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Preparation of a magnetic graphene oxide–Ag_3PO_4 composite photocatalyst with enhanced photocatalytic activity under visible light irradiation

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ABSTRACT

Magnetic graphene oxide–Ag_3PO_4 (MGO–Ag_3PO_4) nanocomposites were prepared by a facile method, and used as photocatalysts for the degradation of methylene blue (MB) in water under visible light irradiation. The MGO–Ag_3PO_4 hybrids were characterized by X-ray diffraction spectroscopy, field emission scanning electron microscopy and UV–vis diffuse reflectance spectra. The results indicated that the as-prepared samples exhibited an enhanced photoactivity toward MB degradation compared to bare Ag_3PO_4. Further study showed that the dominate radicals was the photogenerated holes in the degradation process of MB. GO can suppress the recombination of electron–hole pairs, and improve the photocatalytic performance. Furthermore, the composites can be separated easily by an external magnet. At the same time, the MGO–Ag_3PO_4 composite exhibited higher stability compared to Ag_3PO_4.

1. Introduction

Semiconductor photocatalysts have attracted increasing attention during the past decades due to their application to solving energy and environmental problems [1–4]. Among semiconductor photocatalysts, titanium dioxide (TiO_2) has been widely studied for its high efficiency, stability, low cost and nontoxicity [5,6]. However, as the band gap of TiO_2 is 3.2 eV, it can only be excited by the UV light (wavelength $\lambda < 388$ nm), which account for only 4% of the solar spectrum [7]. To extend the absorption of TiO_2 to the visible light region, some strategies have been explored, including non-metal doping [8,9], metal deposition [10–12] and synthesis of coupled semiconductors [13–15]. However, the photoactivity of visible-light-driven TiO_2 is low for the high recombination rate of photo-generated electrons and holes [16,17]. Therefore, many scientists paid the main attention to the development of a new generation of visible-light-driven catalyst without chemical modifications. Recently, the silver orthophosphate (Ag_3PO_4) has been proven to be a promising alternative which can oxide water or degrade organic pollutants in aqueous solution under visible light irradiation [18]. It has been reported that Ag_3PO_4 has significantly higher photoactivity than that of currently known photocatalysts under visible light illumination. The excellent performance of Ag_3PO_4 can be ascribed to its highly dispersive band structure of the conduction-band minimum [19].

Graphene has attracted much attention owing to its remarkable property, such as superior conductivity, large adsorptive capacity and high specific surface area [20–22]. Furthermore, graphene can be easily obtained from graphite through chemical oxidation–reduction procedure at a low cost. These advantages make graphene as excellent supporters to load nanocrystals for wide applications. Recently, great efforts have been made in employing graphene or graphene oxide (GO) as a support material to synthesis new composite photocatalysts with enhanced photoactivity. It has been reported that grapheme–TiO_2 composite photocatalyst is more effective than bare P25 for H_2 evolution [23] and removal of pollutants [24]. Graphene was also introduced to other semiconductor to improve the photocatalytic performance, such as ZnO [25], CdS [26], and Bi_2MoO_6 [27].

Generally, suspended powders are applied in photocatalytic reaction, owing to the larger specific surface area than that of immobilized system. But in practical application, the removal of the catalyst from the suspension is still a problem. Recently, magnetic materials, especially Fe_3O_4 nanoparticles, are of considerable interests. With the assistance of an external magnetic field, the magnetic materials were believed to separate catalysts from

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liquor more conveniently. Some scientists have demonstrated that the magnetic photocatalysts have high photocatalytic activity and easy separation properties [28,29]. Recently, Guo et al. [30] reported the preparation of Fe nanoparticles@graphene composites and their decolorization performance for MB by adsorption. In this work, a simple and facile method was employed for the synthesis of Fe_3O_4–GO composite (MGO) as the support for Ag_3PO_4. Different from the work by Guo, our purpose is to prepare a composite with high visible light responsive photocatalytic activity. Furthermore, during the preparation process in our work, the MGO maintained good hydrophilicity. Therefore, the favorable dispersion in water provided advantages to combine with Ag^+ and react with PO_4^{3-}. The obtained samples not only exhibited the adsorption capacity of graphene oxide but also the magnetic separability of Fe_3O_4 and excellent photocatalytic activity of Ag_3PO_4. The photocatalytic activity of the resulting samples was evaluated by degradation of methylene blue (MB) under visible light irradiation. In addition, the optimum content of MGO on the photocatalytic performance was also obtained.

2. Experimental

2.1. Materials

Graphite powder, hydrogen peroxide (H_2O_2, 30%), potassium permanganate ($KMnO_4$), iron(III) chloride hexahydrate ($FeCl_3{\cdot}6H_2O$), iron (II) sulfate heptahydrate ($FeSO_4{\cdot}7H_2O$), silver nitrate ($AgNO_3$), p-benzoquinonyl and ethylene diamine tetraacetic acid (EDTA) were purchased from Sinopharm Chemical Reagent Co., Ltd. Sulfuric acid (H_2SO_4, 98%) was purchased from Shanghai Zhongshi Chemical Factory. Sodium phosphate (Na_3PO_4) was purchased from Shantou Xilong Chemical Factory. Ammonia water ($NH_3{\cdot}H_2O$, 25%) and *tert*-butanol was purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd. All the chemical were reagent grade or above and used without further purification. The ultrapure water was produced from Milipore Milli-Q water purification system.

2.2. Preparation of GO

GO was synthesized from graphite powder by a modified Hummers method [31], where 2 g graphite powder was added to 100 mL of H_2SO_4 (98%); then 8 g $KMnO_4$ was slowly added while stirring in an ice bath. The obtained dark black mixture was kept stirring for 2 h below 10 °C. Subsequently, the solution was heated to 35 °C and kept for 1 h. 100 mL of distilled water was dropwise added to the mixture in an ice bath to keep the temperature blow 100 °C. After stirring for 1 h, 100 mL of water and 30 mL of H_2O_2 (30%) was added. A mount of bubble was rising and the color of mixture was turned to bright yellow. The resultant mixture was washed by 5% HCl (aq) and water for several times, and freeze-dried.

2.3. Preparation of MGO

5.4 g $FeCl_3{\cdot}6H_2O$ and 3.3 g $FeSO_4{\cdot}7H_2O$ was added into 200 mL of distilled water which was bubbled with N_2 for 10 min. After stirring for about 10 min, the dilute ammonia solution was slowly added to adjust the pH to 9. The black product was washed for several times and ultrasonic dispersed in definite amount of water, to obtain the Fe_3O_4 suspension. Then a certain amount of GO was dispersed in water, mixed with the Fe_3O_4 suspension, and stirred for 4 h. The obtained liquid was centrifuged and washed for several times, then dried in vacuum. The weight ratio of Fe_3O_4 to GO was 1:1.

2.4. Preparation of MGO–Ag_3PO_4

The as-prepared MGO was dispersed by ultrasonication in 50 mL of water. 100 mL of $AgNO_3$ solution (0.03 mol/L) was added dropwise into the GO solution and kept stirring for 1 h. Subsequently, 50 mL of Na_3PO_4 solution (0.02 mol/L) was added slowly into the mixture liquor and kept stirring for 5 h. The product was washed for three times and dried at 60 °C. The weight ratio of MGO to Ag_3PO_4 was 5%, 10%, 20%, 30% and 40%, which were defined as M-A-5%, M-A-10%, M-A-20%, M-A-30% and M-A-40%, respectively.

2.5. Instruments and analysis method

The crystalline structures of as-prepared samples were determined by an X-ray diffractometer (XRD, Shimadazu, XD-3A) over the 2θ range 10–90°. The surface morphologies were characterized with a field emission scanning electron microscopy (SEM, Hitachi, S-4800). The microstructures of the samples were examined through a transmission electron microscopy (TEM, JEOL, JEM-2100F), which was equipped with an energy dispersive X-ray detector (EDX). The Brunauer–Emmett–Teller (BET) specific surface areas of the samples were analyzed by nitrogen adsorption in a nitrogen adsorption apparatus (Micromeritics, ASAP-2020). The UV–vis absorption spectra of the samples and the concentrations of dye were both measured by a UV–vis spectrophotometer (Shimadzu, UV-3600). Magnetic measurements were performed on a vibrating sample magnetometer (VSM).

2.6. Photocatalytic activity

Photocatalytic behavior of MGO–Ag_3PO_4 composites was performed by degrading methylene blue (MB) in aqueous solution under visible light irradiation. For comparison, the photocatalytic performance for Ag_3PO_4 alone was also measured. 25 mg of the photocatalysts was added into 50 mL of MB solutions whose initial concentration was 20 mg/L. To reach the adsorption equilibrium and compare the adsorption ability of photocatalysts, the resultant suspension was placed in the dark under stirring for 30 min before the light illumination. The visible light source used in the experiments was a 250 W halogen lamp with a 400 nm cut-off glass filter (Instrumental Corporation of Beijing Normal University, MVL-210). After given time intervals, 1 mL solution was withdrawn from the reactor and centrifuged before being analyzed by UV–vis spectrophotometer. The absorbance at

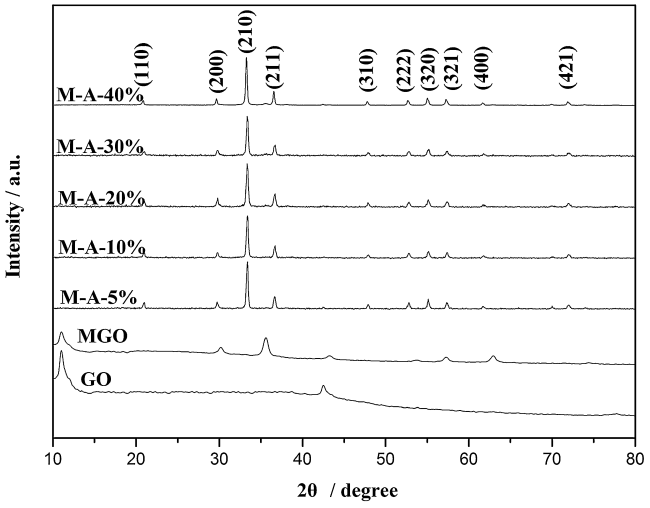

Fig. 1. XRD patterns of different samples.