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Synthesis of hierarchical bismuth-rich $Bi_4O_5Br_xI_{2-x}$ solid solutions for enhanced photocatalytic activities of CO_2 conversion and Cr(VI) reduction under visible light

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ABSTRACT

Bismuth oxyhalides (BiOX, X = Br, I) photocatalysts are rarely applied for photocatalytic reduction reaction withthe photo-induced electron, as this is impeded by their low conduction band. As a widely used approach for enhancing the photocatalytic reduction activity, bismuth-rich strategy results the bismuth content of BiOX photocatalysts increasing. In this paper, a solid solutions of bismuth-rich $Bi_4O_5Br_xI_{2-x}$ were prepared applying the molecular precursor method. $Bi_4O_5Br_xI_{2-x}$ were characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), element mapping, Brunauer–Emmett–Teller surface analysis (BET), UV–vis diffuse reflectance spectroscopy (DRS), and X-ray photoelectron spectroscopy (XPS). The obtained photocatalytic data showed that $Bi_4O_5Br_xI_{2-x}$ solid solutions had higher photocatalytic activities than $Bi_4O_5Br_2$ and $Bi_4O_5I_2$. At an optimal ratio of x = 1, the Bi_4O_5BrI photocatalyst showed the highest photocatalytic reduction activity for CO_2 conversion (22.85 $\mu mol\ h^{-1}\ g^{-1}$ CO generation, AQE was 0.372 at 400 nm) and Cr(VI) removal (88%). CO_2 adsorption data and CO_2 temperature programmed desorption (CO_2-TPD) revealed that Bi_4O_5BrI exhibited the highest chemical adsorption ability of CO_2 molecules Photocurrent and electrochemical impedance (EIS) spectroscopy demonstrated the enhanced photo-induced carrier separation efficiency of Bi_4O_5BrI. These mechanistic studies suggest that $Bi_4O_5Br_xI_{2-x}$ solid solutions are excellent photocatalysts for solar fuel generation and environmental remediation.

1. Introduction

Energy and environmental resources are the most critical factors for human livelihood. Therefore, worldwide research focuses more and more on new technologies for developing new means of energy generation and environmental remediation. Recently, photocatalysis technology displayed great prospects for environmental remediation and solar fuel generation [1–5]. Photocatalysis technology uses semiconductor nanomaterials to decompose toxic pollutants, convert carbon dioxide (CO_2), and split water under solar light irradiation. For example, oxide-based (TiO_2 [6], ZnO [7], SnO_2 [8]), sulfide-based (CdS [9], ZnS [10], SnS [11]), silver-based (AgX (X = Cl, Br, I) [12,13], Ag_3PO_4 [14], Ag_2CrO_4 [15]), and bismuth-based semiconductors (Bi_2MoO_6 [16], $BiVO_4$ [17], BiOX (X = Cl, Br, I) [18,19], $Bi_2O_2CO_3$ [20]) were used for photocatalysis. However, most oxides cannot absorb visible light [21,22]; sulfide- and silver-based semiconductors are unstable due to the leak of ion under light irradiation [23,24]; and bismuth-based semiconductors were rarely used for solar fuel generation due to their low photocatalytic reduction activity [25–27]. Among the above three types of photocatalysts, bismuth-based semiconductors of the type BiOX were suggested to be most promising due their unique layered structure [25–27], and more and more few-layer BiOX nanosheets are applied for photocatalytic reduction in solar fuel generation [28–30].

In order to enhance the photocatalytic reduction activity of BiOX semiconductors more effectively, the bismuth content of BiOX was increased. This bismuth-rich strategy exploits that the

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conduction band (CB) potential can be altered by changing the bismuth content, as the CB of BiOX is mainly determined by the Bi 6p state [31–33]. Depending on the respective bismuth content, different bismuth-rich BiOX photocatalysts may display different photocatalytic reduction activities. For example, $Bi_{24}O_{31}Br_{10}$ can photoreduce Cr(VI) [34], Bi_3O_4Br, Bi_5O_7X (X = Br and I), and $Bi_{24}O_{31}Cl_{10}$ can effectively activate molecular oxygen [35–38], and Bi_3O_4Cl and $Bi_{12}O_{17}Cl_2$ exhibit efficient photocatalytic reduction activities for H_2 generation under visible light [39,40]. Recently, our group synthesized $Bi_4O_5X_2$ (X = Br and I) photocatalysts applying the molecular precursor method [41–43]. These photocatalysts showed high photocatalytic reduction activities for CO_2 conversion. Furthermore, we improved the activity of bismuth-rich BiOX photocatalysts ($Bi_xO_yX_z$) by performing coupling, using a co-catalyst and applying doping [43–46]. However, no solid solution of bismuth-rich BiOX has been reported so far. At present, the different bismuth-rich $Bi_xO_yX_z$ with same atom ratio and different halogen are obtained by the hydrothermal process at different pH values [47–49]. However, the non-uniform synthesis conditions of this approach cause difficulties in the synthesis of solid solutions of bismuth-rich BiOX.

In this paper, solid solutions of bismuth-rich $Bi_4O_5Br_xI_{2-x}$ were prepared via the molecular precursor method based on our previous work, and their enhanced photocatalytic mechanism was discussed in detail [42,43]. To the best of our knowledge, no solid solution of $Bi_4O_5Br_xI_{2-x}$ photocatalysts has been reported to date. At an optimal ratio of x = 1, Bi_4O_5BrI showed the highest photocatalytic reduction activity for CO_2 conversion (22.85 μmol h^{-1} g^{-1} CO generation) and Cr(VI) removal (88%).

2. Experimental section

2.1. Materials

$Bi(NO_3)_3{\cdot}5H_2O$, KBr, KI, glycerol, and ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). These reagents were of analytical grade and were used without further purification.

2.2. Synthesis

2.2.1. Complex precursor

Each of the reagents KX (X = Br or/and I; 2 mmol) and $Bi(NO_3)_3{\cdot}5H_2O$ (2 mmol) was dissolved in 20 mL glycerol. Then, the KX solution was added dropwise to the $Bi(NO_3)_3{\cdot}5H_2O$ solution while stirring continuously. The resulting suspension was transferred into Teflon-lined stainless steel autoclaves (50 mL) and kept at 160 °C for 16 h. After the reaction was completed, the formed complex precursor precipitate was obtained by centrifugation and then washed with ethanol. Finally, the obtained complex precursor was dried at 80 °C under air atmosphere.

2.3. Bi4O5BrxI2-x

$Bi_4O_5Br_xI_{2-x}$ compounds were synthesized by a simple hydrolytic process from an aqueous solution of their complex precursor molecules (0.3 g in 100 mL deionized water). The obtained $Bi_4O_5Br_xI_{2-x}$ compounds were washed successively with deionized water and finally dried at 80 °C.

2.4. Characterization

X-Ray diffraction patterns (XRD) of the samples were recorded at room temperature with a Bruker D8 advance X-ray diffractometer using Cu Kα radiation and a 2θ scan rate of 6 min^{-1}. Diffraction patterns were taken over an angular range of 2θ = 5–70°. A Sigma Zeiss field-emission scanning electron microscope (FESEM) was used to take FESEM images, and a JEOL JEM-2100F (RH) field-emission electron microscope was used to take transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images. X-ray photoelectron spectroscopy (XPS) measurements were carried out with a Thermo Scientific ESCALAB 250XI X-ray photoelectron spectrometer (Al Ka, 150 W, C1s 284.8 eV). UV–vis diffuse reflectance spectra (DRS) were obtained by UV–vis spectroscopy (Perkin Elmer, Lambda 650s, $BaSO_4$ as a reference). A Quantachrome Autosorb-IQ automated gas sorption system, operated at 77 K, was used to measure the Brunauer–Emmett–Teller (BET) surface areas and CO_2 adsorption properties. CO_2 temperature programmed desorption (CO_2-TPD) was carried out on the instrument AutoChem II 2920 (Micrometrics). The CO_2-TPD curves were obtained by gradually increasing the temperature to 500 °C with a ramping rate of 1 °C min^{-1}.

2.5. Photocatalytic CO_2 conversion

Photocatalytic CO_2 conversion was carried out in an off-line system. The used reactor. In the first step, 50 mg photocatalyst were uniformly dispersed on a glass sheet (about 25 cm^2 surface area). A mixture of CO_2/H_2O vapor was produced by passing compressed high purity CO_2 gas (99.99%) through a water vaporizer. This CO_2/H_2O vapor served as reaction gas and was introduced into the reaction system for several times to remove air. The reactor was purged for 15 min with CO_2/H_2O vapor and subsequently irradiated with a 300 W high-pressure Xenon lamp (PLS-SXE300C, Beijing Perfectlight Technology Co., Ltd., Beijing, China.) equipped with a 400 nm filter. The photoreaction temperature was maintained at 15 °C with a DC-0506 low-temperature thermostat bath (Shanghai Sunny Hengping Scientific Instrument Co., Ltd., Shanghai, China). 1 mL of gas was taken from the reaction cell at each time interval for qualitative analysis using an Agilent 7890 gas chromatograph equipped with a flame ionization detector (FID, Porapak N 80/100 columns) and a thermal conductivity detector (TCD, MoleSieve 13 × 60/80 columns). The production yield was quantified using a calibration curve. The outlet gases were determined to be mainly CO, CH_4, and small quantities of O_2 and H_2.

400 nm monochromatic light (400 nm band-pass filter, the illumination intensity of the light at the sample surface was 1.23 mW/cm^2) was used to test the apparent quantum efficiency (AQE) by the following equation.

$$\mathrm{AQE}\ (\%) = \frac{N_{\text{Solar fuels}}}{N_p} = \frac{2 \times \text{number of CO molecules} + 8 \times \text{number of } CH_4 \text{ molecules}}{\text{the number of incident photons}} \times 100\%$$

$$= \frac{2 \times N_a \times \left(M_{CO} + M_{CH_4}\right)}{\frac{Pst\lambda}{hc}}$$

Where, $N_a = 6.02 \times 10^{23}$ mol^{-1}, $P = 1.23$ mW/cm^2, $S = 25$ cm^2, $t = 3600$ s, $\lambda = 400 \times 10^{-9}$ m, $h = 6.626 \times 10^{-34}$ J s, and $c = 3 \times 10^8$ m s^{-1}.

2.6. Photocatalytic Cr(VI) removal

$Bi_4O_5Br_xI_{2-x}$ powders (20 mg) were added to the prepared Cr(VI) solution (50 mL, 60 mg L^{-1} $K_2Cr_2O_7$) while stirring (about 30 min) to attain adsorption equilibrium. A 300 W high-pressure xenon lamp equipped with a 400 nm filter (PLS-SXE300C, Beijing Perfect