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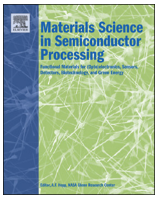

Visible-light-responsive γ-Fe_2O_3/PMMA/S-TiO_2 core/shell nanocomposite: Preparation, characterization and photocatalytic activity

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ABSTRACT

Organic-inorganic composite materials have demonstrated many potential applications in environmental field. This paper presented a facile preparation method for γ-Fe_2O_3/PMMA/S-TiO_2 nanocomposite with core-shell structure and its application in degradation of phenanthrene under visible light irradiation. Firstly, γ-Fe_2O_3/PMMA nanoparticles were synthesized by the modified-suspension-polymerization method. Then γ-Fe_2O_3/PMMA/S-TiO_2 core-shell nanocomposites were prepared by adding as-synthesized γ-Fe_2O_3/PMMA nanoparticles into the sol solution formed by sol-gel method using tetrabutyltitanate as Ti source and thiourea as sulfur source. The characterization result of the obtained products by X-ray diffraction, scanning electron microscopy, transmission electron microscopy and X-ray photoelectron spectroscopy indicated that the layer of sulfur doped titania was successfully coated onto the surface of γ-Fe_2O_3/PMMA nanoparticles. Thermogravimetry (TG) analysis presented that the layer of sulfur doped TiO_2 could efficiently reduce the decomposition of polymethylmethacrylate (PMMA) even at higher temperature up to 500 °C. UV–vis diffuse reflectance spectroscopy showed that γ-Fe_2O_3/PMMA/S-TiO_2 nanocomposite clearly exhibits the red-shift of the absorption edge compared with γ-Fe_2O_3/PMMA/TiO_2. The photocatalytic activity evaluation showed that the γ-Fe_2O_3/PMMA/S-TiO_2 nanocomposite exhibited the best photocatalytic activity for degradation of phenanthrene under the conditions of 0.8 mol% of sulfur doping, calcination temperature at 300 °C and the addition concentration of 1.0 g/L. Moreover, the nanocomposites have good recovery ability by the recovery experiment.

1. Introduction

In the field of advanced oxidation technologies (AOPs), semiconductor TiO_2 has attracted much attention due to its high efficiency as a photocatalyst for environmental remediation and energy conversion. Many studies have been carried out on the application of TiO_2. However, its practical application is limited due to its drawbacks of only response to UV light and difficult recycling [1–4]. Many efforts have been made to extend TiO_2 absorption into visible light region to utilize solar or indoor light such as metal doping [5], nonmetal doping [6–8], dye sensitization [9], and establishment of heterojunction structure with narrow band gap semiconductor [10].

A common approach to enhance the photocatalytic activity of TiO_2 is to increase its surface area by immobilization of TiO_2 on porous silica [11–13] and porous carbon [14,15] because these porous carriers have superior characteristics, such as chemically inert, possessing high surface areas and high physical stability. It is notable that graphene based TiO_2 nanocomposite systems also have been utilized to increase the efficiency of TiO_2 photocatalyst, which is attributed to the higher light absorption ability of the composites, as well as, the reduced recombination rates of electron-hole pairs [16].

In addition, the method of the combination of TiO_2 with sonolysis has obtained extensive attention by applying the ultrasonic irradiation to create turbulence inside the solution overcoming the main disadvantages of UV light such as its low penetration rate in highly colored solutions and shielding effects of catalyst particles in water [17,18].

In recent years, magnetic catalysts have been proposed as a means to solve the difficulty of photocatalyst separation from the treated water by applying an external magnetic field. However, the report on the photocatalyst possessing of magnetic separation and visible light

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activity is hardly found. To that end, our work tried to obtain a magnetically separable photocatalyst, γ-Fe_2O_3/PMMA/S-TiO_2 nanocomposite, which not only exhibits enhanced photocatalytic activity under visible light irradiation but also easily separated to recover from a suspension solution with the aid of magnetic γ-Fe_2O_3. In order to avoid the reduction of γ-Fe_2O_3 ($Fe^{3+} \rightarrow Fe^{2+}$) by photogenerated electron produced by S-TiO_2, the non-conducting polymer PMMA was selected as the isolation layer. In addition, the photocatalytic activity for the degradation of phenanthrene was also investigated.

2. Experimental

2.1. Synthesis of γ-Fe_2O_3 nanoparticles

Magnetic γ-Fe_2O_3 nanoparticles were prepared by sol-gel method. Briefly, an excess of 0.1 M NaOH (AR, Damao Chemical Reagent Factory of Tianjin.) solution was added dropwise to 0.08 M $FeCl_3$ (AR, Sinopharm Chemical Reagent Co.) solution and kept constantly stirred for 1 h. A deep orange precipitate was obtained and further centrifuged, washed with deionized water and dried in air at 80 °C. Finally, γ-Fe_2O_3 was obtained by annealing the above dried powder at 500 °C for 2 h.

2.2. Synthesis of γ-Fe_2O_3/PMMA nanoparticles

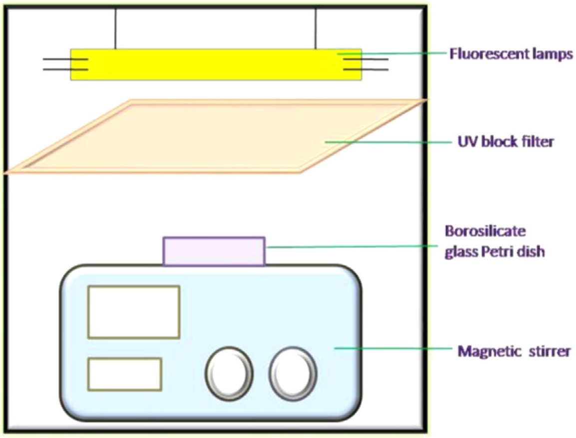
The γ-Fe_2O_3/PMMA nanoparticles were prepared by modified-suspension-polymerization method. Firstly, the organic phase, which comprised of 1 g BPO (Benzoyl peroxide, AR, Sinopharm Chemical Reagent Co.), 45 mL MMA (Methyl methacrylate, AR, Sinopharm Chemical Reagent Co.), 5 mL DVB (Divinylbenzene, CR, Darui fine chemicals of Shanghai.) and 15 mL hexane (AR, Damao Chemical Reagent Factory of Tianjin.), mixed with an appropriate amount of γ-Fe_2O_3 by strong stirring to assure the homogeneous dispersion. For the water phase, it consisted of 13 g PVA (Polyvinyl alcohol, AR, Damao Chemical Reagent Factory of Tianjin.) and 500 mL deionized water. Secondly, the organic phase and the water phase were mixed at a stirring speed of 500 rpm and kept oxygen-free by continuously purging with nitrogen gas in the reactor equipped with three vertical baffles. Finally, the reactive temperature rose to 50 °C within 1 h, maintained at 60 °C for 2 h and held at 80 °C for 1 h. After the synthesis process was completed [19–22], the γ-Fe_2O_3/PMMA nanoparticles were separated from the solution magnetically. Subsequently the product was washed by deionized water and acetone successively and dried at 60 °C for 12 h.

2.3. Synthesis of γ-Fe_2O_3/PMMA/S-TiO_2

The γ-Fe_2O_3/PMMA/S-TiO_2 core/shell nanocomposites were prepared by sol-gel method. Briefly, 1.2 g γ-Fe_2O_3/PMMA nanoparticles were dispersed in a mixture of 20 mL ethanol and 5 mL tetrabutyl titanate (AR, Zhiyuan Chemical Reagent Factory of Tianjin.) with stirring for 30 min, and then added 40 mL deionized water and 0.25 g thiourea (AR, Damao Chemical Reagent Factory of Tianjin.), followed by adding 1.0 M hydrochloric acid (AR, Damao Chemical Reagent Factory of Tianjin.) dropwise to adjust pH 1.8. After the synthesis process was completed, the obtained γ-Fe_2O_3/PMMA/S-TiO_2 was washed by ethanol and deionized water for several times, and then dried at 60 °C in oven for 12 h. The synthesized procedure of γ-Fe_2O_3/PMMA/TiO_2 nanocomposites was similar with that of γ-Fe_2O_3/PMMA/S-TiO_2 in the absence of thiourea.

2.4. Characterization

The X-ray diffraction (XRD) patterns were recorded by step scanning using a BRUKER D8 ADVANCE XRD-6000 X-ray diffractometer (Bruker Germany) with Cu Kα radiation ($\lambda = 1.54056$ Å). A transmission electron microscope (TEM, JEM-2100HR) and a scanning electron microscope (SEM, ZEISS Ultra 55) were used to observe the morphology of the nanocomposites. To determine the fine elemental composition and electronic structure, X-ray photoelectron spectroscopy (Axis Ultra DLD, Kratos) with Mono AlKα X-rays at vacuum pressure of $\sim 5 \times 10^{-9}$ Torr was employed. The binding energies were corrected based on C1s level peak at 284.6 eV. The thermal degradation behaviors of the nanocomposites were monitored using a Perkin-Elmer TGA -DSC 7 apparatus under a stream of nitrogen gas. Optoelectronic properties were derived from diffuse reflectance spectra obtained on a UV–vis spectrophotometer (Shimadzu 2501PC) equipped with an integrated sphere attachment (ISR 1200). $BaSO_4$ was a reference standard material.



Scheme 1. Schematic illustration of the photocatalytic experiment.

2.5. Photocatalytic experiment

The photocatalytic activity of synthesized samples was evaluated through the degradation of phenanthrene in a photodegradation chamber (Scheme 1) fixing a Philips 25 W Fluorescent lamp (wavelength > 390 nm, light intensity 8×10^{-5} W cm^{-2}) as a visible light source at its top, a UV block filter (UV400, Opticology) was mounted under the light source. A borosilicate Pyrex glass Petri dish (I.D. = 5 cm) was used as the reactor. The glass reactor was sealed with Parafilm and cooled with a fan to prevent evaporation and maintain a constant temperature ($T = 25 \pm 1$ °C). The initial concentration of phenanthrene was 2 mg L^{-1} and the total volume of the solution in the reactor was 15 mL. A certain amount of synthesized nanocomposites was placed in the phenanthrene solution to form the photocatalyst suspension. For all experiments, deionized water was used. This suspension was magnetically stirred in the dark for 60 min before light irradiation to ensure the establishment of an adsorption/desorption equilibrium of phenanthrene on the surface of photocatalysts.

The slurry of reaction sample was taken out at pre-determined intervals, filtered using Milipore 0.22 μm membrane filter to separate the photocatalyst and analyzed using an Agilent model 1200 HPLC with a variable wavelength detector set at 254 nm. The mobile phase used was methanol: water (90:10, V/V) at a flow rate of 1 mL/min.

2.6. Recovery of photocatalyst

The beaker containing photocatalyst suspension placed on the magnet base. After the magnetic photocatalyst is completely sucked to the bottom of the beaker, discarding the supernatant, drying at 80 °C