-C₃N₄ and its swelling and shrinking caused by changes in the hydrogen bonds between the amido groups of the PNIPAM and H₂O at different temperature.

troscopy (FT-IR), transmission electron microscopy (TEM), Raman spectroscopy, UV-visible spectroscopy (UV-vis), elemental analysis, thermo-gravimetric analysis (TGA), and vibrating sample magnetometry (VSM). Photoluminescence (PL) spectra and the transient photocurrent responses were also measured. Finally, the degradation mechanism and intermediate products of tetracycline were also determined by mass spectrometry (MS).

2. Experimental

2.1. Materials

Melamine powder (99.0%), $\text{CH}_3\text{COOHNa}\cdot 3\text{H}_2\text{O}$ (98.0%), polyethylene glycol 1500 (PEG, 1500), and ethylene glycol (98.0%) were supplied by Aladdin Chemistry Co. Ltd. (Shanghai, China). Azobisisobutyronitrile (AIBN, CP), *N*-isopropylacrylamide (NIPAM, 98.0%), *N,N*-methylenebis(acrylamide) (MBAA, 97.0%) were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ (98.0%), ethanol (95.0%), tetracycline, and all other chemicals used in the experiments were purchased from Shanghai Chemical Reagent Co., Ltd. (China). Distilled water was used throughout.

2.2. Synthesis

Pure $\text{g-C}_3\text{N}_4$ was synthesized by annealing melamine in a muffle furnace. Briefly, 2.0 g melamine was placed in an open crucible, heated to 500 °C from room temperature and held for 2 h, then heated to 550 °C by a ramping rate of 2.3 °C/min and held for another 2 h. After the alumina crucible cooled to room temperature, the as-prepared $\text{g-C}_3\text{N}_4$ was ground into powder for further use.

$\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ was synthesized as follows: Firstly, 0.5 g $\text{g-C}_3\text{N}_4$ powder was added to 30 mL ethanediol containing 0.18 g $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$, 0.25 g $\text{C}_2\text{H}_3\text{O}_2\text{Na}\cdot 3\text{H}_2\text{O}$, 0.05 g PEG, and 0.005 g PVP, and ultrasonically dispersed for 1 h. The suspension was then transferred into a 50 mL Teflon-lined stainless steel autoclave and heated to 200 °C for 15 h. Finally, the $\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ product was obtained.

PNIPAM/ $\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ was synthesized as follows: Appropriate amounts of $\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ and NIPAM were added to 100 mL of a distilled water/methanol mixture (25/75, V/V). The mixture was sonicated for 10 min, and 0.01 g MBAA and 0.005 g AIBN were then quickly added. The polymerization was conducted at 65 °C under the nitrogen protection for 5 h. After completion of the reaction, the suspension was separated with a magnet and then dried.

2.3. Characterization

XRD patterns of the samples were recorded at room temperature using a powder X-ray diffractometer (Rigaku, Japan) with Ni-filtrated $\text{Cu K}\alpha$ radiation (40 kV, 200 mA) at 10°–80° with a scanning step of 0.02°/0.2 s. FT-IR spectra were obtained on a Nicolet Magna-IR 550 within the wavelength range of 500–4000 cm^{-1} . KBr was used as the reference sample. TEM

images were obtained with a JEM-2100 transmission electron microscopy (JEOL, Japan). The magnetic properties of the samples were measured with a VSM (HH-15, Jiangsu University, China). TGA was carried out using a thermal analyzer (NETZSCH-Gerätebau GmbH, Germany) in air, from room temperature to 800 °C with heating rate of 5 °C/min. Raman experiments were performed using the 532 nm laser of a DXR spectrometer at room temperature. The elemental content of each sample was analyzed using an elemental analyzer (EA-1112A, Thermos, Italy). The PL spectra of the as-prepared samples were investigated using a Cary Eclipse Spectrophotometer (VARIAN, USA) equipped with xenon lamp at an excitation wavelength of 343 nm. UV-vis diffuse reflectance spectra (DRS) were obtained at room temperature for dry-pressed disk samples using a 2450 spectrometer (Shimadzu Co., Japan) equipped with an integrated sphere accessory, and using BaSO_4 as the background. The degradation intermediate products of aqueous tetracycline solution were determined using a Thermo LXQ ion trap mass spectrometer (MS).

2.4. Adsorption experiments

To investigate the adsorption capability of the photocatalysts, adsorption experiments were carried out in a GHX-2 photochemical reactor (Yangzhou University Technology Ltd, Yangzhou, China). The reactor consisted of a quartz reactor and an illumination source. The quartz reactor was connected to a DFY-5 low temperature cooling liquid reaction bath (Gongyi City Yuhua Instrument Co., Ltd. Gongyi, China) to keep the solution at a certain temperature. 0.1 g photocatalyst was added to 100 mL 20 mg/L tetracycline solution in the photochemical reactor and stirred for 70 min in the dark at 20 °C or 45 °C, during which the absorbance of the tetracycline was monitored every 10 min.

2.5. Photocatalytic experiments

The photocatalytic activity of the samples was evaluated using the decomposition of tetracycline under visible light irradiation (300 W Xe lamp). The photo-degradation was performed as follows: the binding experiments were carried out at 20 °C and 45 °C. The tetracycline solution (20 mg/L, 100 mL) containing 0.1 g photocatalyst was ultrasonicated for 5 min and kept in the dark for 1 h under continuous magnetic stirring to achieve adsorption-desorption equilibrium between the tetracycline and photocatalyst. At 20 min intervals, 6 mL of the reaction suspension was sampled and magnetic separated, and the absorbance of the tetracycline was measured. Additionally, radical capture experiments were carried out by adding 0.1 mmol triethanolamine (TEOA, a quencher of h^+), 0.1 mmol isopropanol (IPA, a quencher of $\bullet\text{OH}$), or 0.1 mmol benzoquinone (BQ, a quencher of $\bullet\text{O}_2^-$).

2.6. Analysis

The concentration of tetracycline in reaction solutions were determined by UV-vis spectroscopy at a wavelength of 357 nm.

The photocatalytic efficiency of tetracycline degradation was calculated using the following formula: $\eta = (C_0 - C_t)/C_0$, where η is photocatalytic efficiency, C_0 is the concentration of reactant before illumination, and C_t is the reactant concentration after illumination time t .

3. Results and discussion

3.1. Characterization results of the samples

Fig. 2 shows the XRD patterns of the as-prepared g-C₃N₄, Fe₃O₄/g-C₃N₄, and PNIPAM/Fe₃O₄/g-C₃N₄. Each sample exhibited an intense diffraction peak at $2\theta = 27.4^\circ$, corresponding to the (002) interplanar stacking structure of crystalline graphite [30]. The XRD pattern of Fe₃O₄/g-C₃N₄ exhibited the characteristic peaks of Fe₃O₄ at $2\theta = 30.2^\circ, 35.5^\circ, 43.2^\circ, 53.4^\circ, 57.3^\circ$ and 62.6° [28]. The diffraction peak at 27.4° was slightly lower in intensity than that of the pure g-C₃N₄, which resulted from the Fe₃O₄ restraining the stacking of g-C₃N₄ perpendicular to the (002) direction. The peak intensity of Fe₃O₄ (35.5°) was remarkably weakened in the diffraction pattern of PNIPAM/Fe₃O₄/g-C₃N₄. This result implies that PNIPAM was formed on the surface of the Fe₃O₄/g-C₃N₄, and further indicated the successful formation of PNIPAM/Fe₃O₄/g-C₃N₄ ternary composites. The presence of PNIPAM was subsequently confirmed by FT-IR, EDS, TEM, and elemental analysis.

The functional groups of pure g-C₃N₄, Fe₃O₄/g-C₃N₄, and PNIPAM/Fe₃O₄/g-C₃N₄ were analyzed by FT-IR spectroscopy. As shown in Fig. 3, all the materials demonstrated a series of multiple bands. Those located in the 1200–1600 cm⁻¹ region (1250, 1329, 1419, 1577, and 1635 cm⁻¹) corresponded to the typical stretching modes of CN heterocycles [31], such as C–N and C=N stretching [32]. The sharp band at 808 cm⁻¹ was assigned to the characteristic typical bending vibration of tri-s-triazine units [33]. The broad peaks from 3400 to 2800 cm⁻¹ arose from the stretching vibrational modes of primary amines. In the FT-IR spectrum of Fe₃O₄/g-C₃N₄, the absorption peaks of g-C₃N₄ become slightly weaker, which indicated that the hydrothermal treatment had no effect on the chemical structure of g-C₃N₄. The absorption peaks of

Fig. 2. XRD patterns of pure g-C₃N₄ (1), Fe₃O₄/g-C₃N₄ (2), PNIPAM/Fe₃O₄/g-C₃N₄ (3).

Fig. 3. FT-IR spectra of pure g-C₃N₄ (1), Fe₃O₄/g-C₃N₄ (2), PNIPAM/Fe₃O₄/g-C₃N₄ (3).

PNIPAM/Fe₃O₄/g-C₃N₄ indicated that the g-C₃N₄ retained the same chemical structure as pure g-C₃N₄ after coating with PNIPAM. Peaks at 2969, 1657, and 1390 cm⁻¹ from C–H, O=C–NH₂, and –CH(CH₃)₂, respectively, could be seen clearly, and were caused by introducing PNIPAM to the Fe₃O₄/g-C₃N₄ surface [34]. In brief, it could be inferred from the FT-IR results, that the incorporation and existence of Fe₃O₄ and PNIPAM in the composite would not affect the chemical functionality of g-C₃N₄.

Fig. 4. Raman spectra of Fe₃O₄/g-C₃N₄ (1) and PNIPAM/Fe₃O₄/g-C₃N₄ (2).

In the Raman spectra shown in Fig. 4(a), peaks located at 468 cm^{-1} , 974 cm^{-1} , 1248 cm^{-1} , and 1485 cm^{-1} that stemmed from the vibration modes of CN were clearly seen for both $\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ (1) and $\text{PNIPAM}/\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ (2). The prominent peak at 684 cm^{-1} represents the symmetric stretch of oxygen atoms along the Fe–O bond, which indicates that the Fe_3O_4 was successfully loaded on the surface of the $\text{g-C}_3\text{N}_4$ [22]. A series of modes could be detected in the amplified Raman spectrum of $\text{PNIPAM}/\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ in Fig. 4(b), including CH_3 twisting (838 cm^{-1}), CH_3 rocking (tert-butyl, 918 cm^{-1}), C–C skeletal in-phase stretching (1106 cm^{-1}), N–C bond stretching (1146 cm^{-1}), CH_3 bending (scissor deformation, 1449 cm^{-1}) amide 2 N–H deformation (1544 cm^{-1}), and amide 1 C=O stretching (1646 cm^{-1}) [35]. These results confirmed the existence of $\text{g-C}_3\text{N}_4$, Fe_3O_4 , and PNIPAM in the composite.

The morphology and microstructure of the prepared photocatalysts were characterized by TEM and EDS. As shown in Fig. 5(a), $\text{g-C}_3\text{N}_4$ exhibited a stacked pimple-like structure and consisted of aggregates of several micrometers in size resulting from the thermal polycondensation of melamine. Fig. 5(b) shows that in $\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$, the $\text{g-C}_3\text{N}_4$ sheets served as a support and surfactant to bind with the Fe_3O_4 , which was mainly present as 3D microspheres with an average diameter of $0.05\text{--}0.1\text{ }\mu\text{m}$. After hybridization with the pure $\text{g-C}_3\text{N}_4$, the Fe_3O_4 microspheres were well interwoven with the $\text{g-C}_3\text{N}_4$, forming a 3D hybridized structure expected to facilitate the transfer of photogenerated carriers and improve the photocatalytic performance. In the image of $\text{PNIPAM}/\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ displayed in Fig. 5(c), a thin layer appeared to be assembled on the surface of the $\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$, and the Fe_3O_4 3D microspheres could not be seen clearly. This change from the morphology seen in Fig. 5(b) must have been caused by the covering of the

Table 1

Elemental composition of samples from elemental analysis.

Sample	N (%)	C (%)	H (%)
$\text{g-C}_3\text{N}_4$	54.09	39.99	2.34
$\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$	48.69	31.38	1.31
$\text{PNIPAM}/\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$	50.73	34.26	1.92

material with PNIPAM. Therefore, the TEM image further confirmed the existence of PNIPAM in the composite. Accordingly, the EDS results obtained for the different samples were also different. As shown in Fig. 5(a₁), the EDS spectrum of the pure $\text{g-C}_3\text{N}_4$ samples revealed the existence of C and N elements. For $\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ (Fig. 5(b₁)), besides N and C elements, Fe and O elements were also detected, indicating that the samples consisted of Fe_3O_4 and $\text{g-C}_3\text{N}_4$. Compared with those of $\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$, the C and N intensities of the $\text{PNIPAM}/\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ were enhanced, while the Fe intensity was decreased. These results further indicated that thermo-sensitive PNIPAM was successfully introduced to the composite.

The elemental contents of the different samples are shown in Table 1. The C/N molar ratio in $\text{g-C}_3\text{N}_4$ was nearly 3/4, close to the theoretical value. This further proved that $\text{g-C}_3\text{N}_4$ was successfully prepared [36]. Furthermore, the contents of N, C, and H in $\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ were decreased compared with those in pure $\text{g-C}_3\text{N}_4$. The content of Fe_3O_4 was nearly 20%, which was consistent with the initial dosage, meaning that Fe_3O_4 was successfully attached to the surface of the $\text{g-C}_3\text{N}_4$. Moreover, the contents of N, C, and H in $\text{PNIPAM}/\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ were significantly higher than those in $\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$, indicating that the surface of $\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ was successfully modified with

Fig. 5. TEM images and EDS spectra of pure $\text{g-C}_3\text{N}_4$ (a, a₁), $\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ (b, b₁), $\text{PNIPAM}/\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ (c, c₁).

Fig. 6. Thermogravimetric analysis of PNIPAM/Fe₃O₄/g-C₃N₄.

PNIPAM.

Fig. 6 displays the TG and DSC curves of PNIPAM/Fe₃O₄/g-C₃N₄. The TG curve of PNIPAM/Fe₃O₄/g-C₃N₄ exhibited a slight mass loss of about 4.31% from room temperature up to 200 °C. This mass loss may have been caused by the evaporation of water [37]. As the temperature was increased to 300 °C, a further mass loss of 10.09% was obtained, which may have been caused by the loss of PNIPAM from the surface of the Fe₃O₄/g-C₃N₄. Finally, the mass of the sample decreased rapidly in the temperature range from 450 °C to 600 °C, indicating that 71.02% of the sample was g-C₃N₄, which underwent combustion in the air [38,39]. The remaining mass (15.0%) was attributed to Fe₃O₄, because the melting point of Fe₃O₄ is much higher than the experimental temperature. From the DSC curves, it could be seen the thermal decomposition of PNIPAM/Fe₃O₄/g-C₃N₄ occurred at 300 and 550 °C. Hence, this analysis demonstrated that PNIPAM/Fe₃O₄/g-C₃N₄ had good thermal stability and that its composition was consistent with the original materials.

The magnetic properties of PNIPAM/Fe₃O₄/g-C₃N₄ were measured by sweeping an applied field over the sample from 10 to 10000 kOe at room temperature. Fig. 7(a) shows the hysteresis loop of the as-prepared sample, the magnetization saturation value of which reached 13.80 emu/g. Good superparamagnetism is essential for the collection and reuse of the photocatalyst in multiple cycles. The inset of Fig. 7(a) shows that the photocatalyst was strongly attracted to a permanent mag-

Fig. 7. Hysteresis loop of PNIPAM/Fe₃O₄/g-C₃N₄ under magnetic field (a), and results of tetracycline degradation cycling experiment with PNIPAM/Fe₃O₄/g-C₃N₄ (b).

net. Therefore, the PNIPAM/Fe₃O₄/g-C₃N₄ photocatalyst could be rapidly separated from suspension under an applied magnetic field. To further examine the stability of the as-prepared intelligent PNIPAM/Fe₃O₄/g-C₃N₄, its reusability was tested in five successive tetracycline degradation experiments. As shown in Fig. 7(b), the as-prepared photocatalyst retained over 80% of its original photocatalytic activity after five successive experimental runs, which is very important for practical application. Therefore, the PNIPAM/Fe₃O₄/g-C₃N₄ can be used efficiently in environmental protection.

PL measurements and photocurrent-time tests have been widely used to evaluate the photocatalytic quantum efficiency of photocatalysts [40,41]. As shown in Fig. 8(a), pure g-C₃N₄ exhibited luminescence in a broad range (400–600 nm) centered at 450 nm at room temperature with an excitation wavelength of 330 nm. This finding suggested that photoinduced e⁻-h⁺ pairs were generated and recombined within the pure g-C₃N₄. The PL intensity of PNIPAM/Fe₃O₄/g-C₃N₄ was obviously decreased compared with that of the pure g-C₃N₄, suggesting a decreased recombination rate of photogenerated e⁻-h⁺ pairs in PNIPAM/Fe₃O₄/g-C₃N₄. The above results indicated that efficient separation, transport, and capture of the photo-generated carriers were realized after the formation of Fe₃O₄ and introduction of PNIPAM to the composite. The photocurrent-time (*I*-*t*) curves are displayed in Fig. 8(b). The generated photocurrents were reproducible and stable during three intermittent on-off irradiation cycles. The prompt increase in the photocurrent response from the light-off to the light-on state was ascribed to the quick separation and transport of photo-generated electrons. PNIPAM/Fe₃O₄/g-C₃N₄ exhibited a higher photocurrent response than pure g-C₃N₄. The results of the photo-electrochemical experiments were consistent with the PL measurements, further indicating that PNIPAM/Fe₃O₄/g-C₃N₄ effectively slowed the combination rate of photo-generated e⁻-h⁺ pairs.

The UV-vis diffuse reflectance spectra of Fe₃O₄, pure g-C₃N₄, and PNIPAM/Fe₃O₄/g-C₃N₄ are shown in Fig. 8(c). The pure g-C₃N₄ exhibited photo-absorption from the UV light range to visible light shorter than 460 nm. Notably, PNIPAM/Fe₃O₄/g-C₃N₄ exhibited a red shift in its absorbance edge up to 800 nm, indicating a smaller band gap, and its absorption intensity in the visible light region was higher than that of pure g-C₃N₄. The prominent red shift of the composite

photocatalyst compared with pure g-C₃N₄ can be attributed to the presence of PNIPAM and Fe₃O₄ on the g-C₃N₄ surface, which improved its optical absorption [42–44]. Firstly, the good conductivity of Fe₃O₄ effectively promoted the separation of electron-hole pairs, which accounts for the band gap transition of the photo-generated electrons, and then enhanced the absorption of the composite in the visible light region. Secondly, the change in the color of the sample also cause an increase in ab-

slightly when IPA was added as scavenger of •OH [45], indicating that •OH was not the major oxidative species in the PNIPAM/Fe₃O₄/g-C₃N₄ photocatalytic reaction system. However, the photocatalytic performance decreased upon the addition of BQ as a scavenger for photogenerated superoxide radical species in the solution [46,47]. The tetracycline photo-degradation rate was significantly decreased to only 49%, which indicated that superoxide radicals were the main active

Fig. 8. PL spectra (a), photocurrent response curves (b), UV-vis diffuse reflectance spectra (c) of Fe₃O₄ (1), pure g-C₃N₄ (2), and PNIPAM/Fe₃O₄/g-C₃N₄ (3), and photo-degradation rate of tetracycline over PNIPAM/Fe₃O₄/g-C₃N₄ in the presence of different scavengers (d).

sorbance.

Next, the active species generated by visible-light irradiation were investigated by adding different scavengers to the photocatalytic system. The results are shown in Fig. 8(d). The photocatalytic performance of PNIPAM/Fe₃O₄/g-C₃N₄ changed

species. When TEOA, which is a scavenger for h⁺ [48], was added to the reaction system, the photocatalytic reaction was significantly inhibited. These results indicated that superoxide radicals and h⁺ were the predominant contributors to the photocatalytic reaction.

Fig. 9. Adsorption curves (a) and degradation dynamic curves (b) of tetracycline over PNIPAM/Fe₃O₄/g-C₃N₄ at different temperatures.

Fig. 9(a) shows the absorption curves of tetracycline molecules by PNIPAM/Fe₃O₄/g-C₃N₄ at different temperatures. The solution systems almost reached adsorption equilibrium within 60 min. PNIPAM/Fe₃O₄/g-C₃N₄ exhibited the highest adsorption capacity of 9.0 mg/g at 20 °C. Interestingly, the adsorption capacity of PNIPAM/Fe₃O₄/g-C₃N₄ was reduced at 45 °C, which may have been because PNIPAM is hydrophilic and swells in water at lower temperatures ($T < 32$ °C), so the tetracycline molecules could reach the surface of PNIPAM easily. In contrast, at high temperatures ($T > 32$ °C), PNIPAM shrinks and becomes hydrophobic [49–52], preventing the tetracycline molecules from being adsorbed on the surface of PNIPAM/Fe₃O₄/g-C₃N₄. Therefore, the absorption capacity of PNIPAM/Fe₃O₄/g-C₃N₄ was increased by the change in polarity of the PNIPAM induced by its volume transition. Moreover, a superior adsorption capacity is beneficial for photocatalytic activity because of the increased contact between target molecules and photocatalyst. PNIPAM/Fe₃O₄/g-C₃N₄ had a higher adsorption capacity at 20 °C than at 45 °C and exhibited a higher degradation rate of about 80%. As shown in Fig. 9(b), the degradation rate decreased to 54% when the temperature was increased to 45 °C. This results provides direct evidence that the thermo-sensitive composite had a switchable organic pollutant degradation ability based on temperature control.

The variation in the absorbance of tetracycline on PNIPAM/Fe₃O₄/g-C₃N₄ was also measured. Fig. 10(a) illustrates that the absorbance of tetracycline decreased obviously with increasing light irradiation time at 20 °C. No absorbance peak was observed after visible-light irradiation of 120 min, which indirectly confirmed that the tetracycline molecules were destroyed or decomposed into smaller molecules [53,54]. These results further indicated that the swelling of the polymer at low temperature made it more hydrophilic and more lacunose, which allowed the tetracycline molecules to reach the surface of the PNIPAM easily for photocatalytic degradation by active species. A similar experiment was conducted at 45 °C (Fig. 10(b)), and the results showed that the absorbance was slightly changed compared with that at 20 °C. This result can be attributed to the lower binding ability of PNIPAM at higher temperature meaning that the tetracycline molecules could not be adsorbed on the PNIPAM/Fe₃O₄/g-C₃N₄ surface, as dis-

Fig. 11. Schematic illustration of the mechanism of photogenerated charge carrier transfer in PNIPAM/Fe₃O₄/g-C₃N₄ under visible light irradiation.

cussed above. Therefore, PNIPAM/Fe₃O₄/g-C₃N₄, showed temperature responsive intelligent binding properties and the temperature was a crucially important factor for its efficient degradation of organic pollutants. Therefore, from the experimental results, catalytic activity of the intelligent PNIPAM/Fe₃O₄/g-C₃N₄ photocatalyst was controllable by adjusting the temperature.

Based on the experimental results and theoretical analysis, a possible mechanism for the photo-degradation of tetracycline by PNIPAM/Fe₃O₄/g-C₃N₄ is illustrated in Fig. 11. As previously reported, based on density functional theory (DFT), g-C₃N₄ has appropriate conduction band (CB) and valence band (VB) edge potentials at -1.13 and 1.57 eV, respectively [55,56]. Under visible light irradiation, electrons are excited from the VB to the CB of g-C₃N₄, and then migrate to the surface of the Fe₃O₄, which effectively inhibits the direct recombination of electrons and holes and thus enhances the photocatalytic activity [20]. The photo-generated holes (h^+) in g-C₃N₄ can react with tetracycline, causing it to degrade into small inorganic molecules

Fig. 10. Time-dependent absorption spectra of tetracycline solution in the presence of PNIPAM/Fe₃O₄/g-C₃N₄ (a): 20 °C; (b): 45 °C.

Fig. 12. Photodegradation mechanism of tetracycline.

such as CO_2 and H_2O . Meanwhile, the photo-generated electrons in g- C_3N_4 are transferred to Fe_3O_4 . In the Fe_3O_4 crystals, the electrons are good reductants that can capture adsorbed oxygen molecules, well-known electron acceptors, onto the composite catalyst surface and react with them, generating superoxide radicals $\bullet\text{O}_2^-$ [57]. The generated $\bullet\text{O}_2^-$ may also react with H^+ to further produce $\bullet\text{OH}$. Both superoxide radicals and $\bullet\text{OH}$ have high oxidation activity, and can finally decompose tetracycline. Therefore, the efficient photocatalytic degradation of tetracycline proceeds smoothly. Based on the above analysis, the charge carrier transfers and degradation reactions are proposed as follows:

MS is widely used to probe the possible mechanism of photodegradation and identify the intermediates. In the mass spectrum obtained for tetracycline degradation, many extra peaks appeared alongside that of tetracycline (including $m/z = 478, 401, 373, 359, 348, 292, 246, 164$). As time went on, the characteristic peak of tetracycline ($m/z = 445$) decreased in intensity. This result meant that the tetracycline molecules were decomposed into other intermediate degradation prod-

ucts, which were gradually decomposed to CO_2 , H_2O , and other small molecules. The mechanism speculated according to the MS results is illustrated in Fig. 12.

Under visible light excitation, B was formed by the loss of the $-\text{CONH}_2$ group from A (tetracycline). The process of "A to C" occurred through the loss of $-\text{CONH}_2$ and $-(\text{CH}_3)_2$ from the tetracycline. The formation of "D" must have been caused by $\bullet\text{OH}$ substitution for H in $-\text{N}(\text{CH}_3)_2$. "B, C, and D to E" resulted from the removal of the $-\text{CONH}_2$, $-\text{CH}_3$, and $-\text{N}(\text{CH}_3)_2$ groups from tetracycline, respectively. The degradation process of "E to F" occurred through the breakage of a $\text{C}=\text{C}$ double bond and loss of $\bullet\text{OH}$. Likewise, "F to G" was caused by the breakage of a $\text{C}=\text{C}$ double bond, following which $\bullet\text{OH}$ and $-\text{NH}_2$ were easily lost and a rearrangement reaction occurred. Along with this reaction, the formation of "H" resulted from the breakage of the σ bond and rearrangement reaction. "I" was formed from "H" by the opening of $\text{C}=\text{C}$ bonds, and the loss of molecular $\text{C}_6\text{H}_{11}\text{O}$. Finally, under visible-light irradiation, these products were further decomposed into small gaseous components.

4. Conclusions

In summary, an intelligent PNIPAM/ Fe_3O_4 /g- C_3N_4 composite photocatalyst was successfully fabricated by a hydrothermal method and thermal photoinitiation technology. The photocatalyst exhibited reversible thermo-induced swelling/shrinking transition, and its catalytic activity could be modulated through the corresponding temperature-dependent binding behaviors. The rate of tetracycline degradation over the catalyst was more significant at 20°C than at 45°C . Moreover, PNIPAM/ Fe_3O_4 /g- C_3N_4 could be easily separated from the reaction system and exhibited little deactivation after five repeated use. Importantly, the tetracycline was decomposed into harmless small molecules, as confirmed by MS. The results of this study prove the feasible and promising use of thermo-sensitive composites in the photo-degradation of organic pollutants and intelligent catalysis.

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Graphical Abstract

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Preparation and characterization of ternary magnetic g-C₃N₄ composite photocatalysts for removal of tetracycline under visible light

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A stable and magnetic PNIPAM/Fe₃O₄/g-C₃N₄ photocatalyst was fabricated by a hydrothermal method and thermal photoinitiating technology. Its activity could be modulated by temperature, showing promise for use in intelligent catalysis.

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三元磁性氮化碳复合光催化剂的制备和表征及其在可见光下去除四环素的应用

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摘要: g-C₃N₄作为一种新型有机半导体材料,由于其良好的化学稳定性和可直接利用可见光等优点已经引起了人们的广泛关注,近年来已逐渐将其应用于光催化氧化环境污染物等方面.同时在实际应用中因其光能利用率低、难回收、电子-空穴复合等缺点也受到了限制.研究发现将三氧化二铁与氮化碳相结合,可以有效提高复合催化剂的光催化活性,而且可回收再利用很大程度上降低成本.采用光催化氧化技术处理实际环境污染物废水时,将光催化剂投入到废水中后,环境及水体的温度往往会对催化剂的催化活性产生一定的影响,导致无法实现最佳的光催化处理效果.制备一种催化活性不受外界温度影响的智能光催化材料是当今面临的一项挑战.我们研究制备了一种具有温度响应的磁性复合光催化剂PNIPAM/Fe₃O₄/g-C₃N₄,其可根据外界温度的不同而表现出不同的光催化活性.温敏型聚合物PNIPAM是一类结构、性能和形态随温度变化而做出响应的功能材料,将光催化材料与温敏型PNIPAM智能高分子材料相结合,实现了智能催化的效果. PNIPAM温敏聚合物在水溶液中存在一个低临界溶解温度,其可以作为开关,通过改变温度实现对光催化过程的控制,达到过程智能化的效果.随着温度的改变,温敏聚合物的溶解状态在临界点附近会发生变化.不同温度对催化速率影响很大,当温度升高到临界值以上,催化反应速率降低很多;当温度降低到临界值以下,催化活性随之升高.这样不仅随时控制反应的进行,还可以通过改变温度控制反应速率.同时,温敏聚合层又相当于一个保护层,可以增强其抗腐蚀能力,提高对内部光催化材料的保护,进而提高其稳定性.众所周知四环素等抗生素类药物生产废水,属于高浓度有机废水,具有一定的毒性,一般较难处理.我们将制备的PNIPAM/Fe₃O₄/g-C₃N₄复合光催化材料用于四环素废水的处理取得了很好的效果.

XRD, FT-IR、Raman等表征手段充分证明了我们所制备的三元复合材料PNIPAM/Fe₃O₄/g-C₃N₄的组成及各个组分的存在.并对PNIPAM/Fe₃O₄/g-C₃N₄复合光催化剂在不同温度(20和45 °C)条件下处理四环素废水进行了系统的研究,从20和45 °C的吸附曲线结果可以看出,低温时PNIPAM/Fe₃O₄/g-C₃N₄的吸附性较强,高温时吸附较差.同时PNIPAM/Fe₃O₄/g-C₃N₄低温时具有较高的催化活性,高温时催化活性较低.经过分析可知这种对温度响应的特殊性能与PNIPAM的亲水及疏水性密切相关.另外,通过对PNIPAM/Fe₃O₄/g-C₃N₄复合材料的VSM测试及5次循环实验测试可以看出,PNIPAM/Fe₃O₄/g-C₃N₄复合材料由于Fe₃O₄的引入而表现出较好的磁性,且在外加磁铁的作用下很容易实现分离回收.另外,PNIPAM/Fe₃O₄/g-C₃N₄在经过5次重复利用后其催化活性几乎没有减退,说明催化剂具有很好的稳定性.另一方面,说明我们的复合光催化剂在工业废水等污染治理方面有一定的潜在应用价值.

关键词: 三氧化二铁/氮化碳; 四环素; 磁性; 中间产物; 光催化剂

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