



ZnO-reduced graphene oxide nanocomposites as efficient photocatalysts for photocatalytic reduction of CO₂

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Abstract

A series of zinc oxide/reduced graphene oxide nanocomposites (ZnO-rGO) were fabricated by a facile one-step hydrothermal method. The composite materials were characterized by X-ray diffraction (XRD), Transmission scanning electron microscopy (TEM), Energy dispersive X-ray analysis (EDX), X-ray photoelectron Spectroscopy (XPS), nitrogen adsorption-desorption isotherms, photoluminescence spectra (PL) and UV–vis diffuse reflectance (DRS). The photocatalytic performance of the ZnO-rGO composites was investigated towards photoreduction of CO₂ to CH₃OH. The yield of CH₃OH on ZnO-rGO was five times as high as that on pure ZnO. The ZnO-rGO nanocomposites possess excellent reusing and cycling property.

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1. Introduction

CO₂ is an inevitable product of fossil fuel combustion, which has led to climate changes and posed a serious impaction on our environment. How to reduce the concentration of CO₂ has received much attention. The conversion of CO₂ to value-added fuels or chemical products by direct use of sunlight is considered to be one of the most attractive strategies [1–3]. Thus many research efforts have been made to develop efficient photocatalysts for the reduction of CO₂. Considerable photocatalysts have been researched containing semiconductors, such as TiO₂ [4–6], ZnO [4,7], CdS [8], Ta₂O₅ [9], InTaO₄ [10]. Among these semiconductors, most investigated photocatalytic materials are TiO₂ and ZnO. ZnO has attracted great attention due to its suitable band-gap of 3.37 eV, low cost, environmental friendliness [11]. Additionally, the electron mobility of ZnO is higher than that of TiO₂ [12]. But, it can only absorb ultraviolet (UV) light to yield photoelectrons and holes and photoinduced electron-hole pairs recombined

easily. To solve these problems, many approaches have been designed to enhance the photocatalytic activity of ZnO, such as preparing quantized ZnO nanocrystallites [13], surface photosensitization [14], depositing noble metals [15], and forming carbon-based composites [16,17].

Graphene, as a new carbon material, is regarded as one of the most promising additive for hybrid materials, because of its large theoretical specific surface area, excellent electron mobility, and high transparency [18]. Meanwhile, incorporating semiconductor nanocrystals with rGO not only can reduce the restocking of ultrathin graphene sheets [19], but also can prevent the aggregation and photocorrosion of nanocrystals [20]. Thus, it is believed to be a credible way to obtain a promising photocatalyst for CO₂ reduction. For example, graphene bonded with TiO₂ [21], WO₃ [22], or CdS [3] composites have been widely investigated.

Recently, graphene-based ZnO hybrids have been fabricated by several methods. Hur et al. have prepared a graphene-zinc oxide hybrid by a electrochemical deposition with excellent photocatalytic activity toward methylene blue [23]. Su et al. reported that reduced graphene oxide decorated with ZnO

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nanoparticles have been synthesized by a two-step hydrolysis–calcination method, and a greatly enhanced photocatalytic activity to decompose organic dyes has been achieved [24]. Xu et al. have presented a graphene-ZnO nanorod heterostructure by hydrothermal approach [20]. It is well known that the hydrothermal method has advantages, such as simple, low cost and easy to scale up. However, most of the graphene-ZnO composites are used for the photodegradation of organic molecules. The use of graphene-ZnO composites on the photoreduction of CO₂ has not been reported in detail and further researches are necessary.

In this article, we have successfully prepared ZnO-rGO composites through a simple one-step hydrothermal process. The ZnO-rGO composites showed enhanced photocatalytic activity for converting CO₂ to CH₃OH. The effect of the content of graphene and dosage of catalysts on photocatalytic activity, and the stability of ZnO-rGO composites were investigated systematically.

2. Experimental

2.1. Preparation of graphite oxide

GO was prepared by a modified Hummers' method [25,26]. In detail, 3 g graphite was put into a mixture of 15 mL H₂SO₄, 2.5 g K₂S₂O₈, and 2.5 g P₂O₅. The solution was heated to 80 °C and kept stirring for 5 h in water bath. Then the mixture was diluted with 700 mL water, filtered and washed. The product was dried under room temperature. Thereafter, 15.0 g KMnO₄ was slowly added with magnetic stirring, to prevent the temperature of the mixture from exceeding 10 °C by ice bath. Then ice bath was then removed and the mixture was stirred at 35 °C for 2 h. The reaction was terminated by adding 800 mL of water and 25 mL H₂O₂ solution. The mixture was filtered and washed with 1:10 HCl aqueous solution to remove metal ions followed by DI water to remove the acid. Finally, the GO was obtained by drying.

2.2. Preparation of ZnO/rGO composites

The ZnO/rGO composites were prepared using a simple one-step hydrothermal method. In a typical synthesis, 3 mmol zinc nitrate was added to 60 mL deionized water and continuously stirred for 10 min. A certain amount of GO was added into the zinc nitrate solution and then it was sonicated for 1 h. Then, the pH value was adjusted to 8 by ammonia. After being stirred for 0.5 h, the obtained solution was sealed into a Teflon-lined autoclave and maintained at 160 °C for 10 h. Subsequently, the autoclave was cooled to room temperature naturally. The resulting samples were washed with deionized water and ethanol several times, and then dried in a vacuum oven under 50 °C for 8 h. A series of ZnO-rGO nanocomposites with different weight addition ratios of GO to nanocomposites (1%, 5%, 10%, 20%) were obtained. For comparison, the blank ZnO was prepared in the absence of GO using the same experimental conditions.

2.3. Characterization

X-ray diffraction (XRD) patterns were obtained using a D/MaxRB X-ray diffractometer (Japan) with Cu K_α irradiation source ($\lambda=1.5418 \text{ \AA}$) through the 2θ range from 5° to 80°. The morphologies of the nanocomposites were done by a Japan transmission electron microscopy (TEM, JEM-1400). Energy dispersive X-ray spectrum of samples were obtained by scanning electron microscopy (SEM, HITACHI S-4800 combined with EDX). X-ray photoelectron spectroscopy (XPS) data were taken by a Thermo ESCALAB250 system with a monochromatic Al K_α source and a charge neutralizer. The measurements of N₂ adsorption were carried out by using a USA Micromeritic ASAP 2020 nitrogen adsorption apparatus. Fourier-transform infrared (FTIR) spectra of KBr powder-pressed pellets were recorded by Nicoletis 10 (China). The optical properties of the samples were characterized by a UV-2600 ultraviolet/visible diffuse reflectance spectrophotometer (DRS), during which BaSO₄ was employed as the internal reflectance standard. The photoluminescence spectra (PL) were recorded with a HITACHI F-2500 fluorescence spectrophotometer.

2.4. Photocatalytic activity measurements

The CO₂ reduction reaction was performed by using a quartz glass tube with a volume of 60 mL. A 300 W Xe lamp was used as the light source. First, 100 mg photocatalysts were added into 50 mL 1.0 M NaOH solution in the glass reactor with magnetic stirring. Then CO₂ gas was bubbled through the solution in the reactor for 0.5 h to remove the oxygen. The Xe lamp was turned on to start the photoreaction. During the reaction process, the liquid products were taken out per 45 min, then were centrifuged to remove catalysts. The concentration of methanol was analyzed by a gas chromatograph (GC-7900) equipped with a flame ionization detector and capillary column. Control experiments were carried out in the dark or without catalyst under the same experimental conditions. No methanol was detected in the absence of light irradiation or catalysts.

3. Results and discussion

3.1. XRD analysis

The phase structure of the products was identified by powder XRD. Fig. 1 shows the XRD patterns of the GO, ZnO and ZnO-rGO composites. It can be seen that GO shows a diffraction peak (002) at a 2θ value of 10.3°, which indicates that most of the graphite powder was oxidized into GO. The ZnO and ZnO-rGO samples present almost the same profiles and all the diffraction peaks match well to the hexagonal wurtzite ZnO (JCPDS no. 36-1451). For ZnO-rGO composite, diffraction peak at 10.3° disappears and a weak and low intensity diffraction peak appears around 25.9°, indicating the reduction of GO into rGO [27,28].

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