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Short Communication

Graphene–WO_3 nanobelt composite: Elevated conduction band toward photocatalytic reduction of CO_2 into hydrocarbon fuels

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ABSTRACT

Graphene oxide (GO), tungsten trioxide (WO_3) and graphene–WO_3 nanobelt composites (GW) were synthesized and characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), UV–vis diffuse reflection spectra (DRS) and X-ray photoelectron spectroscopy (XPS) valence band spectra. We demonstrated that the graphene can elevate the conduction band of WO_3 toward photocatalytic reduction of CO_2 into hydrocarbon fuels under visible-light irradiation. And the photocatalytic activity of GW is higher than that of GO, WO_3 and P25 TiO_2.

1. Introduction

Increasing anthropological emissions of greenhouse gasses, in particular carbon dioxide (CO_2) into the atmosphere is widely recognized to be one of the primary causes of global environmental issue [1–3]. The idea of mimicking the overall natural photosynthetic cycle of the chemical conversion of CO_2 into useful fuels has been consistently gaining attention [4,5]. Such artificial photosynthesis allows the direct conversion of CO_2 in order to reduce atmospheric CO_2 concentrations while providing renewable carbon fixation and energy storage [6–8]. And the photocatalysis process can be sustainable by harnessing solar energy, making it economically feasible and environmentally benign. To this end, we face an energy intensive challenge in its reduction since CO_2 is very stable [9,10]. Developing an efficient photocatalyst appears to be a promising methodology to meet this challenge, and this has been a prominent quest to convert CO_2 into hydrocarbon fuels [2–10]. Among the present photocatalysts for conversion, TiO_2-based semiconductor photocatalysts have been the most popular. In spite of above mentioned advantages, CO_2 photoreduction, however, still suffers from very low conversion efficiencies, resulting from the fast electron–hole recombination rate and visible light absorption in the photocatalysts. So, the two major barriers are needed to be overcome.

Several strategies have been proposed to solve the above problems, such as use of facet engineering, mesoporous structures and new visible light photocatalyst using [11–13]. Tungsten trioxide (WO_3) with a bandgap of ca. 2.7 eV is considered as a promising visible-light photocatalyst, harmless and stable in aqueous media over a very wide pH range. Due to its very deep valence band (VB) maximum, WO_3 is usually used for oxygen evolution in the presence of an electron acceptor (i.e. $AgNO_3$) [14–16]. However, a rather low conduction band (CB) minimum (lower than -0.1 V vs. NHE, $pH = 7$) has inherently limited its application in many important reactions such as, reduction of CO_2 to CH_4 ($CO_2 + 8e^- + 8H^+ \rightarrow CH_4 + 2H_2O$, -0.24 V) [17].

Graphene, a new carbonaceous material with two-dimensional (2D) π-conjugation structure, has been applied in various aspects such as electronic, optical and catalytic fields because of its outstanding mechanical, optical and electrical properties [18–20]. In particular, the excellent mobility of charge carriers and an extremely high theoretical specific surface area have spurred the increasing interest to synthesize the graphene-semiconductors and investigate its application in photocatalytic [21,22]. Furthermore, graphene can elevate CB minimum of photocatalyst, such as Bi_2WO_6 [23]. So, the photocatalytic reduction of CO_2 to CH_4 can be occurred. However, hitherto only two studies reported the synthesis of WO_3-graphene composites and their application in gas-sense and water splitting [24,25]. To the best of our knowledge, no previous work regarding the fabrication of graphene WO_3-nanobelt composite and its application on photocatalytic reduction of CO_2 into hydrocarbon fuels has been reported.

In this work, we obtained the graphene–WO_3 nanobelt composites by a facile in situ hydrothermal method. It has higher photocatalytic activity for photocatalytic reduction of CO_2 into hydrocarbon fuels than TiO_2 and WO_3. The mechanism for photocatalytic reduction of CO_2 on the graphene–WO_3 nanobelt composites was also proposed and confirmed.

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2. Experimental section

2.1. Preparation of grapheme-WO_3 nanobelt composites

Graphene oxide (GO) was prepared from the natural graphite by a modified Hummers method [26]. Briefly, 0.5 g graphite power (SP) was reacted with a mixture of 2 g $NaNO_3$, 12 mL concentrated H_2SO_4 and 3 g $KMnO_4$ followed by an addition of 40 mL H_2O and 10 mL H_2O_2 (30%). The product was filtered and washed with 5% HCl solution and deionized water to obtain a brown power. An exfoliated GO aqueous dispersion was achieved after sonication for 2 h and subsequent dialysis for a week. The resulting GO aqueous solution was 0.85 mg/mL.

The graphene–WO_3 nanobelt (GW) composites were prepared by a facile hydrothermal method. In a typical process, 1 g $(NH_4)_5H_5[H_2(WO_4)_6]\cdot H_2O$ (CP, Sinopharm Chemical Reagent Co., Ltd) was dissolved in deionized water (38 mL) and the solution was adjusted to pH = 1 with H_2SO_4 (1:1). Then a desired GO solution was added into the above solution and stirred for 1 h to obtain the transparent solution. The solution was transferred into a 50 mL Teflon-lined autoclave and held at 180 °C for 12 h. After the solution was cooled to room temperature, the precipitation was collected by vacuum-filtration and then rinsed with deionized water several times. The product was dried in an oven at 70 °C for a day. The obtained sample was designed as GW-wt.%, here, wt.% is the weight percentage of graphene to WO_3. For comparison, the pure WO_3 nanobelts without graphene were prepared under the same experimental condition.

2.2. Characterization

X-ray diffraction patterns of the samples were recorded at room temperature, by a Bruker D8 advance X-ray diffractometer using Cu Kα radiation and 2θ scan rate of 6 min^{-1}. Diffraction patterns were taken over the 2θ range of 20–70°. Transmission electron microscopy and high-resolution transmission electron microscopy images were obtained by a JEOL JEM-2010FEF Field Emission Electron Microscope. The UV–vis diffuse reflection spectra were obtained for the dry-pressed disk samples on a UV–vis spectrophotometer (UV-3600) by $BaSO_4$ as the reflectance sample. Valence band spectra were analyzed using X-ray photoelectron spectroscopy (Thermo Escalab 250, a monochromatic Al Ka X-ray source). All binding energies were referenced to the C 1s peak (284.6 eV) arising from adventitious carbon. Raman spectra were recorded on an inVia-Reflex Raman microprobe with 514 nm laser excitation.

2.3. Photocatalytic conversion of CO_2 into CH_4

In the photocatalytic reduction of CO_2, 0.1 g of the catalyst was uniformly dispersed onto the glass reactor with an area of 5.4 cm^2. The light source in the above photoreactivity experiments was a 300 W Xe lamp (Beijing Trusttech Co. Ltd, PLS-SXE-300UV). Visible light irradiation was obtained by using a 400 nm long pass glass filter to remove UV. The volume of the reaction system was about 270 mL. The reaction setup was vacuum-treated several times, and then the high purity of CO_2 gas was followed into the reaction setup for reaching ambient pressure. A total of 1 mL of deionized water was injected into the reaction system as the reducer. Photocatalysts were allowed to equilibrate in the CO_2/H_2O atmosphere for several hours to ensure that the adsorption of gas molecules was complete. During irradiation at room temperature, about 0.5 mL of gas was continually taken from the reaction cell at given time intervals for subsequent CH_4 concentration analysis by using a gas chromatograph (GC-14B and GC8A; Shimadzu Corp., Japan). Control experiments that showed no appreciable reduced C1 or C2 products were detected in the absence of H_2O, CO_2, photocatalyst or light irradiation, illustrating that H_2O, CO_2, photocatalyst and light irradiation were necessary for the photocatalytic CO_2 reduction.

3. Results and discussion

The crystallographic structures of all GW composites and bare GO are confirmed by X-ray diffraction (XRD) technique. Fig. 1 clearly shows that all diffraction peaks of the GW composites and pure WO_3 patch well with the hexagonal reflections (JCPDF card no: 85-2460). For GO, a sharp diffraction peak (002) appears at 10.80°, which indicates that most of the graphite power was oxidized into GO by expanding *d*-spacing from 3.5 Å to 6.78 Å [27,28]. Moreover, the peak of GO disappears in GW composites, which is likely due to the thimbleful GO in GW composites.

To obtain the microscopic information, transmitting electron microscopy (TEM) is carried out together to analyze the GW, pure WO_3 and bare GO for comparison. TEM images clearly reveal the structure of samples. As shown in Fig. 1a, graphene sheets are flaky. The length distribution of the pure WO_3 nanobelts is from 30 nm to a few hundreds of nanometers with widths of 5–15 nm (Fig. 2b). The 1D WO_3 nanobelts were formed because sulfate ions were adsorbed on the faces parallel to the c-axis of WO_3 nanocrystals [29]. Compared with the pure WO_3, WO_3 nanobelts with the addition of graphene become shorter and well-decorate on the curly graphene surface (Fig. 2c). The HRTEM image (Fig. 2d) indicates that the lattice fringe separations are 0.634 and 0.383 nm respectively, which can be indexed as (100) and (002) planes of hexagonal WO_3 and in agreement with XRD results. Obviously, the presence of graphene restrains the WO_3 nanobelt growth along the (002) axis and results in the shorter WO_3 nanobelts of GW composite compared with pure WO_3.

Fig. 3 shows a comparison of bare GO and GW composite. In the case of GO, Raman spectrum shows two prominent bands at 1348 cm^{-1} and 1599 cm^{-1}, which correspond to the well-documented D and G band respectively[30]. For GW, the characteristic bands of hexagonal WO_3 (ν (O–W–O); 790 cm^{-1}) and the D-band (1348 cm^{-1}) of graphene oxide can be observed. However, the G band up-shifts from 1599 cm^{-1} to 1607 cm^{-1}, which gives an evidence for the chemical doping of carbon materials [31,32]. Compared with the I_D:I_G (0.855) of bare GO, the intensity ratio I_D:I_G of graphene–WO_3 composite increases to 0.964. This change suggests the formation of graphene after a hydrothermal treat from the reduction of GO [33].

We perform CO_2 and gaseous H_2O photocatalysis in a gas-solid system over GO, TiO_2, GW and WO_3 under visible-light irradiation in the absence of any co-catalysts. Gas chromatographic analysis shows that CH_4 was exclusively obtained as the reduction product without detectable CH_3OH, H_2, and CO as secondary products. A control experiment that showed no appreciable reduced C1 or C2 products was detected in the absence CO_2 over GW under light irradiation (Fig. 4a), illustrating that graphene is an electron donor for the CO_2 reduction

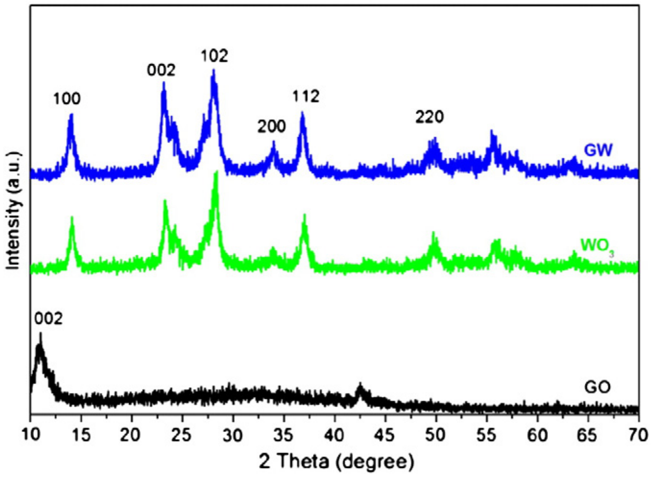

Fig. 1. XRD patterns of GO, WO_3 and GW.