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A metal-free composite photocatalyst of graphene quantum dots deposited on red phosphorus

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ABSTRACT

A simple approach to enhance the photocatalytic activity of red phosphorus (P) was developed. A mechanical ball milling method was applied to reduce the size of red P and to deposit graphene quantum dots onto red P. The product was characterized by scanning electron microscopy, transmission electron microscopy, contact angle measurements, zeta-potential measurements, X-ray diffraction and UV–vis absorption spectroscopy. The product exhibited high visible-light-driven photocatalytic performance in the photodegradation of rhodamine B.

Introduction

Semiconductor-mediated photocatalysis has been widely studied in environmental remediation such as degradation of organic pollutants and reduction of toxic metal ions (Zhang et al., 2010; An and Yu, 2011; Bhatkhande et al., 2002). In the past decades, researches focused on the fabrication of photocatalysts based on metal oxide (Akpan and Hameed, 2009; Ibhadon and Fitzpatrick, 2013) and sulfide (Fang et al., 2011). Various strategies were applied to achieve high photocatalytic activity. A well-known example is the coupling of different semiconductor systems to form composite photocatalysts (Sudha and Sivakumar, 2015; Li et al., 2009). However, the practical applications of these materials are limited due to their high cost, low availability or the release of toxic ions from the photocatalysts. In recent years, photocatalytic metal-free materials are of particular interests. For example, the potential of red phosphorus (P) as a visible-light-driven photocatalyst was discovered recently (Wang et al., 2012; Shen et al., 2014; Xia et al., 2015; Hu et al., 2016). As a metal-free elemental photocatalyst, red P is advantageous over most of the traditional metal-based photocatalysts for its high abundance and availability (Ceppatelli et al., 2013). It is also stable under ambient conditions and possesses low toxicity (Young, 2004). As a result, it has a great potential in various fields of material science (Ballistreri et al., 1983; Koch, 2008). Composite materials such as red P/TiO_2 (Xiao et al., 2014) and red P/active carbon (Wang et al., 2015a) have been fabricated for lithium-ion batteries. A composite of red P and CdS has also been reported for photocatalytic hydrogen evolution (Shi et al., 2016). However, the use of a highly toxic CdS is undesirable in environmental remediation.

Graphene quantum dots (GQDs) are layered graphene with lateral dimensions smaller than 100 nm (Li et al., 2013). They possess interesting optical and electronic properties due to quantum confinement and edge effects (Huang et al., 2014; Peng et al., 2012). The surface of GQDs is rich in oxygenated functional groups including carboxyl, epoxide and hydroxyl

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(Yang et al., 2012; Luo et al., 2013). As a result, GQDs are highly soluble in water (Shen et al., 2012). They can be surface-modified or conjugated to other materials for further applications (Cho et al., 2015; Qian et al., 2013; Ali et al., 2014; Zheng et al., 2013). Being metal-free materials with high photostability and low toxicity, GQDs show great potential in various applications including sensing (Sun et al., 2013) bioimaging and drug delivery (Wang et al., 2014; Nigam et al., 2014). GQDs have been combined with traditional metal oxides to enhance their photocatalytic performances (Guo et al., 2013; Chan et al., 2014; Qu et al., 2015).

In this work, a composite photocatalyst of GQDs/red P was fabricated by a facile mechanical ball milling approach. The experimental data revealed that the deposition of GQDs onto red P not only resulted in a more negative surface potential in water, but also enhanced the visible light photocatalytic performance of red P.

1. Materials and methods

1.1. Preparation of GQDs

The 10 mg of graphene oxide (GO, Xfnano, China) was dispersed into 5 mL of water and sonicated for 10 min. The 20 mL of 30% H_2O_2 (Scharlau, Spain) and 5 mL of 28% NH_3 (Scharlau, Spain) were added to the dispersion. The mixture was then stirred at room temperature for 24 hr followed by centrifugation for 10 min to remove large GO fragments. The supernatant was heated under reduced pressure to remove H_2O_2, NH_3 and water. The solid GQDs were re-dispersed into water for further use.

1.2. Preparation of GQDs/red P

Red phosphorus was first purified using a hydrothermal method. The 2 g of commercial red phosphorus (AR, >99%, Farco, China) was dispersed into 20 mL water and put into a Teflon-lined stainless steel autoclave, The autoclave was heated at 200°C for 12 hr to remove surface oxide layers. GQDs/red P was prepared by a wet milling approach with a planetary ball mill (QM-35P04, Nanjing NanDa Instrument Plant, China). 0.5 g of purified red P, 10 mL of GQDs solution (1 mg/mL) and 20 g of agate balls (diameter: 3/16 in.) were put into an agate vial of 50 mL. The process was carried out under Ar atmosphere at a rotation speed of 400 r/min for 12 hr. The product was collected by centrifugation and being washed with DI water for several times. To prepare ball-milled red P, the above procedures were repeated with GQDs solution being replaced by 10 mL DI water in the ball milling process.

1.3. Characterization

The morphologies of the products were characterized by transmission electron microscopy (TEM) (Tecnai, FEI, USA) and field-emission scanning electron microscopy (SEM) (Quanta 400 FEG, FEI, USA). The chemical structures were characterized using a Fourier-transform infrared (FT-IR) spectrometer (Nicolet iS10, ThermoFisher, USA). UV–vis spectra were recorded on a UV–vis spectrometer (Cary 100, Agilent, USA). The photoluminescence (PL) measurements were performed using a fluorescence spectrometer (F-4500, Hitachi, Japan). Zeta potentials were measured on a zeta potential analyzer (ZetaPlus, Brookhaven Instruments Corporation, USA) at 25°C. Contact angle measurements were carried out using a contact angle meter (FACE CA-XP, Kyowa Interface Science, Japan). X-ray diffraction (XRD) patterns were recorded using a diffractometer (SmartLab, Rigaku, Japan) with high-intensity Cu $K\alpha_1$ irradiation (λ = 1.5406 Å).

1.4. Photocurrent response measurements

The photo-electrochemical measurements were performed in a three-electrode electrochemical cell by using an electrochemical workstation (660D, CHI). Pt foil (1.0 cm × 1.0 cm) and Ag/AgCl were the counter and reference electrodes. The electrolyte was a 0.1 mol/L Na_2SO_4 (Farco, China) aqueous solution. A 300 W xenon arc lamp was used as the irradiation source and the average light intensity was about 100 mW/cm^2. The photocurrent responses under illumination of visible light (400 nm cutoff filter) were analyzed.

1.5. Photocatalytic activity evaluation

The photocatalytic activities of catalysts were evaluated by measuring the photodegradation of rhodamine B (RhB). In a typical measurement, 5 mg of photocatalyst powders were dispersed into 40 mL of 10 ppm aqueous solution of RhB. The suspension was stirred in the dark for 1 hr to reach the adsorption/desorption equilibrium. The suspension was then illuminated with a 300 W xenon arc lamp with a 400 nm cutoff filter. Photodegradation of RhB was monitored by measuring the change in UV–vis absorption of the suspensions with time. The suspension was centrifuged for 2 min to remove the photocatalyst before measurement. The peak absorbance of RhB at 553 nm was used to determine its concentration.

1.6. Detection of photogenerated hydroxyl radicals

0.4 mmol/L terephthalic acid (Merck, Germany) was used as a fluorescence probe for the generation of OH radicals (Wang et al., 2012). The reaction was carried out by dispersing 10 mg of photocatalyst powders into 40 mL of 2.0 mM NaOH (RFCL, India) aqueous solution. A 300 W xenon arc lamp with a 400 nm cutoff filter was used as the irradiation source. The formation of 2-hydroxyterephthalate ion was monitored by the change in PL intensity of the solution at 420 nm. The excitation wavelength was 320 nm.

2. Results and discussion

2.1. Characterization of graphene quantum dots

Fig. 1a is a typical TEM image of GQDs with diameters of about 10 nm. No apparent aggregation can be observed. To provide evidence for the existence of oxygenated functional groups in GQDs, FT-IR spectra of GQDs were obtained (Fig. 1b). The measured zeta-potential of GQDs is −34.0 mV in water. The negative value further supports the existence of negatively charged oxygenated functional groups (Wu et al., 2013).

Similar to other reported UV–vis absorption spectra of GQDs (Li et al., 2013), Fig. 1c shows a broad absorption below

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