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Two novel Bi-based oxychloride photocatalysts: Synthesis, optical property and visible-light-responsive photocatalytic activity

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ABSTRACT

Two novel visible-light-responsive bismuth oxychloride photocatalysts Bi_2EuO_4Cl and Bi_2NdO_4Cl have been successfully developed via a solid-state reaction route. Their crystal structures and optical properties were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM), diffuse reflectance spectra (DRS), and photoluminescence (PL) spectra. Fascinatingly, both the compounds possess considerable optical absorption in a broad region ranging from UV light to visible light. The indirect-transition optical band gaps of Bi_2EuO_4Cl and Bi_2NdO_4Cl are estimated to be 2.21 and 1.89 eV, respectively. For the first time, their photocatalytic activities were determined by photodecomposition of methylene blue (MB) in aqueous solution under visible light ($\lambda > 420$ nm). The results revealed that both Bi_2EuO_4Cl and Bi_2NdO_4Cl can be used as effective visible-light-driven photocatalysts. In addition, theoretical calculations on the electronic structure, orbital constitutions and optical absorption of Bi_2NdO_4Cl were also performed. These findings shed light on the exploration of new photocatalytic materials activated by visible light.

1. Introduction

Photocatalysis has attracted ever increasing attentions for its incomparable advantages such as unlimited resources, low cost, and environmental friendliness [1–5]. Now, it is regarded as one of the most promising solutions to the severe problems of environmental crises and energy shortages. Though TiO_2 offers a powerful oxidation in the treatment of organic contamiants, a great effort has still been made to develop new photocatalysts [6–9]. In particular, exploration of photocatalyst that responds to visible light is very meaningful for maximizing the utilization of solar spectrum.

Over decades, the research on bismuth compounds has been very active for their strong photooxidation ability [10–24]. These Bi-based photocatalysts, including Bi_2XO_6 (X=W and Mo) [10,11], BiOX (X=Cl, Br and I) [12,13], $BiVO_4$ [14], $BiPO_4$ [15], $Bi_2O_2CO_3$ [16], $BiIO_4$ [17,18], etc., all exhibit good performance in degradation of organic pollutants [19,20]. The high photocatalytic efficiency of Bi-containing compounds is mainly due to their unique layered crystal structure. The self-built internal electric fields derived from the layered structure are considered to facilitate the separation of charge carriers, which can subsequently induce redox reactions at the surface of semiconductors and contribute to the highly efficient photocatalytic activity [25]. Nevertheless, most of the reported Bi-based photocatalysts suffer from the drawbacks of insufficient photoabsorption in visible region. Thus, the development of new bismuth compounds as photocatalysts with visible-light response is highly desirable.

In this work, we for the first time report the visible-light-responsive photocatalytic activity of two rare-earth-containing bismuth compounds Bi_2EuO_4Cl and Bi_2NdO_4Cl. They are synthesized via a solid state reaction route and their microstructure and optical properties have been determined. The two compounds were found possessing a broad range of optical absorption. The photocatalytic performance of Bi_2EuO_4Cl and Bi_2NdO_4Cl was investigated by photodegradation of methyl blue (MB) under visible light irradiation ($\lambda > 420$ nm). Our preliminary experimental results indicated that Bi_2EuO_4Cl and Bi_2NdO_4Cl can be used as visible-light-active photocatalyst. To the best of our knowledge, this is the first investigation of photocatalytic activity of Bi_2EuO_4Cl and Bi_2NdO_4Cl.

2. Experimental

2.1. Synthesis of the photocatalysts

Bi_2EuO_4Cl and Bi_2NdO_4Cl samples were synthesized by a solid state reaction method. BiOCl, Bi_2O_3, Eu_2O_3 and Nd_2O_3 were used as

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the starting materials and BiOCl was prepared by a hydrolysis method. In a typical synthesis of BiOCl, a total of 0.01 mol Bi $(NO_3)_3 \cdot 5H_2O$ was dissolved in 20 ml ethanol. Then, the solution was added dropwise to 20 ml of aqueous solution containing 0.01 mol NaCl. The mixture was vigorously stirred for 5 h to ensure a complete reaction. After that, the products were filtered and dried at 80 °C in a vacuum oven. The as-prepared BiOCl, Bi_2O_3, Eu_2O_3 or Nd_2O_3 were mixed in stoichiometric proportions and ground in a mortar. After that, the well-mixed powders were calcined at 800 °C for 4 h, then grinded and calcined once again.

2.2. Characterization

X-ray diffraction(XRD) spectroscopy was performed on a Bruker D8 ADVANCE X-ray diffractometer with Cu Kα radiation. The morphology and microstructure of Bi_2EuO_4Cl and Bi_2NdO_4Cl products were observed with a S-4800 scanning electron microscope (SEM) and high-resolution transmission electron microscopy (HRTEM,JEM-2100). UV–vis diffuse reflectances pectra (DRS) of samples were performed by using a Varian Cary 5000 UV–vis spectrophotometer. Photoluminescence (PL) spectra were obtained on a fluorescence spectrophotometer (HITACHI, F-4600) an excitation wavelength of 300 nm at room temperature.

2.3. Photocatalytic measurement

Photocatalytic activities of BiOCl, Bi_2EuO_4Cl and Bi_2NdO_4Cl were evaluated by degradation of MB under visible light irradiation ($\lambda > 420$ nm, 300 W). 50 mg of photocatalyst was dispersed in an aqueous solution of MB (2^*10^{-5} M, 50 mL). Before illumination, the suspensions were magnetically stirred in the dark for 1 h to reach an absorption–desorption equilibrium between dye and photocatalyst. About 3 mL of the liquid was sampled at certain time intervals, and centrifuged to remove the particles. The concentration of MB was analyzed by recording the absorbance of MB on a Cary 5000 UV–vis spectrophotometer.

2.4. Theoretical calculation

The calculations of band structure, partial density of states and optical absorption were performed using CATSEP code [26]. Because of the strong correlation of f electrons of Nd and Eu ion, we adopt spin polarized LDA+U approach, the value of Hubbard U for the f electrons is 6.8 eV [27]. The ultrasoft pseudopotentials were implemented and the energy cutoff was set to be 500 eV. A density of $4 \times 4 \times 2$ Monkhorst–Pack k-point mesh in the Brillouin zone of the unit cell were used for the calculation of geometric optimization, and more k-points of $8 \times 8 \times 4$ were adopt to calculate the partial density of state and optical absorption.

3. Results and discussion

3.1. XRD analysis

Bi_2EuO_4Cl and Bi_2NdO_4Cl crystallize in the P4/mmm space group with the same tetragonal crystal structure [28]. Different from other layered bismuth compounds, the Bi-containing layers of Bi_2EuO_4Cl and Bi_2NdO_4Cl are $[Bi_2XO_4]^{2+}$ (X=Eu or Nd) instead of $[Bi_2O_2]^{2+}$ layers as depicted in Fig. 1. The $[Bi_2XO_4]^{2+}$ layers are composed of the double $[BiXO_2]^{2+}$ layers via sharing the X atom. The $[Bi_2XO_4]^{2+}$ layers and interbedded Cl^- ions are stacked through electrostatic interaction to form three-dimensional crystal structure. Fig. 2a and b shows the XRD patterns of as-prepared Bi_2EuO_4Cl and Bi_2NdO_4Cl samples, respectively. Their diffraction peaks all can be indexed into the tetragonal Bi_2EuO_4Cl (ICSD #92401) and Bi_2NdO_4Cl (ICSD #92399), indicating that the two target compounds have been successfully synthesized [28]. The sharp diffraction peaks are indicative of high crystallinity of the samples. Meanwhile no other peaks were found, suggesting the high purity of Bi_2EuO_4Cl and Bi_2NdO_4Cl products.

3.2. SEM analysis

The microstructure and surface morphologies of Bi_2EuO_4Cl and Bi_2NdO_4Cl were studied by a S-4800 scanning electron microscope (SEM). As shown in Fig. 3a and c, their products consist of irregular blocks with crystal sizes of 100–500 nm. The enlarged SEM images (Fig. 3b and d) demonstrated that Bi_2EuO_4Cl and Bi_2NdO_4Cl bulk crystals are stacked by many nanoplates with diameters of approximately 100–150 nm. The surface morphology observed here is in good accordance with their layered crystal configuration. Fig. 4 shows the high resolution transmission electron microscopy (HRTEM) image of Bi_2EuO_4Cl. The clear and uniform lattice fringes demonstrate the high crystallinity of crystals. The HRTEM image indicates the lattice fringe with a spacing of 0.274 nm, which can be indexed to (110) plane of Bi_2EuO_4Cl.

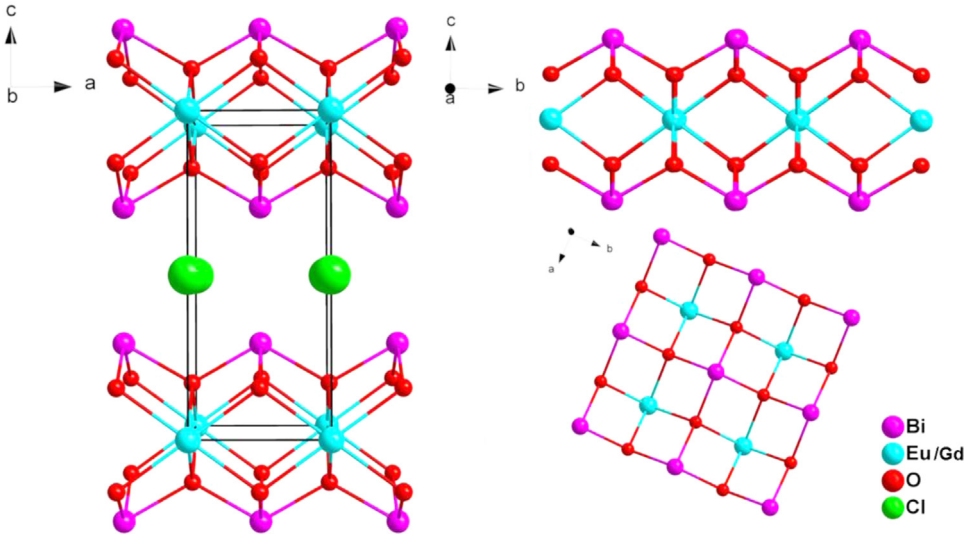

Fig. 1. Crystal structures of Bi_2Eu/NdO_4Cl.