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A bismuth based layer structured organic–inorganic hybrid material with enhanced photocatalytic activity

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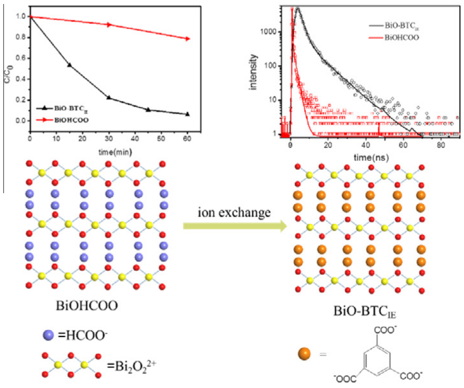
GRAPHICAL ABSTRACT

BiO-BTC$_{IE}$ is obtained via the ion exchange reaction, i.e. the HCOO$^-$ in BiOHCOO is changed to be BTC anions. The obtained BiO-BTC$_{IE}$ remains the layered structure of BiOHCOO, except a distortion of the $Bi_2O_2{}^{2+}$ layer. The distortion is assigned to the origin of the enhanced photocatalytic activity and longer life time of photogenerated charge carriers of BiO-BTC$_{IE}$.



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ABSTRACT

A bismuth-based organic–inorganic hybrid material with layered structure (BiO-BTC$_{IE}$) was synthesized by taking advantage of an ion exchange reaction. The structure of BiO-BTC$_{IE}$ was examined by XRD, EXAFS, FT-IR, TG/DTA, etc. By replacing the HCOO$^-$ with BTC anions in the $Bi_2O_2^{2+}$ interlayer, the $Bi_2O_2^{2+}$ layer is distorted as revealed by the EXAFS, which lead to a longer life time of the photogenerated charge carriers and a higher photocatalytic activity of BiO-BTC$_{IE}$ (more than 10 times).

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1. Introduction

Renewable energy substitutes and environmental decontamination using semiconductor based photocatalysis have attracted intensive research interest because they are economic and ecologically safe options for solving energy and pollution problems. Bismuth-based semiconductors accounts for a very large proportion of the various photocatalysts, and most of them display layered structure, such as Bi_2WO_6, $BiVO_4$, BiOX (X = Cl, Br, I) and $Bi_2O_2CO_3$, $BiOIO_3$ [1–14].

Bismuth based organic inorganic hybrid materials, combining features of organic molecular and bismuth ions, are interesting systems due to their manifold properties ranging from photoluminescence, medicine to catalysis, photocatalysis, gas sorption and high dielectric constant materials [15–23]. Nevertheless, few bismuth based organic inorganic hybrid materials were reported to display significant photocatalytic activity [19,20]. Bi^{3+} cations are known for their stereoactive lone pair leading to interesting and versatile coordination geometries. The coordination number is irregular ranging from 3 to 10 [24,25], making the preparation of bismuth-based organic–inorganic hybrid materials time consuming and uneconomic.

In addition, distorted BiOx polyhedral are usually observed for bismuth based organic inorganic materials [26]. The lone pair distortion has a great influence on the separation of photo-generated charge carriers. For example, monoclinic $BiVO_4$ displays higher photocatalytic activity than the tetragonal phase due to the distortion of BiO_8 dodecahedron in the monoclinic phase [27,28]. However, as far as we know, no investigation was reported about the effect of BiOx polyhydra on the photocatalytic activity.

In this paper, a new bismuth based organic inorganic hybrid material has been synthesized via a facile ion exchange reaction. The $HCOO^-$ ions in BiOHCOO is replaced by trimesic acid anions (BTC), and the as-prepared BiO-BTC_{IE} remains the layered structure of BiOHCOO, except a distortion of the $Bi_2O_2^{2+}$ layer. Photogenerated charge carriers in BiO-BTC_{IE} show higher photocatalytic activity and longer life time. The distortion of the $Bi_2O_2^{2+}$ layer is assigned to the origin of the improved photocatalytic activity.

2. Experimental section

All chemicals used were of analytical grade, and were used without further purification.

2.1. Synthesis of BiOHCOO, $Bi_2O_2[NC_5H_3(CO_2)_2]$, and BiO-BTC_{IE}

BiOHCOO and $Bi_2O_2[NC_5H_3(CO_2)_2]$ (the organic linker is 3,5-pyridinedicarboxylate) were synthesized according to the literature [29,30].

Synthesis of BiO-BTC_{IE}: BiOHCOO was used as the starting material and the details are as follows. BiOHCOO and H_3BTC in a molar ratio of 1:9 were added in a mixture of 5 ml DMF and 15 ml methanol. After being stirred for 0.5 h, the mixed solutions were sealed in a 100 ml Teflon-lined autoclave, maintained at 150 °C for 48 h and cooled down to room temperature. The resultant solid was washed by DMF, water, ethanol and then dried in air at 60 °C.

Synthesis of BiO-BTC_{IE} using $Bi_2O_2[NC_5H_3(CO_2)_2]$ as the starting material was the same except that BiOHCOO is replaced with $Bi_2O_2[NC_5H_3(CO_2)_2]$.

2.2. Characterization

The X-ray power diffraction (XRD) data of the as-prepared samples was collected on an X-ray powder diffraction (Bruker AXS D8). The Bi L_3-edge extended X-ray absorption fine structure (EXAFS) spectra were collected in transmission mode at beamline 1W2B of the Beijing Synchrotron Radiation Facility in China. A fixed-exit Si(1 1 1) double crystal monochromator was used. The incident and transmit X-ray beam were measured by ionization chambers filled with 25% Ar and 75% N_2. The EXAFS raw data were then background-subtracted, normalized and Fourier transformed by the standard procedures with the IFEFFIT package [31]. Thermogra vimetric–differential thermal analysis (TG/DTA) was carried out using a diamond TG/DTA analyzer under air atmosphere with a heating rate of 5 °C/min. Fourier transform infrared (FT-IR) spectra was performed on a Bruker ALPHA-T spectrometer using KBr pellets. The UV–vis diffuse reflectance spectra (DRS) were obtained by a Shimadzu UV-2550 recording spectrophotometer with $BaSO_4$ as the reference. Steady state photoluminesce (PL) spectra were recorded by a high sensitivity fluorometer (Edinburgh FS920). The pump source is an Opolette HE 355 II tunable laser system with a laser pulse width of 5 ns and repetition rate of 20 Hz. The time resolved PL spectra were conducted on Edinburgh FLS920 PL. The decay curve was fitted by using a biexponential decay function to obtain deconvolution of the instrument response function. The average life time was calculated by using the following equation: $\langle \tau_{av} \rangle = a_1\tau_1 + a_2\tau_2$, ($\tau_1$ and τ_2 are the life time, a_1 and a_2 are normalized pre-exponential factors). For BiO-BTC_{IE}, the biexponential decay fitting suggests the lifetime values are 2.04 ns (76.97%) and 8.69 ns (23.03%).

2.3. Photocatalytic reaction

The photocatalytic degradation of Rhodamine B (RhB) was carried out at room temperature. Before photoirradiation, a solution of 50 mg catalyst dispersed in 50 mL of RhB solution (20 mg L^{-1}) was stirred for 2 h to reach adsorption/desorption equilibrium. A 300 W Xe arc lamp (PLS-SXE300, Beijing Trusttech Co., Ltd.) was used as the light source and the concentration of RhB was measured by UV/visible spectrophotometer (UV-2550, Shimadzu).

The examination of active species was the same as above, except that 1 mmol benzoquinone (BQ) or tert butanol (TBA) was added into the RhB solution.

Photocatalytic oxygen evolution from water was performed in a top-irradiation vessel which is connected to a glass-enclosed gas circulation system. In the procedure, 30 mg catalyst and 30 mg $AgNO_3$ were mixed in 30 mL aqueous solution with constant stirring. The reaction temperature was kept at 5 °C. The amount of O_2 evolution was determined by a gas chromatograph (Techcomp GC7890 II).

3. Results and discussion

In our previous work, we reported a bismuth based MOFs (Bi-BTC), which possesses H_3BTC as the organic linker and a unique $\{Bi_2O_{14}\}$ unit acts as metal dots, and H_3BTC acts as organic linker. The as-prepared Bi-BTC exhibits high photocatalytic activity of O_2 evolution from water [20]. A further investigation using BiOHCOO as the starting material found a material which displays totally different XRD patterns from Bi-BTC (Fig. 1), and the materials was denoted as BiO-BTC_{IE}. BiOHCOO is an important sillenite oxide possessing layered structure ($Bi_2O_2^{2+}$ layer and $HCOO^-$ layer). Anion exchange reaction between $HCOO^-$ and BTC is most likely to occur, which is a common phenomenon for these bismuth based sillenite compounds [32–35].

The following experiments further confirm the anion exchange reaction mentioned above. When the starting material was changed from BiOHCOO to $Bi_2O_2[NC_5H_3(CO_2)_2]$, almost identical XRD patterns to BiO-BTC_{IE} is observed (Fig. 2). The little difference of