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Synthesis of $ZnFe_2O_4/ZnO$ nanocomposites immobilized on graphene with enhanced photocatalytic activity under solar light irradiation

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ABSTRACT

Magnetically recyclable $ZnFe_2O_4/ZnO$ nanocomposites immobilized on different content of graphene with favorable photocatalytic activity under solar light irradiation were successfully prepared on the basis of an ultrasound aided solution method. The molar ratio of $ZnFe_2O_4$ to ZnO and the content of graphene could be controlled by adjusting the amount of zinc salts and graphene oxide dispersions. The most excellent photocatalytic activity under solar light irradiation was displayed when the molar ratio of $ZnFe_2O_4$ to ZnO was 0.1 and the weight ratio of graphene to $ZnFe_2O_4/ZnO$ was 0.04. Furthermore, the presence of magnetical $ZnFe_2O_4$ will facilitate the recycling process of photocatalyst nanoparticles.

1. Introduction

Environmental problems such as air pollution, soil contamination, especially refractory wastewater produced by some noxious organics, have aroused much attention in the area of environmental remediation [1]. Over past few decades, nano-semiconductor photocatalysts offer an extremely convenient route for eliminating the crisis of water pollution inasmuch as various organic pollutants can be easily degraded under UV or solar light irradiation in the presence of photocatalysts [2–4].

Nano zinc oxide (ZnO) with features of high activity, chemical stability, morphology controllable preparation, and environmental friendly has been widely used as photocatalysts [5]. Unfortunately, ZnO has a wide bandgap of 3.2 eV, which is unfavorable for absorption and utilization of visible light region of solar light. Namely light with shorter wavelength (below 385 nm) can be employed to drive ZnO to generate electron–hole pairs [6,7]. It is well known that the major hindrance for enhancing photocatalytic efficiency of pure semiconductor photocatalysts is the fast recombination of photogenerated electron–hole pairs [8,9]. One of effective strategies to address this problem is to prepare semiconductor nanocomposites, which will facilitate the charge migration [10]. Especially, the combination of P-type semiconductor and N-type semiconductor, as well as non-mental doping semiconductors will improve the photocatalytic activity significantly. In recent years, some researchers have devoted to this area and many semiconductor nanocomposites such as SnO_2–ZnO [11], ZnO/CdS [12], ZnO/In_2O_3 [13], NiO/ZnO [14], Cu_2O/ZnO [15], and N doped Cu_2O [16] have been successfully synthesized.

At the same time, it is noteworthy that some spinel materials, including $ZnFe_2O_4$, are a class of semiconductors with narrow bandgaps. These semiconductors exhibit characteristics of excellent visible-light response, good photochemical stability, as well as favorable magnetism [17,18]. Although these materials with such superior properties open up a promising gate for applications in photocatalysis oxidation, they are seldom used as photocatalysts independently due to the lower valence band potential and poor property in photoelectric conversion [19]. Based on the fundamental theory of photocatalysis, it is not difficult to envisage that another profitable pathway to improve the photocatalytic activity is looking for some supporting medium with outstanding electric conductivity. Photoinduced electrons can be transferred rapidly by conductive supporters, simultaneous leaving more positive holes, so as to remarkably enhance the photocatalytic efficiency [20]. Among various conducting materials, carbon material, especially two-dimensional (2D) graphene which was first obtained by Geim et al., has been received extensively concern for use in the area of photocatalysis [21–24].

Recently, hot semiconducting materials have aroused many interests [25–27]. It had been reported that the $ZnFe_2O_4/TiO_2$ nanomaterial could be served as photocatalyst and modified electrode [28–30]. However, the preparation process usually involved high temperatures or some complicated fabricating methods, which would limit the production in a large scale. Meanwhile, the photocatalytic activity of $ZnFe_2O_4/TiO_2$ nanocomposite under

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solar light irradiation was also restrained [31]. On the other hand, some researchers also had conducted a series of investigations on the ferrite–graphene-based magnetical photocatalysts with visible-light-response, such as $ZnFe_2O_4$/graphene [32], $NiFe_2O_4$/graphene [33], and $CoFe_2O_4$/graphene [34]. Unfortunately, in the absence of H_2O_2, the composite photocatalysts exhibited inferior photocatalytic activity under solar light irradiation. Namely H_2O_2 played crucial roles in the photocatalysis oxidation but it was considered as introduced contaminant to some extent.

Therefore, from views of protecting the environment, enhancing the photocatalytic activity and improving the visible light absorption region of solar light spectrum, the conjugation between semiconductor nanocomposites and graphene seems tremendously meaningful. In the present work, we selected the nanocomposite of P-type $ZnFe_2O_4$ and N-type ZnO as photocatalyst, successfully synthesized $ZnFe_2O_4$/ZnO nanocomposites immobilized on graphene and investigated their photocatalytic activity under solar light irradiation, including the effects of $ZnFe_2O_4$ content and graphene content on the photocatalytic efficiency. The molar ratio of $ZnFe_2O_4$ to ZnO could be adjusted easily because of the growth-tunable of ZnO. On the other hand, the excellent photocatalytic activity of the novel material was exhibited without any assisted reagents. The formation of $ZnFe_2O_4$/ZnO nanocomposites as well as the presence of graphene efficiently facilitated the charge transfer and improved the photocatalytic reactivity under solar light irradiation. Meanwhile, the existence of magnetic $ZnFe_2O_4$ nanoparticles provided a convenient route for recycling the photocatalyst by an external magnetic field. The prepared samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDS), UV–vis diffuse reflectance spectra (UV–vis DRS), fourier transform infrared (FT-IR) and X-ray photoelectron spectroscopy (XPS). Photochemical experiments of the obtained samples were carried out by choosing methylene blue (MB) as a model target under UV and solar light irradiation. To our best knowledge, the novel composite material had never been reported previously.

2. Experimental

2.1. Materials

All chemicals and reagents were of analytical purity and used as received without further purification. Distilled water was used throughout.

2.2. Preparation of graphene oxide (GO) dispersions

The detailed fabrication process of GO dispersions has been described in reported literature [35]. In a typical synthesis, 2.00 g of flake graphite, 2.00 g of $NaNO_3$ and 96 mL of concentrated H_2SO_4 were mixed and magnetically stirred in an ice bath. Then, 12.00 g of $KMnO_4$ was gradually added to the above mixture. The formed pasty suspension was first stirred at nearly 0 °C for 90 min and then at 35 °C for 2 h. After that, 80 mL of distilled water and 10 mL of 30 wt% H_2O_2 were added dropwise to the mixture with continuous stirring. The mixture solution was vigorously agitated for another 10 min and then centrifuged at a high speed of 14000 rpm, the collected graphite oxide was washed with distilled water until pH = 7. The exfoliation process of graphite oxide was carried out in a mild ultrasonic environment (80 W, 5 min), and the formed suspension after ultrasonic treatment was centrifuged for 5 min at a relatively low speed of 5000 rpm. GO, namely the supernatant was obtained. Moreover, the concentration of GO suspension was determined by the method of weighing, and the resultant concentration of GO was 0.8 mg/mL.

2.3. Synthesis of $ZnFe_2O_4$/ZnO nanocomposites

The preparing procedure of $ZnFe_2O_4$/ZnO nanocomposites was according to our previous study [36]. Briefly, at first, pure $ZnFe_2O_4$ nanoparticles were synthesized via a hydrothermal method accompany with $Zn(NO_3)_2 \cdot 6H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ as the main salts. Then, a certain amount of pure $ZnFe_2O_4$ nanoparticles and $Zn(NO_3)_2 \cdot 6H_2O$ were dispersed in 110 mL of ethanol, the mixture was ultrasonic agitated for several minutes. KOH ethanol solution was used to adjust the pH value of the above suspension. After reaction at 80 °C for 5 h, the $ZnFe_2O_4$/ZnO nanocomposite was finally obtained. The optimum molar ratio of $ZnFe_2O_4$ to ZnO had been investigated in literature [32]. The sample prepared under optimum condition was labeled with MZ-1 and was chosen as raw material for the preparation of $ZnFe_2O_4$/ZnO nanocomposites immobilized on graphene.

2.4. Preparation of $ZnFe_2O_4$/ZnO nanocomposites immobilized on graphene

20 mL of of prepared GO dispersions was transferred into 180 mL of distilled water containing 0.4 g of sample MZ-1. The suspension was ultrasonic agitated for 10 min (120 W, 40 KHz) and then mechanically stirred for 24 h at room temperature. After that, 200 μL of ammonia and 38 μL of 80 wt% hydrazine hydrate were added, reacting at 95 °C for 1 h. The obtained precipitate was collected by a magnet and washed with distilled water thoroughly and dried in vacuum oven at 40 °C. The sample was designated as MZG(4%). Similarly, samples with different graphene content were also prepared. For comparison, bare $ZnFe_2O_4$ and bare ZnO immobilized on graphene were obtained using the same preparing method. The detailed information was presented in Table 1.

2.5. Photochemical experiments

Photocatalytic activity of the obtained samples was evaluated at a photochemical reaction apparatus, the schematic diagram was shown in Fig. 1. A 500 W xenon lamp (the wavelength distribution was similar to that of solar light) was used as the light source. For each experiment, 70 mg of photocatalyst was dispersed in 500 mL of 10 mg/mL of MB aqueous solution, Prior to the irradiation, the suspension was magnetically stirred in the dark for 30 min to ensure the adsorption/desorption equilibrium of MB solution with the photocatalyst. 5 mL of the aliquots were sampled and analyzed by recording variations in the absorption band (663 nm) in the UV–vis spectra of MB.

2.6. Characterization

X-ray diffraction (XRD) patterns were recorded on a DX2700 diffractometer using Cu Kα radiation (λ = 0.154056 nm) at 40 kV and 35 mA in the range of 2θ value between 5° and 80°. The morphology and grain size of the obtained products

Table 1
Summarized sample designations of $ZnFe_2O_4$/ZnO immobilized on graphene with different mass ratio of GO to $ZnFe_2O_4$/ZnO nanocomposites.

Constituent of photocatalysts	Mass ratio of GO to $ZnFe_2O_4$/ZnO (%)	Lable
$ZnFe_2O_4$	4	MG(4%)
ZnO	4	ZG(4%)
$ZnFe_2O_4$ + ZnO(MZ-1)	2	MZG(2%)
$ZnFe_2O_4$ + ZnO(MZ-1)	4	MZG(4%)
$ZnFe_2O_4$ + ZnO(MZ-1)	6	MZG(6%)

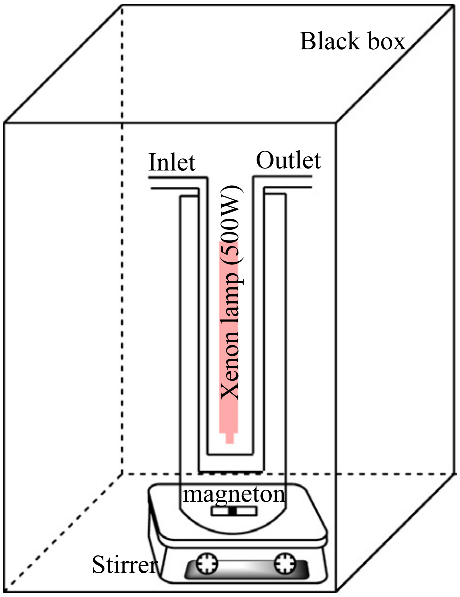

Fig. 1. Schematic diagram of photocatalytic apparatus.