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Facile synthesis of highly active reduced graphene oxide-CuI catalyst through a simple combustion method for photocatalytic reduction of CO_2 to methanol

Wenjun Zhang*, Yingjie Li, Xiaoxiong Zhang, Cuiluo Li

School of Chemical Engineering, Hebei University of Technology, Tianjin 300130, China

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ABSTRACT

We report a facile combustion method synthesis of reduced graphene oxide/CuI composites as a photocatalyst, in which CuI nanoparticles were homogeneously distributed on the surface of reduced graphene oxide (rGO), showing a good visible light response. The rGO-supported and unsupported CuI hybrids were tested over the photocatalytic reduction of CO_2 for methanol evolution in visible light. In the current study rGO-CuI composites have shown excellent yields (19.91 μmol g-cat^{-1}). rGO provides a light-weight, charge complementary and two-dimensional material that interacts effectively with the CuI nanoparticles.

1. Introduction

With the continuous development of human society, the demand for fossil fuel resources has become more and more substantial [1–3]. Research has revealed that in the past few decades the global temperature has increased significantly during the high consumption of fossil fuel resources that produced large amounts of carbon dioxide which creates global warming. Traditional semiconductor-mediated TiO_2 photocatalytic CO_2 conversion driven by solar energy has attracted much attention as it can solve global energy and environmental problems [4–13]. In recent years, emerging semiconductor materials such as rGO and CuI have also attracted the enthusiasm of researchers [14,15].

Both graphene oxide (GO) and rGO contain oxygen functional groups, but rGO contains a less amount of oxygen functional groups than GO [16]. Nevertheless, a small amount of functional groups can still give rGO good dispersity and adsorption properties. It is more important that rGO are deemed to be an electron transfer channel. Thus enhancing phototransformation efficiency of the photocatalytic materials [17–21]. The CuI, a P type semiconductor material, is steadily existed as γ crystalline phase when temperatures below 642 K which has attracted much attention due to its potential applications in light dye-sensitized solar cell and catalysis of the organic reaction [22]. However, the band gap of CuI is 3.1 eV, only UV light can stimulate the CuI nanoparticles to produce electron-hole pairs, greatly impeding its widespread application. Such drawbacks could be obviated by using rGO-supported CuI [23].

Farnoush Tavakoli et al. described the successful synthesis of CuI-graphene nanocomposites via a combination of coprecipitation and hydrothermal methods [24]. Wang et al. used graphite oxide, $CuSO_4 \cdot 5H_2O$ and KI and aniline through multiple steps of reactions to synthesize rGO/CuI/PANI composites which were used to degrade Rhodamine B and generate H_2 in the presence of illumination [23]. Despite all the above efforts, simple synthesis of composites material quickly is still a challenge.

Accordingly, we developed a new approach of synthesizing rGO-CuI composites by a naked flame. The GO was successfully reduced to rGO and CuI was supported on the surface of the rGO at the same time. So the combustion method is simple and rapid for preparation of composites in large quantities. Subsequently, we have studied the catalytic properties of the composites. rGO-CuI composites were used for reducing carbon dioxide under the irradiation of simulated sunlight and the methanol were detected successfully by gas chromatography. The product also contains other compounds, but we only concentrate on the main product of methanol. The experimental result proves that rGO-CuI have excellent catalytic performance under visible light. Morphology and ingredient of rGO-CuI were carefully characterized by XRD, SEM, TEM, UV–vis and FT-IR.

2. Experimental

2.1. Reagents and materials

All reagents used in the experiments were analytical reagent grade and used without further purification. Crystalline flake graphite was

* Corresponding author.
E-mail address: wjzhang@hebut.edu.cn (W. Zhang).

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purchased from Qingdao Jinrilai graphite Corporation. $NaNO_3$ was obtained from Tianjin Viktor Chemical Corporation·H_2O_2 (30%) was supplied by Tianjin Bot Chemical Corporation. $KMnO_4$ was purchased from Tianjin Jiangtian Chemical Corporation. HCl and Concentrated H_2SO_4 (98 wt%) were obtained from Beijing Chemical Works. CuI was supplied by Tianjin Damao Chemical Reagent Corporation. CO_2 (99.995%) was obtained from Tianjin Sizhi Gas Corporation.

2.2. Catalysts characterization

Fourier transform infrared spectroscopy (FT-IR) were registered in a Bruker Ten-sor27 spectrometer (Germany) with a KBr disc in the wavelength range of 4000–400 cm^{-1}. The X-ray diffraction (XRD) patterns were taken on Germany Bruker AX in the range of 5–90°. Morphology of rGO-CuI was investigated using scanning electron microscopy (NanoSEM 450) and transmission electron microscopy (NanoTEM). The UV–visible transmittance spectrum was obtained on an Agilent Carry 100 UV–vis spectrometer, from 200 to 800 nm. The gas chromatography (GC) analyses were performed on a Shandong Lunan Ruihong SP-6860(SE 54 column (30 m ×0.5 μm), Inj. Temp. 80 °C, FID Temp. 260 °C and Oven Temp. 80 °C).

2.3. Synthesis of rGO-CuI composites

Hummers' method was initially adopted to synthesize graphite oxide as our group previously synthesized [25]. Graphite oxide 100 mg and CuI 0.3 g were added into a 25 mL beaker. Then 20 mL ethanol is added to the mixture that was treated as one hour with ultrasonic wave. The resulting material was subsequently removed, evenly spread over the surface of the watch glass and dry 24 h with 50 °C in the drying oven. Then the dried product were quickly passed through a naked flame from a burning alcohol lamp(time 1 s, utilizing the internal flame of the alcohol lamp) [25]. The internal flame of the alcohol lamp has the ability to reducing. After passing through the flame quickly, the sample was immediately placed in a bottle filled with argon.

3. Results and discussion

3.1. X-Ray powder diffraction

The phase structures of GO, rGO, CuI and rGO-CuI were tested by X-ray diffraction (XRD) measurement. Fig. 1a, b, c and d compare the XRD patterns of samples in the range of 5–90° (2θ). In Fig. 1a, the obvious and strong characteristic broad (002) peak at 11.806° corresponding to GO. The GO sheets were observed increase in layer distances because both sides of the GO sheets have a large number of oxygen-containing functional groups. As shown in Fig. 1, we can see the b curve in 23.655° has a width of the characteristic peaks and the characteristic peak at 11.806 is disappeared which indicate the π-π stacking interaction of rGO is weakened severely. So it is indicated that when GO was handled through the naked flame. The GO would soon be reduced to graphene. According to Fig. 1, the diffraction peaks of c curve at 2θ of 25.558°, 42.266° and 50.009° corresponding to the (111), (222) and (311) plane reflections of cubic crystal structure CuI, which agrees well with the reported data (JCPDS Card no. 06-0246). The diffraction peaks of rGO-CuI almost the same as with CuI and the intensity of these peaks is also more than strong. It proves that CuI still has a good crystal structure undergoing flame treatment. Nevertheless, it did not detect the diffraction peaks of the rGO, which owing to the addition of copper iodide affects rGO crystal structure. Therefore, it manifests that we successfully reduced GO to rGO by a naked flame, and CuI is supported on the surface of rGO through a simple one-step method.

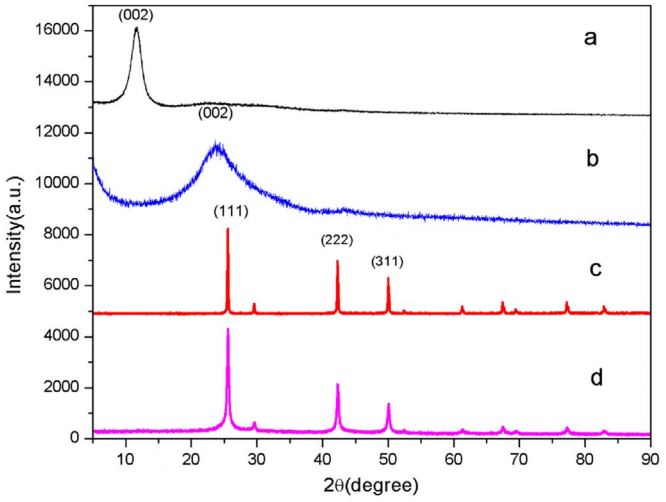

Fig. 1. XRD patterns corresponding to GO(a), rGO(b), CuI(c), rGO-CuI(d).

3.2. Scanning electron microscope (SEM) characterization

To further investigate the structure and morphology of the as-prepared samples, SEM observations were employed as shown in Fig. 2. It can be seen that the rGO exhibits a good three-dimensional and loose structure when GO was reduced to rGO through a flame treatment in Fig. 2a and b. This loose structure formation is considered to be in the combustion process GO decomposition produces large amounts of carbon dioxide and water caused by swelling. Lamellar spacing is large and the surface is smooth and slightly wrinkled. As is shown in Fig. 2c and d, the distinct contrast between rGO-CuI composites and rGO is observed, and the CuI nanoparticles were dispersed on the surface of rGO sheets.

3.3. Transmission electron microscopy (TEM) characterization

The morphology and microstructure of the sample are analyzed by TEM. As is shown in Fig. 3a and b, from the figure we can see that the surface of rGO is quite folded without the presence of other particles. The as-obtained rGO presents a transparent structure which indicating it is under a very low number of layers. According to the image of Fig. 3c and d, it demonstrates that a large number of CuI nanoparticles were evenly distributed on the surface of the rGO, which indicating our combustion method is successful. Fig. 1S shows the CuI particle size at the nanoscale level.

3.4. Ultraviolet-visible characterization

UV–vis diffuse reflectance spectra shown in Fig. 4 also carried out in order to understand the optical properties of the rGO based photocatalyst. The rGO and rGO-CuI display typical absorption bands around 200–270 nm and the characteristic absorption from cyclic structure of rGO. In the visible-light region, the CuI has a very weak absorption peak at 440 nm, which originates from the excitation of electrons from the valence band to the conduction band. But the absorption peak at 440 nm in rGO-CuI and rGO are strong obviously than the peak of CuI [26]. After the introduction of CuI species, the absorption of visible-light increased greatly [27]. The rGO absorption strength slightly below the absorption intensity of rGO-CuI, therefore rGO photocatalytic efficiency is lower than rGO-CuI, and this theory was verified in the experiment.

3.5. Fourier transform infrared (FT-IR) characterization

Fig. 5 shows the FT-IR spectra of pure GO and rGO-CuI composites. In the case of GO, the broad and intense peak centered at 3441 cm^{-1}, which is related to the OH groups, and the peak at