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Short Communication

Reduced graphene oxide-cuprous oxide hybrid nanopowders: Hydrothermal synthesis and enhanced photocatalytic performance under visible light irradiation

Niu Zhigang *

Department of Applied Chemistry Engineering, Lanzhou Petrochemical College of Technology, Gansu, Lanzhou 730060, China

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ABSTRACT

Reduced graphene oxide-cuprous oxide (rGO-Cu_2O) hybrid was successfully prepared using a facile and efficient hydrothermal synthesis method, with sodium dodecyl sulfate (SDS) as a dispersing agent, glucose as a reducing agent, and rGO as two-dimensional support. The morphology and microstructure of the as-prepared hybrid were characterized by Scanning electron microscopy (SEM) and Transmission electron microscopy (TEM) images, respectively. The result demonstrated that well monodispersed cube-like Cu_2O particles precipitate on the rGO layer. X-ray powder diffraction (XRD) determined the crystallographic structure of Cu_2O is cubic and X-ray photoelectron spectroscopy (XPS) showed that GO had been reduced to rGO in our hybrid. Moreover, visible photocatalytic activity of the composites was tested using Rhodamine B (RhB) as the model contaminant. Compared with the corresponding bare GO and Cu_2O, rGO-Cu_2O hybrid demonstrated improved photodegradation activity for RhB dye under visible light. The investigation gave a promise to the development of original yet highly efficient graphene oxide-based photocatalysts that utilize visible light as an energy source.

1. Introduction

A great challenge for this century lies in cleaning up the waste generated during industrial, agricultural, and domestic activities. Artificial photocatalystic systems are highly desirable because of abundant sunlight resource and less of carbon emission. Various ultraviolet light catalysts are reported to remove dye pollutants [1,2]. However, the ratio of ultraviolet light about 4% is much lower than visible-light (about 43% of the solar spectrum) in natural light. Therefore, visible-light catalyst is hot-pursued for practical application [3–8]. Semiconductor oxides have been widely used in optical coating and microelectronics devices, their use to purify contaminants in air and water has been recognized more recently [9–11]. In these investigations, various semiconductor materials such as TiO_2, CdS, ZnS, and ZnO have been used to study photocatalytic reduction of pollution in water [12–14]. Moreover, compared with other narrow band gap semiconductors such as metal sulfides, Cu_2O are of low toxicity and low costs, which is environmental friendly and attractive in large scale applications. Cu_2O is a versatile semiconductor with promising applications in many fields, such as solar cells [15], lithiumion batteries [16], gas sensors [17], biosensors [18], and magnetic storage devices [19]. Due to the narrow direct band gap of 2.0–2.2 eV and the suitable energy level position [20], the sunlight can be effectively utilized for photocatalytic degradation of organic compounds [21]. Cu_2O can be also widely applied in water splitting under

* Tel.: +86 18993189179.
E-mail address: niuzhigang666@sina.com

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visible light for hydrogen generation [22,23]. In recent years, Cu_2O was also investigated for photocatalytic degradation of organic contaminants.

Graphene is found to be a two-dimensional semimetal with a tiny overlap between valence and conductance bands [24], and consists of a single atomic sheet of conjugated sp^2 carbon atoms [25], and has revealed cornucopia applications including supercapacitors, photovoltaic devices, sensor, water purification [26–29]. The combination of graphene with the size-tunable properties of metal and semiconductor nanocrystals offers many interesting applications in a wide range of fields including heterogeneous catalysis, nanoelectronics, and devices [30–33]. Specifically, semiconductor nanocrystals of controlled size and shape assembled on the surface of graphene are expected to play major roles in the development of new generation nanostructured solar cells, fuel cells, light-emitting diodes, lasers, sensors, and novel energy conversion devices [34–38].

Because graphene is an analog of a giant aromatic "poly-molecule", it is insoluble in water. To solve this problem, we import graphene oxide (GO) as precursor and reduce it to rGO during hydrothermal process. According to our work, we present a facile, fast, and scalable one-step, hydrothermal synthesis of phase-controlled Cu_2O nanocrystals supported on highly rGO sheets. We also report visible photocatalytic activity of the composite using Rh. B as the model contaminant. Compared with the corresponding bare Cu_2O, the rGO-Cu_2O nanocomposite display distinctly enhanced photocatalytic activities.

2. Experimental sections

All of the chemical reagents were of analytic-grade and used without further purification (purchased from Shanghai Chemical Reagent Co., Ltd., Shanghai, China).

2.1. Synthesis of GO and rGO-Cu_2O hybrid materials

GO was prepared from natural flake graphite powders using a modified Hummer's method (Hummers and Offeman 1958) [39,40]. The rGO-Cu_2O hybrid was synthesized via a hydrothermal process. In a typical procedure, a certain amount of SDS and glucose and $CuCl_2 \cdot 2H_2O$ (1 mmol) were added into 50 mL deionized water. And 2 mL aqueous solution of GO (1 mgmL^{-1}) and were added to the mixture solution and stirred for 2 h to form a homogeneous solution. Then the mixture was transferred to a Teflon-lined stainless steel autoclave (100 mL), heated at 160 °C for 6 h and cooled to room temperature naturally. Finally, the product was centrifuged at 5000 rpm, and dried in a vacuum drier. Pure Cu_2O was also synthesized via a parallel process without the introduction of GO.

2.2. Visible light catalytic degradation of RhB

The visible light catalytic activity of rGO-Cu_2O was estimated by degradation of RhB. A comparative test was also performed on GO and Cu_2O. In every test, the amount of catalyst was 10 mg. In a typical procedure, rGO-Cu_2O nanocomposite was added into 500 mL of RhB (0.02 mg mL^{-1}) solution. The mixtures were stirred moderately on a magnetic stirring apparatus at room temperature for several minutes and then maintained in the dark for 30 min to ensure the adsorption/desorption equilibrium of the organic dye. Then, the solution was exposed to a visible light lamp which was placed 20 cm above the beaker. Samples were withdrawn regularly from the reactor at time t, $t=0$, 30, 60, 90, 120, 150, 180 min, and immediately centrifuged to separate any suspended solid before analysis. The concentration of RhB (c_t and c_0 are the concentrations of the organic dye at time t and $t=0$, respectively) in the solution after the photocatalytic degradation reaction was monitored by measuring the absorbance of the solution samples with a UV–vis spectrophotometer (Optizen POP) at $\lambda_{max}=552$ nm.

2.3. Characterization

The structure and phase purity of rGO-Cu_2O nanocomposites were examined by XRD measurements, which were performed on a Bruker D8 with Cu Kα radiation at 40 kV and 40 mA. The scan rate was 0.02°/s. FTIR analyses were carried out on a Bruker Vector-22 spectrophotometer using a potassium bromide pellet technique. The morphology characterization and microstructure analysis were carried out using SEM measurement on a JEOL-6380LV and TEM measurement on a JEOL-2100. UV–vis adsorption spectra were recorded by the SHIMADZU UV-3600. Nitrogen adsorption–desorption isotherms were obtained on a nitrogen adsorption apparatus (NOVA 4000e, USA) and photoluminescence (PL) spectra of samples were recorded with an FLS 920 Fluorescence and Phosphorescence spectrometer (Edinburgh Instruments Ltd.).

3. Results and discussions

3.1. Growth and characterization of rGO-Cu_2O hybrid materials

Fig. 1 shows the microimage and composition analysis of the as-prepared hybrid. It is observed from Fig. 1(a–b) that the sample is consist of rGO sheets and Cu_2O nanoparticles (NPs). The rGO sheet has a gauze-like morphology with crumpled structure. The TEM image (see Fig. 1(b)) suggests that the rGO sheet has a few stack of layers. And it is so thin and transparent, which contributes the high specific surface area. Cu_2O NPs precipitate thick with good dispersibility on the rGO layers, and they unify the diameter for 300–500 nm. As seen in Fig. 1(a), it is revealed that the Cu_2O NPs have a cube-like feature. What's more, the benign dispersibility Cu_2O NPs of and rGO layers can illustrate that the agglomeration of Cu_2O NPs and recombination of rGO layers are solved by our preparation method. Fig. 1(c) shows the EDS microanalysis and element mass of the rGO-Cu_2O nanocomposite a good combination between graphene and Cu_2O. The graphene sheets act as bridges for the connection between different Cu_2O NPs, which is beneficial for the separation of photo-generated carriers, and enhances the photocatalytic performance. To get information on the elements and element massosites. The main elements such as C, O, and Cu are present. The C signal mainly