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Article

Visible light-responsive carbon-decorated p-type semiconductor CaFe_2O_4 nanorod photocatalyst for efficient remediation of organic pollutants

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ARTICLE INFO

Article history:

Received 18 June 2017

Accepted 12 July 2017

Published 5 October 2017

Keywords:

p-type semiconductor CaFe_2O_4

Carbon coating

Nanorod

Composite photocatalyst

Degradation of methylene blue

ABSTRACT

We report the fabrication and photocatalytic property of a composite of C/ CaFe_2O_4 nanorods (NRs) in an effort to reveal the influence of carbon modification. It is demonstrated that the photocatalytic degradation activity is dependent on the mass ratio of C to CaFe_2O_4 . The optimal carbon content is determined to be 58 wt% to yield a methylene blue (MB) degradation rate of 0.0058 min^{-1} , which is 4.8 times higher than that of the pristine CaFe_2O_4 NRs. The decoration of carbon on the surface of CaFe_2O_4 NRs improves its adsorption capacity of the MB dye, which is specifically adsorbed on the surface as a monolayer according to the adsorption isotherm analysis. The trapping experiments of the reactive species indicate that superoxide radicals ($\cdot\text{O}_2^-$) are the main active species responsible for the removal of MB under visible-light irradiation. Overall, the unique feature of carbon coating enables the efficient separation and transfer of photogenerated electrons and holes, strengthens the adsorption capacity of MB, and improves the light harvesting capability, hence enhancing the overall photocatalytic degradation of MB.

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1. Introduction

As one of the most promising routes for alleviating the environmental pollution and energy crisis, the visible light-driven heterogeneous photocatalysis has attracted extensive attention [1–5]. In recent decades, considerable efforts have been focused on the fabrication of highly efficient semiconductor-based photocatalysts towards the elimination of organic contaminants or hydrogen production through water splitting [6–10]. As a model p-type semiconductor photocatalyst, the nontoxic, inexpensive CaFe_2O_4 with a narrow bandgap (about

1.9 eV) has been proven to be capable of photocatalytic decomposition of organic dyes, reduction of carbon dioxide and photoelectrochemical water splitting [11–14]. Nevertheless, owing to its intrinsic problems, such as p-type character with inefficient hole transfer to the surface, high recombination of photoexcited charge carriers and low charge carrier mobility arising from the existence of defects, usually, a low photo-quantum yield is obtained for the CaFe_2O_4 -based photocatalysts either in water splitting or the degradation of organic pollutants.

One of the strategies for solving these problems is the con-

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This work was supported by the National Natural Science Foundation of China (21503100), Natural Science Foundation of Jiangxi Province (20161BAB213071, 20151BAB213010), Project of Education Department of Jiangxi Province (GJJ150325), and Sponsored Program for Cultivating Youths of Outstanding Ability in Jiangxi Normal University.

DOI: 10.1016/S1872-2067(17)62888-2 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 38, No. 10, October 2017

struction of composite photocatalysts. For example, a series of CaFe_2O_4 -based composites, such as $\text{CaFe}_2\text{O}_4/\text{g-C}_3\text{N}_4$ [15], $\text{CaFe}_2\text{O}_4/\text{Ag}_3\text{VO}_4$ [16] and $\text{CaFe}_2\text{O}_4/\text{MgFe}_2\text{O}_4$ [17], have been fabricated and exhibit enhanced photocatalytic activities. Recently, it was found that carbon/inorganic semiconductor composite photocatalysts exhibit promising photocatalytic activities for the removal of the organic pollutants from water [18–20]. For instance, Zhong et al. [21] reported that carbon-deposited TiO_2 can efficiently degrade Acid Orange 7 and 2,4-dichlorophenol under visible-light irradiation. Chen et al. [22] studied the photocatalytic activity of carbon-coated PbMoO_4 microspheres for the degradation of rhodamine B (RhB) in an aqueous solution under visible-light irradiation. Li et al. [23] observed that modification with an appropriate amount of carbon could significantly improve the photocatalytic activity of Bi_2WO_6 for the degradation of RhB. In general, the major advantages of coupling carbon materials with a semiconductor are as follows: (1) increase of the visible-light absorption of wide bandgap semiconductors, (2) enhancement of electron transport and inhibition of the recombination of photogenerated charge carriers [24,25], (3) high dispersion of semiconductor particles through the wide distribution of hydrophilic groups (such as $-\text{OH}$ and $\text{C}=\text{O}$), and (4) improvement of the adsorption capacity for organic pollutants. However, most of these are composites of carbon with n-type semiconductors [23,26,27], so would be interesting to determine the carbon coating effect on the photocatalytic performance of p-type semiconductors.

In this work, well-defined CaFe_2O_4 nanorod (NR) crystals were prepared by a facile polymerizable complex method in an eutectic mixture of NaCl and KCl molten salts that we have reported earlier [28]. The coating of the carbon layers onto the surface of the CaFe_2O_4 NRs was carried out by the impregnation method. Through a comprehensive study of the relationship between the photocatalytic performance and composite structure, carbon loading, methylene blue (MB) adsorption, and oxidant intermediate, the unique effects of carbon coating on a p-type semiconductor are well addressed. This study will serve as a guide for the construction of highly efficient carbon/p-type semiconductor composite photocatalysts.

2. Experimental

2.1. Materials

Glucose, citric acid, ethylene glycol, NaCl and KCl were purchased from Sinopharm Chemical Reagent Co., Ltd. $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and MB were obtained from Aladdin Industrial Corporation. All chemicals were of analytical grade and used as received without any further purification.

2.2. Preparation of samples

CaFe_2O_4 NRs were synthesized according to the procedure reported in our previous paper [28]. Briefly, 8.406 g of citric acid, 4.723 g of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and 16.160 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were added into 20 mL of distilled water and dissolved com-

pletely under stirring, followed by the addition of ethylene glycol (8 mL) to yield a brown solution. Subsequently, the resulting solution was transferred to an evaporating dish and dried at 130 °C for 20 h to obtain a dry gel. Calcination in air at 500 °C for 2 h yielded the CaFe_2O_4 precursor, which was blended and ground with NaCl and KCl in the molar ratios of 1:5:5 for the molten salt crystallization. The mixture was calcined in air at 800 °C for 20 h and washed with boiling water. After drying at 60 °C for 12 h, the CaFe_2O_4 NRs product was obtained.

The C/ CaFe_2O_4 NRs composite material was prepared as follows. 1.440 g of glucose was dissolved in 60 mL of distilled water. The glucose solution was transferred into a 100-mL Teflon-lined stainless-steel autoclave and kept at 180 °C for 24 h, then allowed to cool naturally to room temperature. Then, the reaction solution was centrifuged several times. The resultant yellow aqueous solution containing carbon was obtained for further use. Subsequently, CaFe_2O_4 (100 mg) was respectively dispersed into 5, 10, 15, 20, 25, 30 mL of the yellow aqueous solution containing carbon, and sonicated for 10 min. After complete evaporation of the solvent at 60 °C under stirring, the collected products were dried at 60 °C overnight. The carbon contents in the as-prepared composite samples were determined by TG analysis to be 28, 41, 49, 58, 67 and 71 wt%, respectively. Therefore, in the following discussion, the samples are labeled as X wt% C/ CaFe_2O_4 , where “X” denotes the content of carbon in the composite.

2.3. Characterization

To determine the crystal structure of the as-prepared samples, powder X-ray diffraction (XRD) measurements were carried out using a Rigaku RINT-2200 diffractometer with a $\text{Cu } K_\alpha$ radiation source at 40 kV and 20 mA and a scanning rate of 4° min^{-1} (2θ from 5° to 90°). TG analysis was performed on a Diamond TG/DTA apparatus in air from room temperature to 1000 °C. The functional groups of the photocatalyst were analyzed by Fourier transform infrared (FTIR) spectroscopy using a Nicolet 6700 spectrometer. The spectra were recorded in the transmission mode ranging from 4000 to 500 cm^{-1} . The morphology and composition of the photocatalyst were studied by scanning electron microscopy (SEM) on a Hitachi SU-8020 cold field emission source and by an energy-dispersive spectroscopy (EDS) detector attached to the scanning electron microscope, respectively. Ultraviolet-visible diffuse reflectance spectroscopy (UV-vis DRS) was performed on a JASCO V-750 instrument equipped with an integrating sphere. X-ray photoelectron spectroscopy (XPS) was conducted on a VG-ESCALAB 250Xi instrument with a monochromic Al K_α source at 1486.6 eV (150 W). The peak of C 1s at 284.6 eV was used as the reference to calibrate the binding energy. Nitrogen adsorption-desorption measurements were performed on a BELSORP-mini II analyzer using the Brunauer-Emmett-Teller (BET) method. The photocurrent response was determined using an electrochemical workstation in a three-electrode photoelectrochemical cell. The photocatalyst film coated on fluorine-doped tin oxide conducting glass was used as the working electrode. A platinum foil and a saturated calomel electrode

(SCE) were employed as the counter electrode and the reference electrode, respectively. 0.5 mol L⁻¹ NaSO₄ aqueous solution was applied as the electrolyte.

2.4. Adsorption and photocatalytic experiments

In a typical experiment, 50 mg of catalyst were added to 100 mL of an aqueous solution containing 50 mg L⁻¹ of MB dye. The suspension was sonicated for 10 min and then stirred for 2 h in the dark to evaluate the adsorption property of the sample. After achievement of the adsorption-desorption equilibrium of MB with the catalyst, the photocatalytic degradation of MB was performed in a 250-mL jacketed cylindrical glass reactor using a 300-W Xe lamp with a UV cutoff filter ($\lambda > 400$ nm) as the irradiation source. The system temperature (25 °C) was maintained with a circulation cooling device. At given time intervals, approximately 4 mL of the suspension was withdrawn and centrifuged to remove the solid particles during the adsorption and photocatalysis experiments. The residual MB in the solution was analyzed by monitoring its maximum absorption band using a UV-vis spectrometer (JASCO V-750). To further evaluate the photocatalytic performance, the removal of methyl orange (MO) and RhB were also conducted under the same experimental conditions.

To determine the active species in the photocatalytic degradation of organic pollutants, isopropanol (IPA), AgNO₃ and methanol were added into the reaction solution (20 mmol L⁻¹) to scavenge hydroxyl radicals, electrons and holes, respectively. In the study of the effect of the superoxide radical, the solution was purged with nitrogen for 120 min to remove oxygen completely before photocatalytic degradation. To detect the generation of hydroxyl radicals, the photoluminescence (PL) studies were carried out in a basic solution of terephthalic acid using a FLS980 fluorescence spectrometer with an excitation wavelength of 315 nm. The experimental procedure was the same as that reported previously [29].

3. Results and discussion

3.1. Composition, phase structure and optical properties

Thermal analysis was employed to quantify the contents of carbon in the composites. TG analysis was carried out in an air atmosphere by increasing the temperature from RT to 1000 °C at a constant heating rate of 10 °C min⁻¹. As shown in Fig. 1, almost no weight loss was observed for CaFe₂O₄ NRs in air at temperatures up to 1000 °C. However, the composite photocatalysts showed an obvious mass loss between 150 and 380 °C, which mainly arose from the combustion of carbon. No distinct weight loss was detected above 400 °C, demonstrating the complete combustion of carbon above this temperature. Therefore, the weight percentage of carbon in the C/CaFe₂O₄ composite can be determined from the weight loss after heating the samples to a temperature above 400 °C. The carbon contents in the composites were calculated to be 28, 41, 49, 58, 67 and 71 wt% for sample (b) to sample (g), respectively. Hence, C/CaFe₂O₄ NRs photocatalysts with different carbon

Fig. 1. TG curves of *X* wt% C/CaFe₂O₄ NRs. (a) *X* = 0; (b) *X* = 28; (c) *X* = 41; (d) *X* = 49; (e) *X* = 58; (f) *X* = 67; (g) *X* = 71.

contents were successfully prepared.

In the XRD patterns of Fig. 2, all samples showed major diffraction peaks at 19.2°, 33.6°, 35.5°, 42.8°, 49.7° and 61.4°, which could be assigned to the (200), (320), (201), (311), (401) and (170) planes of orthorhombic CaFe₂O₄ (JCPDS-32-0168), respectively. As labeled by the dotted box, an intense peak was observed at 20.7° in the composite samples. This peak is very similar to the standard XRD peak of chaoite located at 20.8° (JCPDS-22-1069), indicating the existence of the carbon phase in chaoite [30]. Moreover, the intensity of this characteristic carbon peak increased distinctly with the increase of the carbon content from 41 to 71 wt%. However, this peak of carbon was negligible for 28 wt% C/CaFe₂O₄ NRs, probably owing to the low carbon content. The above results demonstrate that carbon was successfully coated onto the surface of CaFe₂O₄ NRs in the form of chaoite.

The optical absorption property of the photocatalyst is one of the major factors influencing the photocatalytic activity. UV-vis DRS was employed to investigate the absorption edge of the obtained samples. As can be seen from Fig. 3, the CaFe₂O₄

Fig. 2. XRD patterns of *X* wt% C/CaFe₂O₄ NRs. (a) *X* = 0; (b) *X* = 28; (c) *X* = 41; (d) *X* = 49; (e) *X* = 58; (f) *X* = 67; (g) *X* = 71.

Fig. 3. UV-vis DRS of X wt% C/CaFe₂O₄ NRs. (a) $X = 0$; (b) $X = 28$; (c) $X = 41$; (d) $X = 49$; (e) $X = 58$; (f) $X = 67$; (g) $X = 71$.

NRs displayed a strong absorption band between 400 and 670 nm. In contrast, the light absorption edges of C/CaFe₂O₄ NRs moved further into the long wavelength visible region with an increase of the carbon content. Additionally, the light absorption intensity of C/CaFe₂O₄ NRs above 550 nm was obviously enhanced compared with that of the pristine CaFe₂O₄ NRs, indicating that the carbon coating could effectively improve the optical absorption property. As a consequence, the composite photocatalysts exhibit excellent ability for light harvesting, which is beneficial for the improvement of the photocatalytic activity.

3.2. Morphology and surface functional groups of the photocatalysts

The morphology and the dispersity of the photocatalysts were investigated by SEM. As shown in Fig. 4(A)–(C), the pure CaFe₂O₄ exhibited a well-defined rod shape with a length of a few microns and a diameter of approximately 200–500 nm. The surface of the nanorod was smooth, but some were aggregated into bundles side-by-side. The SEM images of C/CaFe₂O₄ NRs are shown in Fig. 4(D)–(F). It can be seen that the surface of the nanorod was relatively rough, suggesting that the deposited carbon layer was tightly anchored on the smooth surface of CaFe₂O₄. The existence of carbon could be further confirmed by the EDS analysis, as shown in Fig. 4(G). Only C, Ca, Fe and O elements were detected in the C/CaFe₂O₄ composite. The observed Si signal arose from the silicon wafer substrate. The absence of other elements indicated that the composite samples were free of impurities, which was in good agreement with the XRD results.

Fig. 5(A) shows the FTIR spectra of the samples. The peaks at approximately 640, 1050 and 1635 cm⁻¹ were assigned to the Fe–O stretching vibration, Fe–O–Ca metal framework stretching vibration and O–H bending vibration of the adsorbed water, respectively [31]. The broad band in the region of 3600–3200 cm⁻¹ was attributed to the O–H stretching vibration of the adsorbed water. Compared with the spectrum of pristine CaFe₂O₄ NRs, several new peaks appeared in the spectrum of C/CaFe₂O₄ NRs. The bands at 838 and 1704 cm⁻¹ corresponded to the C–C stretching vibrations [31] and the C=O stretching

Fig. 4. SEM images of CaFe₂O₄ NRs (A–C) and 58 wt% C/CaFe₂O₄ NRs (D–F); (G) EDS spectrum of 58 wt% C/CaFe₂O₄ NRs.

Fig. 5. (A) FTIR spectra of CaFe_2O_4 NRs and 58 wt% C/ CaFe_2O_4 NRs; (B) High-resolution XPS spectrum of the C 1s of 58 wt% C/ CaFe_2O_4 NRs.

vibration [32,33], respectively. Additionally, the bands between 1020 and 1380 cm^{-1} were associated with the C–OH stretching vibrations [22]. Furthermore, the peaks centered at 2916 and 2942 cm^{-1} were attributed to C–H vibrational modes [31,34]. These results indicate that the surface of CaFe_2O_4 NRs was functionalized by multiple types of carbon groups.

Subsequently, XPS measurement was performed to provide further information regarding the carbon species in C/ CaFe_2O_4 NRs. The deconvoluted C 1s spectrum of C/ CaFe_2O_4 NRs is shown in Fig. 5(B). The peak at 284.6 eV was attributed to the C–C bond, while the peak located at approximately 286.1 eV was a characteristic peak of the C–O band [32,35]. Furthermore, the appearance of a peak centered at approximately 288.4 eV implied the existence of C=O bond [21,36]. These findings together with the FTIR results indicate that the carbon with abundant functional groups was successfully decorated on the surface of CaFe_2O_4 NRs. It should be noted that the carboxyl and hydroxyl groups anchored on the surface of C/ CaFe_2O_4 NRs probably resulted in a negatively charged surface, which would favor the adsorption of MB (a cationic dye) owing to their electrostatic attraction.

3.3. Adsorption and photocatalytic performance

The MB dye was selected as a probe pollutant to evaluate the photocatalytic activity of the as-prepared samples. Before visible-light irradiation, the adsorption property of the photocatalyst for MB was also investigated in the dark condition. As depicted in Fig. 6, the pristine CaFe_2O_4 NRs exhibited a negligible adsorption capacity and low photocatalytic activity for the degradation of the target dye. However, it is noteworthy that C/ CaFe_2O_4 composites display a strong adsorption capability for MB. As a typical example, 67 wt% C/ CaFe_2O_4 NRs yielded a dye removal efficiency of more than 80% in the dark within 120 min. After reaching the adsorption–desorption equilibrium between MB and catalyst under vigorous stirring, the photocatalytic degradation experiment was conducted to eliminate the residual MB in the aqueous solution. It is apparent that CaFe_2O_4 NRs exhibited a very poor activity for MB degradation. However, when CaFe_2O_4 was modified by carbon, the photo-

catalytic performance was enhanced owing to a more efficient adsorption of MB. Furthermore, MO (an anionic dye) and RhB (a cationic dye) were employed to further evaluate the photocatalytic property of C/ CaFe_2O_4 . As shown in Fig. 7, approximately 90% of RhB was removed after adsorption and photocatalytic degradation, while the photocatalyst displayed almost no activity for the elimination of the MO dye. Combining the analysis of FTIR and XPS, we can conclude that the electrostatic attraction between C/ CaFe_2O_4 and the cationic dyes (MB and RhB) plays a dominant role in the adsorption process. However, the electrostatic repulsion between the photocatalyst and anionic dye (MO) results in negligible adsorption of MO.

The pseudo-first-order kinetic model [37] was applied to fit the degradation data and the catalytic activity of the samples was further assessed by the photocatalytic degradation rate constant. Fig. 8(A) shows the linear relationship of $\ln(C_0/C)$ as a function of time, and the corresponding rate constants (k) are displayed in Fig. 8(B). The order of MB degradation rate constants of the photocatalysts was as follows: 58 wt% C/ CaFe_2O_4 > 49 wt% C/ CaFe_2O_4 > 67 wt% C/ CaFe_2O_4 > 71 wt% C/ CaFe_2O_4 > 41 wt% C/ CaFe_2O_4 > 28 wt% C/ CaFe_2O_4 > CaFe_2O_4 . In partic-

Fig. 6. Adsorption and photocatalytic degradation of MB in the presence of X wt% C/ CaFe_2O_4 NRs. (a) $X = 0$; (b) $X = 28$; (c) $X = 41$; (d) $X = 49$; (e) $X = 58$; (f) $X = 67$; (g) $X = 71$.

Fig. 7. Adsorption and photocatalytic degradation of MB, RhB, and MO over 49 wt% C/CaFe₂O₄ NRs.

ular, 58 wt% C/CaFe₂O₄ NRs possessed the highest rate constant (0.0058 min⁻¹), which was 4.8 times greater than that of the pristine CaFe₂O₄ NRs (0.0012 min⁻¹). Considering the fact that the adsorption is a prerequisite step for the photocatalytic degradation of organic pollutants, the improved photocatalytic activity, to a large extent, was ascribed to the enhanced adsorp-

tion capacity of C/CaFe₂O₄ NRs toward MB. Moreover, it is noticeable that C/CaFe₂O₄ exhibited a higher photocurrent response (Fig. 9) compared with that of pure CaFe₂O₄, indicating that the separation efficiency of the photogenerated electron-hole pairs was improved over composite samples. Thus, a more efficient separation of charge carriers is another important factor for the enhancement of the photocatalytic activity.

To further investigate the adsorption property of the photocatalysts toward MB in aqueous solution, the adsorption kinetics curves for MB were analyzed for different samples. It can be seen from Fig. 10(A) that the adsorption amounts for MB increased rapidly by prolonging the contact time of photocatalysts and MB molecules within 20 min, after which the increment of the MB adsorption amounts became slow, indicating that the adsorption-desorption equilibrium of the system was achieved. Hence, the equilibrium adsorption capacity (q_e) was determined by fitting of the adsorption curves using a pseudo-second-order kinetic model [38,39]. As shown in Fig. 10(B), q_e first increased with the increase of carbon content in the composites, reaching the maximum value at sample (f), and then decreased with a further increase of carbon amounts. The equilibrium adsorption capacity of the optimum sample for MB dye was calculated to be 82.0 mg g⁻¹, which was 68.3 times

Fig. 8. First-order kinetic plots (A) and rate constants (B) of MB degradation in the presence of X wt% C/CaFe₂O₄ NRs. (a) $X = 0$; (b) $X = 28$; (c) $X = 41$; (d) $X = 49$; (e) $X = 58$; (f) $X = 67$; (g) $X = 71$.

Fig. 9. Current-potential curves for 58 wt% C/CaFe₂O₄ NRs (A) and CaFe₂O₄ NRs (B).

Fig. 10. Adsorption kinetics curves (A) and equilibrium adsorption capacities (B) for MB in the presence of X wt% C/CaFe₂O₄ NRs. (a) $X = 0$; (b) $X = 28$; (c) $X = 41$; (d) $X = 49$; (e) $X = 58$; (f) $X = 67$; (g) $X = 71$.

higher than that of the pristine CaFe₂O₄ NRs (1.2 mg g⁻¹). Obviously, the improved adsorption ability of the composite sample mainly stems from the coating of the carbon layer on the surface of CaFe₂O₄. As measured by nitrogen sorption isotherms, the BET specific surface areas of 58 wt% C/CaFe₂O₄ and pristine CaFe₂O₄ were 32.2 and 20.0 m² g⁻¹ (Fig. 11), respectively. Thus, the high adsorption capacity of composite sample is likely to result from the increased BET surface area

Fig. 11. Nitrogen adsorption-desorption isotherms of CaFe₂O₄ NRs and 58 wt% C/CaFe₂O₄ NRs.

besides electrostatic attraction.

The adsorption isotherm provides information for the interaction between the dye molecules and the photocatalyst surface at a constant temperature. Fig. 12(A) presents the plot of q_e versus equilibrium concentration (C_e) for MB adsorption on 58 wt% C/CaFe₂O₄ NRs at 25 °C. It can be seen that q_e increased dramatically in the beginning with the increase of C_e , and then reached a plateau when C_e was higher than about 10 mg L⁻¹. Two well-known isotherm models, Langmuir and Freundlich [40,41], were employed to fit the experimental data and the linear fitting curves are shown in Fig. 12(B) and (C), respectively. The correlation coefficient of the Langmuir curve ($R^2 = 0.9998$) was obviously higher than that of the Freundlich curve ($R^2 = 0.6836$), indicating that the Langmuir isotherm was more suitable for the interpretation of MB adsorption on the composite photocatalyst. Furthermore, the maximum adsorption capacity of 58 wt% C/CaFe₂O₄ NRs was calculated to be 74.1 mg g⁻¹ using the Langmuir model. Considering that the Langmuir isotherm theory describes a monolayer adsorption of adsorbate, it can be concluded that the MB adsorption occurs by a monolayer coverage on the photocatalyst surface.

3.4. Mechanism for the photocatalytic degradation of MB

To further explore the degradation mechanism of MB, the major reactive species during the photocatalytic reaction were

Fig. 12. Adsorption isotherm (A) and fitting results of Langmuir (B) and Freundlich (C) isotherm adsorption models for 58 wt% C/CaFe₂O₄ NRs.

identified by the addition of different scavengers. Generally, in a photocatalytic reaction for organic pollutant degradation, the hydroxyl radical ($\cdot\text{OH}$), superoxide radical ($\cdot\text{O}_2^-$) and hole (h^+) may serve as the active species. Hence, IPA, AgNO_3 , methanol and N_2 purging were used as scavengers for the probe of the hydroxyl radical, electron, hole and superoxide radical, respectively. As can be seen from the contrast experiments (Fig. 13), the rate constants showed a slight decrease in the presence of IPA, indicating that the hydroxyl radical did not have a large influence on the degradation of MB. However, the hole was also determined to be a minor active species responsible for the degradation of MB. The rate constant declined obviously when nitrogen gas was bubbled to purge the air in the reaction system, which suggested that the photocatalytic degradation was primarily driven by the participation of superoxide radical. Furthermore, considering the generation of superoxide radical involves the reaction of electron with dissolved oxygen, the observed sharp suppression of photocatalytic activity after addition of AgNO_3 in reaction solution further confirmed that the superoxide radical played a predominant role in the elimination of MB. In addition, the fluorescence technique was applied to detect the hydroxyl radical generated in the photocatalytic reaction. It can be seen from Fig. 14 that almost no obvious change in PL intensity was observed with increased irradiation time, indicating that negligible hydroxyl radicals formed in the C/ CaFe_2O_4 system.

Based on the above analysis, the possible mechanism for the photocatalytic degradation of MB by C/ CaFe_2O_4 NRs was proposed and is depicted in Fig. 15. Under visible-light irradiation, the photo-induced electrons can transfer from the VB to CB of CaFe_2O_4 , leaving holes on the VB. When carbon, which may serve as a potential electron collector [42,43], is coated onto the surface of CaFe_2O_4 NRs, the electrons gathering on the CB of CaFe_2O_4 would further migrate to the carbon layer where oxygen is reduced by the electrons to generate reactive $\cdot\text{O}_2^-$ radicals with strong oxidation ability. As a consequence, the MB molecules adsorbed on the carbon layer can react with $\cdot\text{O}_2^-$ to form the degradation products. Meanwhile, the MB pollutants could also be directly decomposed by the holes on the VB of CaFe_2O_4 . Therefore, it is concluded that the significant en-

Fig. 13. Active species trapping experiments of 58 wt% C/ CaFe_2O_4 NRs under visible-light irradiation.

Fig. 14. Hydroxyl radical trapping PL spectra of 58 wt% C/ CaFe_2O_4 NRs with terephthalic acid solution under visible light-irradiation.

hancement of the photocatalytic activity for C/ CaFe_2O_4 NRs could be attributed to the improvement of the adsorption capacity toward MB as well as the accelerated separation of photo-excited charge carriers arising from the presence of carbon coating on the surface of CaFe_2O_4 NRs.

4. Conclusions

A novel composite photocatalyst, C/ CaFe_2O_4 NRs, is prepared by introducing a carbon coating on the surface of CaFe_2O_4 NRs. The deposition of carbon on the CaFe_2O_4 surface is verified by XRD, UV-vis DRS, SEM, FTIR and XPS spectroscopy. The carbon-decorated CaFe_2O_4 composites exhibit an enhanced photocatalytic activity for the elimination of MB in an aqueous solution under visible light illumination, which can be related to three factors: (1) the carbon coating with abundant functional groups (carboxyl and hydroxyl) improves the adsorption capability for MB molecules; (2) the excellent electrical conductivity of carbon enhances the separation efficiency of the photogenerated carriers; and (3) the introduction of carbon coating greatly extends the light absorption range. The optimum photocatalyst is the 58 wt% C/ CaFe_2O_4 with a degrada-

Fig. 15. Scheme of the mechanism for photocatalytic degradation of MB over composite photocatalysts.

tion rate constant of 0.0058 min^{-1} , which is approximately 4.8 times higher than that of the pristine CaFe_2O_4 (0.0012 min^{-1}). Additionally, the study of the adsorption isotherm suggests that MB adsorption on the surface of composite photocatalysts follows the Langmuir model. The scavenger quenching results indicate that the superoxide radicals ($\cdot\text{O}_2^-$) play an important role in the degradation of MB. Our findings provide new insights into the design and fabrication of efficient carbon-semiconductor composite photocatalysts.

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Graphical Abstract

Chin. J. Catal., 2017, 38: 1770–1779 doi: 10.1016/S1872-2067(17)62888-2

Visible light-responsive carbon-decorated p-type semiconductor CaFe_2O_4 nanorod photocatalyst for efficient remediation of organic pollutants

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Carbon-decorated p-type semiconductor CaFe_2O_4 nanorods exhibit an enhanced photocatalytic activity for the degradation of MB owing to the simultaneous improvement of MB adsorption, separation and transfer of photogenerated charges and light absorption.

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可见光响应的碳修饰纳米棒状p型 CaFe_2O_4 半导体光催化降解有机污染物

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摘要: 制备了C/ CaFe_2O_4 纳米棒复合材料, 并考察了其光催化性能, 同时深入研究了C修饰对 CaFe_2O_4 活性的影响. 研究发现, 复合材料的光催化降解活性与C和 CaFe_2O_4 的质量比密切相关. 其最佳的碳含量为58 wt%, 所得复合光催化剂对亚甲基蓝(MB)的降解速率常数达到 0.0058 min^{-1} , 是铁酸钙的4.8倍. 进一步研究表明, C修饰在 CaFe_2O_4 表面显著提高了样品对亚甲基蓝染料的吸附性能. 吸附等温线结果发现, MB以单分子层形式吸附于 CaFe_2O_4 表面. 总体而言, C覆盖在 CaFe_2O_4 表面可以使光生电子和空穴更有效的分离和传输, 可以显著提高催化剂对MB的吸附性能, 还可以增强样品对光的吸收能力, 因而催化剂光催化降解MB性能增加.

表征结果表明, 复合光催化剂表面含有大量羧基和羟基基团, 导致光催化剂表面带负电荷, 从而有利于阳离子的MB的静电吸附. 为了进一步验证该吸附机理, 我们选择了另外两种染料分子, 阳离子的罗丹明B和阴离子的甲基橙. 结果显示, 该光催化剂对罗丹明B同样具有较强的吸附能力和较好的光催化降解活性, 但对甲基橙几乎没有吸附和光催化性能. 这充分说明亚甲基蓝染料通过静电相互作用的形式吸附于催化剂表面, 较好的吸附性能进一步促进了光催化剂的降解活性.

为了讨论光催化机理, 向反应体系中加入不同的捕获剂来研究光催化反应过程中产生的活性物种. 研究显示, 羟基自由基在光催化降解亚甲基蓝的反应中几乎没有作用, 光生空穴发挥了次要作用, 而超氧自由基在整个反应中发挥了主导作用. 因此, 光催化降解的机理如下: CaFe_2O_4 在可见光激发下产生光生电子和空穴, 电子快速转移到C材料的表面并与空气中的氧气反应生成超氧自由基, 后者再与吸附在光催化剂表面的染料分子反应产生低毒或无毒的降解产物. 此外, CaFe_2O_4 价带上产生的空穴也可以直接将染料分子氧化成小分子产物.

关键词: p型半导体 CaFe_2O_4 ; 碳覆盖; 纳米棒; 复合光催化剂; 亚甲基蓝降解

收稿日期: 2017-06-18. 接受日期: 2017-07-12. 出版日期: 2017-10-05.

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基金来源: 国家自然科学基金(21503100); 江西省自然科学基金(20161BAB213071, 20151BAB213010); 江西省教育厅基金(GJJ150325); 江西师范大学青年英才支持项目.

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