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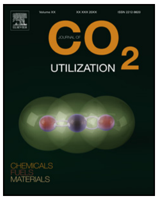

Synthesis of $Bi_xO_yI_z$ from molecular precursor and selective photoreduction of CO_2 into CO

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ABSTRACT

In this paper, different $Bi_xO_yI_z$ photocatalysts ($Bi_4O_5I_2$ and Bi_5O_7I) have been successfully synthesized via two different methods to process molecular precursor. The precursor was papered by solvothermal method with $Bi(NO_3)_3 \cdot 5H_2O$, glycerol and iodine. $Bi_4O_5I_2$ was obtained by hydrolyzing the precursor, and Bi_5O_7I was achieved via calcining the precursor at 400 °C. The as-prepared $Bi_xO_yI_z$ photocatalysts were characterized by X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET), X-ray photoelectron spectroscopy (XPS), scanning electron microscope (SEM), high-resolution transmission electron microscopy (HRTEM) and UV–vis diffuse reflectance spectra (DRS). The photocatalytic results showed that $Bi_4O_5I_2$ and Bi_5O_7I can photoreduce CO_2 into CO selectively. $Bi_4O_5I_2$ (19.82 umol h^{-1} g^{-1}) has higher photocatalytic activity for CO_2 photoreduction than Bi_5O_7I (1.73 umol h^{-1} g^{-1}). The AQY for the solar fuels productions over $Bi_4O_5I_2$ reached 0.37% at 420 nm monochromatic light irradiation. The selectivity of $Bi_4O_5I_2$ was more than 99.9%. Photocatalytic mechanism studies revealed that the higher conduction band (CB) edge of $Bi_4O_5I_2$ resulted in higher photoactivity for CO_2 photoreduction.

1. Introduction

With the rapid development of science and society, environmental pollution and energy crisis have become great issues that human have to confront all over the world. Semiconductor photocatalysis, which could harvest energy directly from sunlight, has drawn considerable attention as a potential green technology for environmental purification and energy generation [1,2]. Now, CO_2 photoreduction was the most typical case for environmental purification and energy generation simultaneously. During the reaction, the concentration of greenhouse gases CO_2 was reduced for environmental protection doing, and solar fuels (CO, CH_4) were obtained for energy generation doing [3,4]. There is no doubt that the photocatalyst is the most important part of the photocatalysis technology. At present, TiO_2 is the most widely semiconductor photocatalyst due to its high photoactivity, low cost, chemical and photochemical stability, non-toxicity, and environmentally friendly features [5,6]. However, it showed very low photocatalytic activity under visible light irradiation due to its wide band gap of 3.2 eV. For improving the application efficiency of TiO_2 in visible light region, many modification strategies have been employed, such as metal or non-metal elements doping [7], noble metal deposition [8], surface functionalization [9], and combination of semiconductor photocatalysts [10]. However, these modification strategies can't enhance the visible-light-driven (VLD) photocatalytic performance to a perfect level. Therefore, besides modification, more new VLD photocatalysts are exploited [11,12]. To date, some active VLD photocatalysts such as oxides, sulfides, element, and polymers semiconductor photocatalysts were studied. However, these new photocatalysts also faced many new problems, such as photo-stabilization of Ag-based photocatalysts [13], and the low quantum yields of the polymer and element semiconductor photocatalysts [14–16]. So, the development of novel, highly efficient and persistently stable VLD photocatalysts remains a major challenge.

Bismuth oxyhalides BiOX (X = Cl, Br, I) belong to a new family of VLD semiconductor photocatalysts. They attract more and more attention due to their layered structure with $[Bi_2O_2]$ slabs and double halogen atoms slabs, which features an internal static electric field perpendicular to each layer that may induce more

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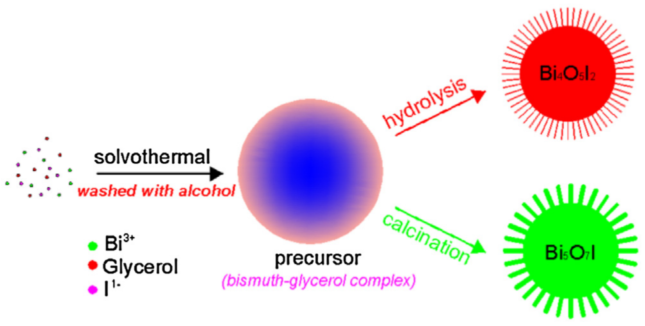
effective separation of photo-induced charge carriers [17–23]. Among all the BiOX samples, BiOI displays the best photocatalytic activity under visible light irradiation [24]. It has also been demonstrated that BiOI nanoplates exhibit more superior activity than commercial TiO_2 (P25, Degussa), BiOCl and BiOBr towards methyl orange (MO) dye degradation under UV–vis or visible light irradiation [24]. The higher photocatalytic activity of BiOI is mainly attributed to its smallest band gap (1.8 eV) among BiOX. In order to improve the photocatalytic activity of BiOI, the composite materials (BiOI/BiOBr [25], $Bi_2O_2CO_3$/BiOI [26], MnO_x–BiOI [27], AgI/BiOI [28]) and the solid solution ($BiOBr_{(1-x)}I_x$ [29], $BiOCl_{(1-x)}Br_x$ [30], and $BiOCl_{(1-x)}I_x$ [31])have been prepared.

In recent studies, another effective way to improve the photocatalytic performance of BiOX was found: new $Bi_xO_yX_z$ (X = Cl, Br, I) materials with bismuth-rich (dehalogenation) strategy [32–34]. Theoretical calculation showed that the position of conduction band minimum (CBM) was mainly determined by the Bi 6p of BiOX [35]. Therefore, the increase in the content of bismuth may decrease the CBM potential, and then, the bismuth-rich bismuth oxyhalide photocatalysts can display high photocatalytic activity. For instances, by bismuth-rich strategy, $Bi_{24}O_{31}Br_{10}$ can photoreduce Cr (VI) and split water [34], Bi_3O_4Br can effectively activate molecular oxygen [36], and Bi_5O_7I exhibited efficient photocatalytic activity for the decomposition of RhB in water and acetaldehyde in air under visible light [37]. Comparing to the constructing hetero-structure, bismuth-rich strategy was more simple and feasible to enhance the photocatalytic properties of BiOI. However, to our best knowledge, the synthesis of $Bi_xO_yX_z$ is rarely investigated via molecular precursor method.

Molecular precursor method has been the main way to prepare inorganic materials [38–40]. But, it was not used to prepare $Bi_xO_yX_z$ yet till now. In this paper, bismuth-iodine-glycerol molecular precursor was synthesized. Furthermore, the as-synthesized molecular precursor can be used to prepare different $Bi_xO_yX_z$ photocatalysts via two different processes (Scheme 1). Bi_5O_7I was achieved via calcining the precursor at 400 °C. Via a simple hydrolytic process, another pure bismuth-rich bismuth oxyiodides $Bi_4O_5I_2$ was obtained. This discovery indicated that glycerol plays an important role in the bismuth oxybromide synthesis process. As an new bismuth-rich bismuth oxyiodides photocatalyst, pure $Bi_4O_5I_2$ was reported rarely [41–43]. In order to study the photocatalytic properties of as-prepared $Bi_xO_yX_z$ samples, the photoreduction of CO_2 were done under UV–vis light irradiation. The photocatalytic mechanism for the excellent photocatalytic activity of $Bi_4O_5I_2$ also was discussed.



Scheme 1. Synthesis process of $Bi_4O_5I_2$ and Bi_5O_7I via different methods processing molecular precursor.

2. Experimental

2.1. Synthesis

2.1.1. Complex precursor

0.002 mol KI and 0.002 mol $Bi(NO_3)_3 \cdot 5H_2O$ were dissolved into 20 mL glycerol, respectively. Then, KI solution was added into the Bi $(NO_3)_3 \cdot 5H_2O$ solution dropwise with continuously stirring. The suspension was transferred into Teflon-lined stainless steel autoclaves (50 mL), and then the autoclaves were kept at 160 °C for 17 h. After reaction, the complex precursors precipitate was obtained by centrifugation, and then washed with ethanol several times. Finally, it was dried at 80 °C in air.

2.1.2. $Bi_4O_5I_2$

0.3 g complex precursor was dispersed in 100 mL deionized water. Then, $Bi_4O_5I_2$ sample was obtained via a simple hydrolytic process, and then washed successively with deionized water. Finally, it was dried at 80 °C in air and heat treatment at 300 °C for 5 h to remove possible residual organic species (glycerol).

2.1.3. Bi_5O_7I

1.0 g complex precursor was calcinated at 450 °C for 5 h. Then, the yellow Bi_5O_7I sample was obtained.

2.1.4. BiOI

1.0 g complex precursor was calcinated at 300 °C for 5 h. Then, the yellow Bi_5O_7I sample was obtained.

2.2. Characterization

The crystalline phase of the samples was characterized by X-ray diffraction (XRD) by a Bruker D8 advance X-ray diffractometer at room temperature with Cu-Ka radiation (λ = 0.15418 nm). Diffraction patterns were taken over the 2θ range 8–70°. SEM images were obtained with scanning electron microscopy (SEM, FEI, QUANTA 200). Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were obtained by a JEOL JEM-2100F Field Emission Electron Microscope with operating at an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were carried out by Thermo ESCALAB 250XI X ray photoelectron spectrometer (Al Ka, 150 W, C1s 284.8 eV). UV–vis diffuse reflectance spectra (DRS) were achieved using a UV–vis spectra (Perkin Elmer, Lambda 650s, $BaSO_4$ as a reference). The infrared spectra were obtained using a Nicolet 5700 Fourier transform infrared (FT-IR) spectrometer (reference sample: KBr; wavelength range: 400–4000 cm^{-1}). The Brunauer-Emmett-Teller (BET) surface areas were measured using Quantachrome Autosorb-IQ automated gas sorption systems at 77 K.

2.3. Photocatalytic reduction of CO_2

The photocatalytic reduction activities for CO_2 conversion was done in Labsolar-III AG (Beijing Perfect light Technology Co., Ltd., China) closed gas system. The volume of the reaction system was 350 mL 1.3 g $NaHCO_3$ was added firstly. Then 0.1 g pholocatalysts were uniformly dispersed onto a watch-glass with an area of 28.26 cm^2, and then the watch-glass was put in mid-air of the reaction cell. Prior to the light irradiation, the above system was thoroughly vacuum-treated to remove the air completely, and then 5 mL 4 M H_2SO_4 was injected into the reactor to react with $NaHCO_3$. Then, 1 atm CO_2 gas was achieved. After that, the reactor was irradiated from the top by a 300 W high pressure xenon lamp with 400 nm cut off filters (PLS-SXE300, Beijing Perfect light Technology Co., Ltd., China), and the photoreaction temperature was kept at