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Synthesis of BiOI flowerlike hierarchical structures toward photocatalytic reduction of CO_2 to CH_4

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ABSTRACT

BiOI flowerlike hierarchical structure was synthesized by the direct hydrolysis method – hydrolysis at room temperature in the presence of polyvinyl pyrrolidone. As-synthesized BiOI was characterized by powder X-ray diffraction, UV–vis diffuse reflectance spectra, X-ray photoelectron spectroscopy spectra, scanning electron microscopy, transmission electron microscopy, and high-resolution transmission electron microscopy. It is a facile way to obtain BiOI flowerlike hierarchical structure photocatalyst for photocatalytic reduction of CO_2 into hydrocarbon fuels under simulated sunlight irradiation without cocatalyst. And the photocatalytic activity of as-synthesized BiOI is higher than that of P25 TiO_2 and bulk BiOI.

1. Introduction

Semiconductor photocatalysis based on harnessing and converting solar energy into chemical energy has been considered to be a green and promising pathway for solving the energy crisis and eliminating most kinds of contaminants [1,2]. Recently, Bi(III)-based semiconductors, such as $BiVO_4$ [3], Bi_2MO_6 [4], Bi_2WO_6 [5], $BiPO_4$ [6] and BiOCl [7,8] have been reported to be promising photocatalysts. BiOI is an important V-VI-VII ternary semiconductor compound with suitable absorption edge at about 680 nm and the estimated band gap energy of about 1.8 eV [9–12]. It is known as a tetragonal layered structure with lattice constants of $a = 0.3994$ nm and $c = 0.9149$ nm. The enough large space of BiOI layered structure can polarize the related atoms and orbitals and induce the presence of internal static electric fields perpendicular to the $[Bi_2O_2]$ slabs and halogen anionic slabs in BiOI. At the end, effective separation of the photoinduced electron–hole pairs along the [0 0 1] direction can be displayed. On the other hand, BiOI has an indirect-transition band-gap so that the excited electron has to travel certain *k*-space distance to be emitted to the valence band (VB) which reduces the recombination probability of the excited electron and the hole [3,4]. So, BiOI can be used as an excellent semiconductor material for solar utilization. Furthermore, our previous study about BiOI nanosheets showed that the {0 0 1} facet-dependent photoactivity of BiOI was found and explained the origin: photoinduced oxygen vacancies and self-induced internal electric fields result in high separation efficiency of photogenerated electron and hole [11,12].

Many routes have been applied to synthesize BiOI with various morphologies. For examples, reverse microemulsions (consisting of heptane, nonionic surfactants, and aqueous salt solutions) were used to synthesize BiOX (X = Cl, Br, I) nanoparticles [13]. BiOI nanosheets synthesized via phase-transfer assisted reaction or precipitation–filtration process [7,14,15]. One-pot solvothermal process was explored to prepare BiOI 3D structure by employing ethylene glycol or ethanol–water mixture as the solvent [9,10]. They exhibit good photoactivity under visible light irradiation.

In this study, we report BiOI hierarchical structures via direct hydrolysis synthesis. As-synthesized BiOI showed an extraordinary photocatalytic activity for photocatalytic reduction of CO_2 into hydrocarbon fuels under visible light. And this is the first paper about photoreduction CO_2 with BiOI.

2. Experimental

2.1. Preparation

$Bi(NO_3)_3{\cdot}5H_2O$, KI and polyvinyl pyrrolidone (PVP) were analytically pure and from Sinopharm Chemical Reagent Co., Ltd. Nano-TiO_2 (Degussa P25, 70% in anatase phase and 30% in rutile, particle diameters: 30–50 nm) was from Degussa Corp.

In a typical experiment, 0.0028 mol solid $Bi(NO_3)_3{\cdot}5H_2O$ was added into 20 mL (0.140 mol/L) KI and (40 g/L) PVP solution with magnetic stirring. After sonicating for 2 min and further magnetic

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stirring for 5 h at room temperature, the BiOI precipitate was centrifuged, washed with distilled water and dried at 60 °C for 8 h. Bulk BiOI was prepared without PVP adding.

2.2. Characterization

X-ray diffraction (XRD) was carried out on a multi-purpose high performance X-ray diffractometer (PANalytical, CuKα radiation, λ = 1.54 Å) at a scanning rate of 0.03° s^{-1} in the 2θ range from 15° to 70°, and the current and the voltage used for the powder XRD are 40 kV and 30 mA, respectively). The morphologies were examined by a scanning electron microscope (FEI Sirion200). The TEM-images and SAED-patterns were recorded on a JEOL 2010 electron microscopy, using an accelerating voltage of 200 kV. X-rays photoelectron spectroscopy (XPS) was performed by using an AXIS-NOVA (CJ109, Kratos Inc.) in the range of 0–1000 eV for surface composition and surface interaction of nanomaterials. The peaks were calibrated using the C1s level at 284.6 eV as an internal standard. UV–vis diffuse reflectance spectroscopy (DRS) was recorded on a UV-2550 (Shimadzu) UV–vis spectrophotometer and converted from reflection to absorbance by the Kubelka–Munk method. BaSO4 was used as a reference in a UV–vis diffuse reflectance experiment.

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 into the glass reactor with an area of 5.4 cm^2. The light source for the above photoreactivity experiments was a 300 W xenon lamp (Beijing Trusttech Co. Ltd., PLS-SXE-300UV). The volume of the reaction system was about 270 mL. The reaction setup was vacuum-treated several times, and then the high purity CO_2 gas was flowed into the reaction setup to reach 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 continuously taken from the reaction cell at given time intervals for subsequent CH_4 concentration analysis by using a gas chromatography (GC-14B and GC8A; Shimadzu Corp., Japan). Control experiments showed that no appreciable reduced C1 or C2 products were detected in the absence of H_2O, CO_2, photo-catalyst or light irradiation, illustrating that H_2O, CO_2, photo-catalyst and light irradiation were necessary for the photocatalytic CO_2 reduction.

3. Results and discussion

The XRD patterns in Fig. 1 show that all of the diffraction peaks were in good agreement with the tetragonal phase of BiOI (JCPDS no. 10-0445); meanwhile no other impurity peaks were observed. It can be found that there are three peaks (0 0 2), (1 0 2) and (1 1 0) at 2θ of 19.36°, 29.57° and 31.71°, respectively. Moreover, the sharp diffraction peaks indicated that the as-prepared samples were well-crystallized. All the diffraction peaks can be indexed to the tetragonal structure of BiOI with space group of *P4/nmm* (JCPDS, 85-0863). The XPS measurements provided further information for the evaluation of the purity and surface composition of the BiOI flowerlike hierarchical structure. The XPS survey spectrum in Fig. 2a demonstrates, no peaks of other elements other than C, O, Bi and I in the sample, a proof of the purity of BiOI flowerlike hierarchical structure. Fig. 2b shows the high-resolution XPS spectra of Bi 4f. The two strong peaks at the Bi region of 159.1 eV and 164.4 eV are assigned to Bi 4f7/2 and Bi 4f5/2 of BiOI, respectively.

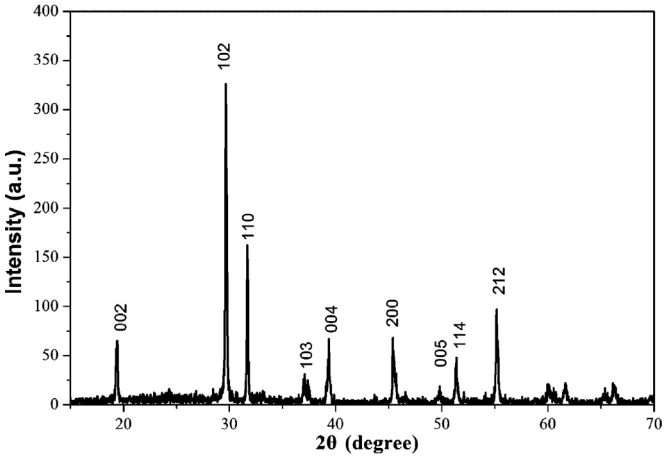

Fig. 1. XRD patten of as-synthesized BiOI.

In order to investigate the detailed crystal structure of BiOI hierarchical structure, FESEM, TEM and HRTEM were carried out, and the results are shown in Fig. 3. The typical overall SEM and TEM image (Fig. 3a and c) shows that the obtained products are uniform flowerlike spheres. These spheres have an average size of 600 nm in diameter. Fig. 3b reveals that the flower is composed of several dozen nanosheets. The nanosheets are ca. 400 nm in plane size and

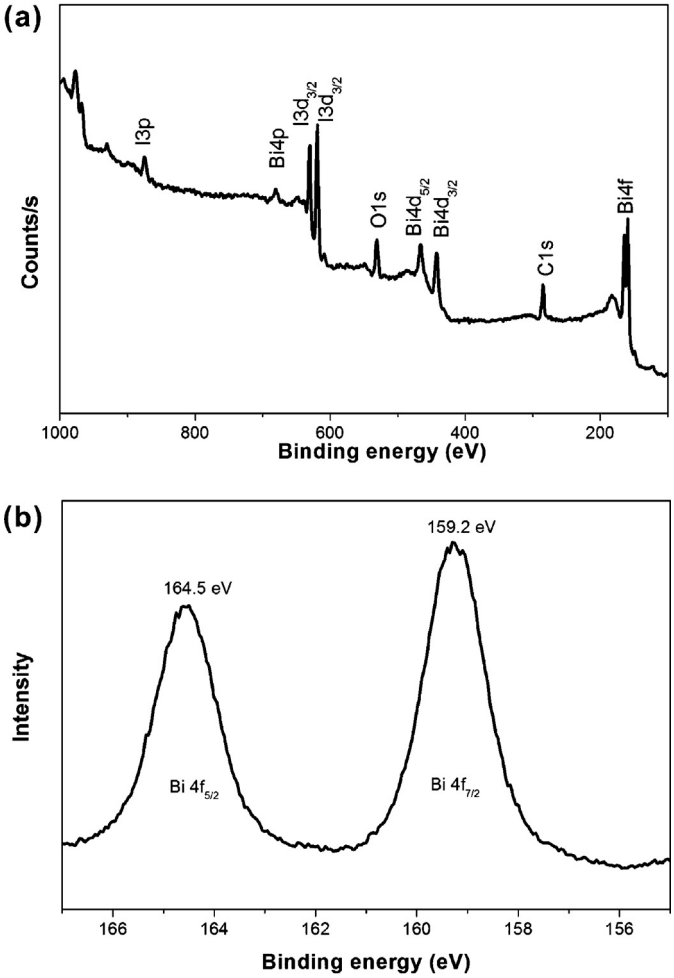

Fig. 2. XPS survey spectrum (a) and high-resolution XPS spectra of Bi 4f (b) of as-synthesized BiOI.