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A novel Bi-based phosphomolybdate photocatalyst $K_2Bi(PO_4)(MoO_4)$: Crystal structure, electronic structure and photocatalytic activity

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ABSTRACT

A novel phosphomolybdate photocatalyst $K_2Bi(PO_4)(MoO_4)$ has been successfully developed via a solid-state reaction. The products were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), diffuse reflectance spectrum (DRS) and photoluminescence (PL) spectra. The photocatalytic activities of the samples prepared at different temperature were determined by the photooxidative decomposition of methylene blue (MB) in aqueous solution. The results revealed that $K_2Bi(PO_4)(MoO_4)$ can be used as an effective photocatalyst under UV–vis irradiation and the nanocubes obtained at 600 °C exhibits the highest photocatalytic activity. The photodegradation of MB by $K_2Bi(PO_4)(MoO_4)$ nanocrystals followed the first-order kinetics. Theoretical calculations on electronic structure confirmed the indirect optical transitions property in the absorption edge region of $K_2Bi(PO_4)(MoO_4)$, and the orbital constitutions of CB and VB were also analyzed.

1. Introduction

Photocatalysts have attracted much attention for counteracting environmental degradation over the past decades [1–5]. Until now, numerous photocatalysts have been discovered, including metal or non-metal ions doped TiO_2, metal oxides or metal sulfide semiconductors [6–9]. However, the known photocatalysts show many disadvantages, e.g. low photocatalytic-activity, instability, or toxicity. Thus, developing a new efficient photocatalyst is still a great challenge in the photocatalysis field so far [10].

Recently, bismuth compounds have received a lot of attentions for their high photocatalytic activities in the degradation of organic pollutants, including Bi_2O_3 with its heterojunctions [11,12], perovskite-structure $NaBiO_3$ and $BiFeO_3$ [13,14], Scheelite-structure $BiVO_4$ [15], pyrochlore-structure Bi_2MNbO_7 (M = Al, Ga, In, Fe and Sm) [16,17], Aurivillius structure Bi_2MoO_6, Bi_2WO_6, Bi_2GeO_5 and Bi_2SiO_5 [18–21], Sillén structures BiOX (X = Cl, Br, I) [22,23] and Sillén-Aurivillius structures Bi_4NbO_8Cl [24]. Especially, Bi_2MoO_6 and Bi_2WO_6 have been shown to be very promising photocatalysts under visible-light irradiation. Very recently, the nonmetal oxy-acid salts $BiPO_4$ [25] has been found possessing excellent photooxidation properties for decomposing organic contaminants under UV light. Thus, it is very meaningful to discover new Bi-based compounds as photocatalysts.

Herein, the phosphomolybdate $K_2Bi(PO_4)(MoO_4)$ was explored as a novel photocatalyst for the first time. Until now, only the crystal structure was reported [26]. In this work, $K_2Bi(PO_4)(MoO_4)$ nanocrystals were synthesized by a solid-state reaction. The crystal structure, micromorphology, and optical properties of the material were characterized. The photocatalytic activities of $K_2Bi(PO_4)(MoO_4)$ were investigated by the photodegradation for methylene blue (MB). The photodecomposition experiments demonstrated that $K_2Bi(PO_4)(MoO_4)$ can be used as an effective photocatalyst under UV–vis irradiation. The electronic structure of $K_2Bi(PO_4)(MoO_4)$ was also calculated.

2. Experimental

2.1. Preparation

$K_2Bi(PO_4)(MoO_4)$ were synthesized by a solid-state reaction, which is different from the flux method reported in Ref. [26]. All chemicals were used as received, without further purification. The raw materials of Bi_2O_3, K_2CO_3, $NH_4H_2PO_4$ and MoO_3 were mixed in stoichiometric proportions, then gradually elevated to sintering temperatures of 500 °C, 600 °C and 700 °C and kept at this temperature in air for 10 h. The calcination procedure was repeated another three times after grinding to ensure a complete reaction.

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2.2. Characterization

X-ray diffraction (XRD) spectroscopy was performed on a Bruker D8 ADVANCE X-ray diffractometer with Cu Kα radiation (λ = 1.5418 Å). The scanning step width of 0.02° and the scanning rate of 0.2 S^{-1} were applied to record the patterns in the 2θ range of 10–70°. The morphology and microstructure were obtained by a S-4800 scanning electron microscope (SEM) and a transmission electron microscopy (TEM and HRTEM; JEM-2100F). UV–vis spectra were performed with sample powder from PerkinElmer Lambda 35 UV–vis spectrometer. The spectra were collected at 200–1000 nm referenced to $BaSO_4$. Room temperature excitation and emission spectra were measured on a JOBIN 10 YVON FluoroMax-3 fluorescence spectrophotometer with a photomultiplier tube 11 operating at 400 V, and a 150 W Xe lamp was used as the excitation lamp.

2.3. Theoretical calculations

The electronic structure, as well as total and partial densities of states (DOS), of $K_2Bi(PO_4)(MoO_4)$ were obtained by the planewave pseudopotential method [27]. The calculations were carried out using the local density approximation (LDA) with a very high kinetic energy cutoff of 500 eV is adopted. The MonkhorstePack k-point [28] with a density of (2 × 2 × 2) points in the Brillouin zone of the unit cell is chosen.

2.4. Photocatalytic evaluation

Photocatalytic activities of $K_2Bi(PO_4)(MoO_4)$ at different sintering temperature were evaluated by degradation of methylene blue under ultraviolet light irradiation of an 300 W metal halide lamp. Powder photocatalyst (50 mg) was dispersed into 100 mL of dye solution (10^{-5} mol/L). Before illumination, the photocatalyst powder and dye solution were vigorously stirred in dark for 0.5 h to achieve the adsorption–desorption equilibrium of suspensions. After that, the light was turned on, and 2 mL of the suspension was taken at certain intervals and separated through centrifugation. The UV–vis spectra of the centrifuged solution were recorded using a U-3010 spectrophotometer.

3. Results and discussion

3.1. Characterization on structure of $K_2Bi(PO_4)(MoO_4)$

$K_2Bi(PO_4)(MoO_4)$ crystallizes in the orthorhombic space group Ibca, the crystal structure was shown in Fig. 1. It was constructed by PO_4 tetrahedra, MoO_4 tetrahedra and cations polyhedra. The XRD patterns in Fig. 2 were all in agreement with that from Inorganic Crystal Structure Database (ICSD) indicating that all the samples synthesized at different temperatures are pure. Compared with the products obtained at 500 °C and 700 °C, the sample synthesized at 600 °C exhibits the diffraction peaks with highest crystallinity.

The surface morphologies and particle sizes of $K_2Bi(PO_4)(MoO_4)$ at 500 °C, 600 °C and 700 °C were observed by SEM. Fig. 3a shows the products at 500 °C were in poor crystallinity, which may be due to the low sintering temperature. Whereas, the sample obtained at 700 °C coheres to make bulks as a result of excessive sintering shown in Fig. 3b. When the sintering temperature was 600 °C, the nano-cubes of $K_2Bi(PO_4)(MoO_4)$ were obtained. The dimension of these cubes was estimated to be 100 nm–1 μm, as illustrated in Fig. 3c and d.

Fig. 4 presented the TEM and HRTEM images of $K_2Bi(PO_4)(MoO_4)$ prepared at 600 °C. The low magnification TEM images in Fig. 4a and b show the nanoparticles distributed in aggregation. In Fig. 4c, the high-magnification HRTEM image obviously

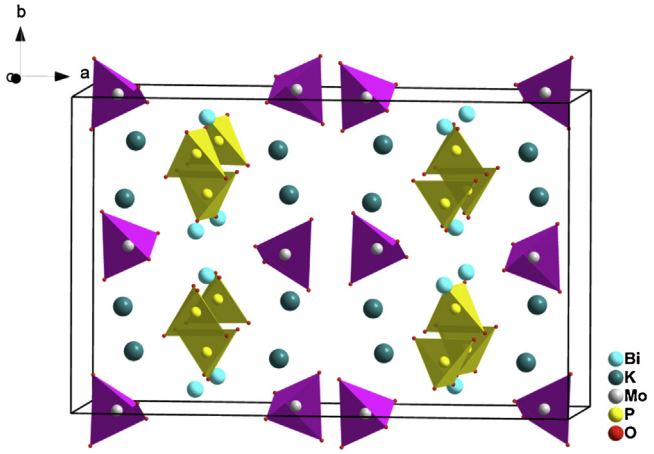

Fig. 1. Crystal structure of $K_2Bi(PO_4)(MoO_4)$.

demonstrated that the particle size of the $K_2Bi(PO_4)(MoO_4)$ nanocubes was about 100 nm. Meanwhile, the lattice resolved HRTEM image shown in Fig. 4d indicates that the spacing of the lattice is 0.262 nm, which is in agreement with the spacing of [341] crystallographic plane of $K_2Bi(PO_4)(MoO_4)$. It is apparent that the $K_2Bi(PO_4)(MoO_4)$ single crystals were successfully synthesized.

3.2. Optical properties

Fig. 5 displayed the diffuse reflectance absorption spectra (DRS) of the $K_2Bi(PO_4)(MoO_4)$ nano-crystals prepared at different temperature. In semiconductors, the square of absorption coefficient is linear with energy for direct optical transitions in the absorption edge region; whereas the square root of absorption coefficient is linear with energy for indirect transitions [22]. Data plots of absorption$^{1/2}$ vs. energy in the absorption edge region for $K_2Bi(PO_4)(MoO_4)$ shown in the inset of Fig. 5 is nearly linear, which indicate the absorption edge of $K_2Bi(PO_4)(MoO_4)$ is caused by indirect transitions. The samples synthesized at 500 °C, 600 °C and 700 °C almost possess the same band gap about 2.93 eV.

3.3. Photocatalytic activities

Fig. 6a showed the photocatalytic performance of the as-prepared samples evaluated by the degradation of MB. It can be

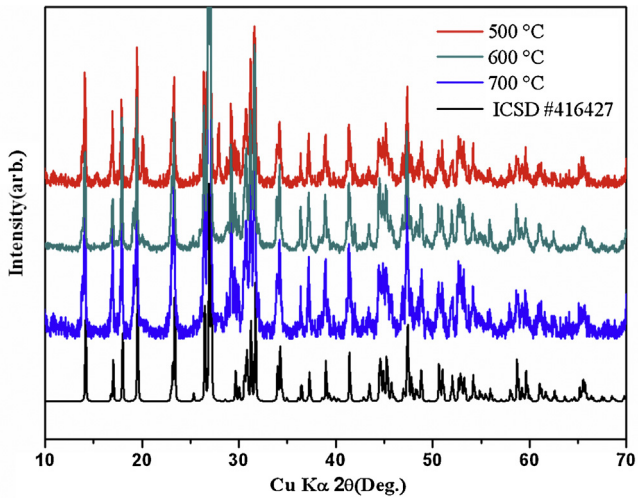

Fig. 2. XRD patterns of $K_2Bi(PO_4)(MoO_4)$ synthesized at different temperatures.