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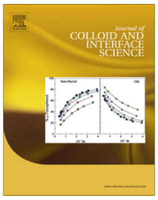

Assembly of Ag_3PO_4 nanocrystals on graphene-based nanosheets with enhanced photocatalytic performance

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ABSTRACT

A facile fabrication of graphene oxide (GO)–Ag_3PO_4 nanocomposites has been achieved through a two-phase self-assembly process. The well anchoring of Ag_3PO_4 nanocrystals (NCs) on the GO nanosheets was confirmed by transmission electron microscopy (TEM), X-ray diffraction (XRD), Fourier transform infrared spectra (FTIR), and Raman spectra. The significantly enhanced photocatalytic activity of the composites in comparison with bare Ag_3PO_4 NCs was revealed by the degradation of methylene blue (MB) under visible light irradiation, which can be attributed to the improved separation of electron–hole pairs and the high adsorption performance due to the presence of GO. The GO–Ag_3PO_4 can also be further photo-reduced into reduced graphene oxide (RGO)–Ag_3PO_4 nanocomposite without the formation of metal Ag. The RGO–Ag_3PO_4 nanocomposite exhibited higher photocatalytic activity and stability than bare Ag_3PO_4 NCs with the reason that the RGO nanosheets with high conductivity can effectively decrease the Ag formation during the cycling processes. This method developed here could be extended to design other high-performance graphene-based photocatalysts for environment and energy applications.

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1. Introduction

The construction and development of new photocatalytic materials with high efficiency and good stability in sunlight has attracted increasing amount of attention during the past decades [1,2]. Recently, silver orthophosphate (Ag_3PO_4) has been demonstrated to show excellent photocatalytic ability for the oxidation of water and degradation of organic contaminants in aqueous solution under visible light [3–6]. The photocatalytic activity of Ag_3PO_4 is demonstrated to be far exceeding those of current known visible light photocatalysts. Despite these advantages, however, there are some limitations in bare Ag_3PO_4 photocatalytic system. On the one hand, Ag_3PO_4 is slightly soluble in aqueous solution, which greatly reduces its structural stability [7]. On the other hand, Ag_3PO_4 is photosensitive. The transformation of Ag^+ into Ag usually takes place due to the combination of the photo-induced electron and interstitial Ag^+ during the photocatalytic process, which results in the photocorrosion of Ag_3PO_4 in the absence of electron acceptors [8]. Furthermore, along with the photocatalytic reaction, the increase in the metallic Ag particles would inevitably prevent visible light absorption of Ag_3PO_4, which decreases the photocatalytic activity [9]. In light of this, it is still a challenge to explore new Ag_3PO_4 photocatalytic systems with good structural and catalytic stability.

Graphene, a monolayer or few layers (<10) of hexagonally arrayed sp^2-bonded carbon atoms, has attracted intense scientific interest mainly due to its large surface area and exceptional electrical, mechanical, thermal, and optical properties [10–12]. To date, various synthetic strategies have been developed for producing graphene. Among them, sonication exfoliation-chemical reduction of graphene oxide (GO) route is both easily scalable, affording the promise for large-scale production, and versatile in realizing abundant chemical functionalization and decoration, benefited from the residual functional groups on them [13]. GO nanosheets were often chemically reduced to reduced graphene oxide (RGO) with various reducing agents [14]. However, chemical reduction often involves the use of toxic chemicals such as hydrazine, hydroquinone, and sulfur-containing compounds [15–17]. Photochemical reduction may overcome the shortcomings, which can provide a “green” reducing environment. Semiconductors with photocatalytic activities could be used to reduce GO through a photogenerated electron transfer process. For example, Kamat et al. reported the photoreduction of GO with the UV irradiation of GO–TiO_2 dispersion in an inert atmosphere using ethanol as a hole scavenger for the TiO_2 photocatalyst [18].

Recently, the synthesis and application of graphene-inorganic nanocomposites have been intensively pursued [19,20]. Among them, novel photocatalysts originating from the combination of graphene nanosheets with photocatalytically active component such as TiO_2 [21,22], ZnO [23], $CoFe_2O_4$ [24], $BiVO_4$ [25], and Ag/AgX(X = Br, Cl) [26] have been reported in degradation of organic

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pollutants for water purification. Previous studies have shown that graphene nanosheets with good conductivity and large surface area could be used as an electron transfer channel to reduce the charge recombination, thus leading to the improved photoconversion efficiency of the photocatalytic materials. Besides, graphene could also increase the adsorbility of photocatalysts toward pollutants and extend the light absorption range of photocatalysts [27].

Herein, we assembled Ag_3PO_4 nanocrystals (NCs) on GO nanosheets through a facile two-phase approach to produce GO–Ag_3PO_4 nanocomposites for enhanced photocatalytic application. The obtained GO–Ag_3PO_4 photocatalysts showed remarkably enhanced photocatalytic activities toward degradation of methylene blue (MB) in comparison with bare Ag_3PO_4 NCs under visible light. The GO–Ag_3PO_4 nanocomposites could be photo-reduced into RGO–Ag_3PO_4 nanocomposites through light irradiation at room temperature. The RGO–Ag_3PO_4 nanocomposites exhibited improved photocatalytic stability in comparison with bare Ag_3PO_4 NCs. Moreover, the mechanisms of the GO reduction and the enhanced photocatalytic performance for the graphene-based nanocomposites were detailedly discussed.

2. Materials and methods

2.1. Materials

Natural flake graphite was purchased from Qingdao Guyu graphite Co., Ltd. with a particle size of 150 μm. All other chemicals are of analytical grade and used without further purification.

2.2. Preparation of graphite oxide

Graphite oxide was synthesized from natural flake graphite by a modified Hummers method [28]. In a typical procedure, 2.0 g of graphite powder was added into cold (0 °C) concentrated H_2SO_4 (100 mL) and $NaNO_3$ (4.0 g) solution in a 500 mL flask. Under vigorous stirring, $KMnO_4$ (10.0 g) was added gradually, and the temperature of the mixture was kept to below 10 °C. The reaction mixture was stirred at 35 °C for 2 h until it became pasty brownish and then diluted with de-ionized water (100 mL). The addition of water was performed in an ice bath to keep the temperature below 100 °C. Then, the mixture was stirred for 30 min, and 20 mL of 30 wt% H_2O_2 was slowly added to the mixture to reduce the residual $KMnO_4$, after which the color of the mixture changed to brilliant yellow. The mixture was filtered and washed with 5% HCl aqueous solution (800 mL) to remove metal ions followed by 1.0 L of de-ionized water to remove the acid. The resulted solid was centrifuged and dried at 60 °C for 24 h. For further purification, the as-obtained graphite oxide was redispersed in de-ionized water and then was dialyzed for 1 week to remove residual salts and acids.

2.3. Synthesis of Ag_3PO_4 NCs

Oleylamine-capped Ag_3PO_4 (OM-Ag_3PO_4) colloidal NCs were synthesized using a simple and reproducible route based on the reaction between silver ions, OM, and phosphoric acid in toluene at room temperature [29]. The removal of OM surfactant from Ag_3PO_4 NCs surface was performed through treating the OM-Ag_3PO_4 NCs with acetic acid. Typically, 1.0 g of the as-synthesized OM-Ag_3PO_4 NCs was dispersed in 100 mL glacial acetic acid ($\geqslant$99.5%). The solution was stirred continually at 25 °C for 24 h. The resultant Ag_3PO_4 NCs were separated by centrifugation, washed with toluene and ethanol several times, and dried at 40 °C in a vacuum oven.

2.4. Synthesis of GO–Ag_3PO_4 nanocomposites

The GO–Ag_3PO_4 nanocomposites were produced through a two-phase approach. In a typical synthesis of GO–Ag_3PO_4 with 0.5 wt% GO, 5 mg graphite oxide was mixed with 50 mL water and then sonicated for 30 min to form uniform GO aqueous dispersion. OM-Ag_3PO_4 NCs (995 mg) were dispersed in toluene (50 mL) and then mixed with the GO aqueous dispersion. The mixture was kept stirring for 12 h at room temperature. The GO–Ag_3PO_4-OM (containing OM) nanocomposites were obtained by diluting the mixture with a large amount of acetone and then centrifugation. The removal of OM from the as-prepared GO–Ag_3PO_4-OM nanocomposites was performed through the same procedure as the removal of OM from OM-Ag_3PO_4 NCs (Section 2.3). GO–Ag_3PO_4 composites with other GO contents were obtained by adjusting the weight ratio of graphite oxide to OM-Ag_3PO_4.

2.5. Photo-reduction of GO–Ag_3PO_4 to RGO–Ag_3PO_4 nanocomposites

A 100 mg of GO–Ag_3PO_4-OM nanocomposites was redispersed in 50 mL of toluene to form homogeneous dispersion. The above solution was irradiated with a 500 W tungsten lamp as visible light for 3 h at room temperature. Then, the resulting black dispersion was diluted with acetone, then centrifuged, and isolated. The removal of OM was performed through the same procedure as in Section 2.3.

2.6. Synthesis of OM-functionalized GO (OM–GO) nanosheets

OM–GO nanosheets dispersed in toluene were obtained through simple phase transfer method we reported before [30]. In a typical experiment, 10 mL of GO aqueous dispersion (1.0 mg mL^{-1}) was mixed with 10 mL of ethanol containing 300 μL of OM. After 2 min of stirring, 20 mL of toluene was added, and the stirring was continued for a few second. The formed OM–GO nanosheets could be extracted upwards to toluene quickly and completely, from which the uniform and stable toluene dispersion of OM–GO nanosheets was obtained.

2.7. Characterization

Powder X-ray diffraction (XRD) measurements were carried out on an X-ray diffractometer (Bruker D8 Advance diffractometer) with Cu Kα radiation. Fourier transform infrared spectra (FTIR) were recorded on a Nicolet FT-170SX spectrometer with KBr pellets in the 4000–400 cm^{-1} region. Raman spectra were measured at room temperature using a DXR Raman microscope with 514.5 nm excitation source from an Ar^+ laser. The morphology and size of the products were examined by transmission electron microscopy (TEM, JEOL JEM-2100). Energy-dispersive X-ray spectrometry (EDS) was recorded with an energy-dispersive spectrometer attached to a scanning electron microscope (SEM, JSM-6480). The X-ray photoelectron spectroscopy (XPS) measurements were performed on a PHI 5000 VersaProbe. Ultraviolet–visible (UV–vis) spectroscopy measurements were performed on a UV-2450 UV–vis spectrophotometer.

2.8. Photocatalytic measurements

The photocatalytic activities of the as-prepared samples were evaluated by photodegradation of methylene blue (MB). Photoirradiation was conducted on a GHX-2 photochemical reactor with a 500 W tungsten lamp as visible light source. Experiments were conducted at 20 °C as follows: 30 mg of photocatalyst was added to 100 mL of 7.5 mg/L dye aqueous solution. The mixed suspension was stirred for 1 h in the dark in order to reach the adsorption–

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