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Two Bi-based phosphate photocatalysts: Crystal structure, optical property and photocatalytic activity

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ABSTRACT

Two Bi-based phosphate photocatalytic materials $Na_3Bi_2(PO_4)_3$ and $Na_3Bi(PO_4)_2$ have been successfully synthesized by a solid-state reaction. Compared to $BiPO_4$ with band gap 3.77 eV, the introduction of Na_3PO_4 resulted in smaller band gaps of 3.6 and 3.01 eV for $Na_3Bi_2(PO_4)_3$ and $Na_3Bi(PO_4)_2$, respectively. The photocatalytic activities of the samples were determined by photooxidative decomposition of methylene blue (MB) in aqueous solution. The results revealed that both $Na_3Bi(PO_4)_2$ and $Na_3Bi_2(PO_4)_3$ can be used as effective photocatalysts under UV irradiation, and the former exhibits a higher photocatalytic activity compared to $BiPO_4$, which may be attributed to more light absorption in the UV range. It is a novel way to regulate the band-gaps of semiconductors and explore new photocatalytic materials.

Over decades, semiconductor photocatalysis as one of the most promising green chemical techniques attracted much attention for providing very potential applications for counteracting environmental degradation [1–3]. Nevertheless, developing a new efficient photocatalyst is still a great challenge in the photocatalysis field so far [4].

Among the vast explorations, the research on bismuth compounds as photocatalysts has been very active for their high photocatalytic activities [5]. In addition, the incorporation of alkali and alkalin-earth metals into Bi-based compound can effectively decrease the optical band gap. For instance, the band gaps of $Na_{0.5}Bi_{1.5}O_2Cl$ [6] and $CaBiO_2Cl$ [7] are 3.04 and 2.73 eV, which are smaller than that of BiOCl ($Eg = 3.44$ eV) [8]. Recently, the nonmetal oxy-acid salts $BiPO_4$ [9] has been found possessing excellent photooxidation properties for decomposing organic contaminants under UV light. It is mainly because that $(PO_4)^{3-}$ ions have a large negative charge which maintains a large dipole in these phosphates preferring the photogenerated charge separation. Thus, it is very meaningful to discover other Bi-based phosphate compounds as photocatalysts. Herein, two Bi-based phosphates $Na_3Bi_2(PO_4)_3$ and $Na_3Bi(PO_4)_2$ were synthesized by a solid-state reaction and explored as photocatalysts. The incorporation of Na_3PO_4 into $BiPO_4$ successfully resulted in the narrow band gaps in $Na_3Bi_2(PO_4)_3$ and $Na_3Bi(PO_4)_2$. The photocatalytic activities of $Na_3Bi_2(PO_4)_3$ and $Na_3Bi(PO_4)_2$ were investigated by the photodegradation for methylene blue (MB).

$Na_3Bi_2(PO_4)_3$ and $Na_3Bi(PO_4)_2$ were synthesized by a solid-state reaction from stoichiometric powder mixtures of Bi_2O_3, Na_2CO_3 and $NH_4H_2PO_4$. The starting materials were mixed in stoichiometric proportions, then gradually elevated to sintering temperatures of 650 °C and kept at this temperature in air for 20 h with several intermediate grindings. $BiPO_4$ samples as references were also synthesized by a similar solid-state reaction. Powder X-ray diffraction (XRD) investigations on the samples were carried out with a Bruker D8 advanced diffractometer. $Na_3Bi_2(PO_4)_3$ and $Na_3Bi(PO_4)_2$ crystallizes in the hexagonal space group *P63/m* and monoclinic space group *P2/c* [10], and their crystal structures of were shown in Fig. 1a and b, respectively. $BiPO_4$ crystallizes in the monoclinic space group P2/n, and the crystal structure of $BiPO_4$ was shown in Fig. S1. They all include the same PO_4 tetrahedra and BiO_n polyhedra. $Na_3Bi_2(PO_4)_3$ contains BiO_9 polyhedra. While in $Na_3Bi(PO_4)_2$ and $BiPO_4$, Bi atoms connect O atoms to form BiO_8 polyhedra. The different symmetry of crystal structures and coordination environment of Bi atoms may influence their photocatalytic activity. The XRD patterns of $Na_3Bi_2(PO_4)_3$ and $Na_3Bi(PO_4)_2$ show that the diffraction peaks can be indexed to the hexagonal $Na_3Bi_2(PO_4)_3$ (JCPDS #46-0251) and monoclinic $Na_3Bi(PO_4)_2$ (ICSD #71362), indicating that the two samples have been successfully synthesized (Fig. 1c and d, respectively). Meanwhile no other peaks are found, suggesting the high purity and crystallinity of the samples. The diffraction peaks of $BiPO_4$ can be indexed to the monoclinic phase (Fig. S2 in the Supporting information).

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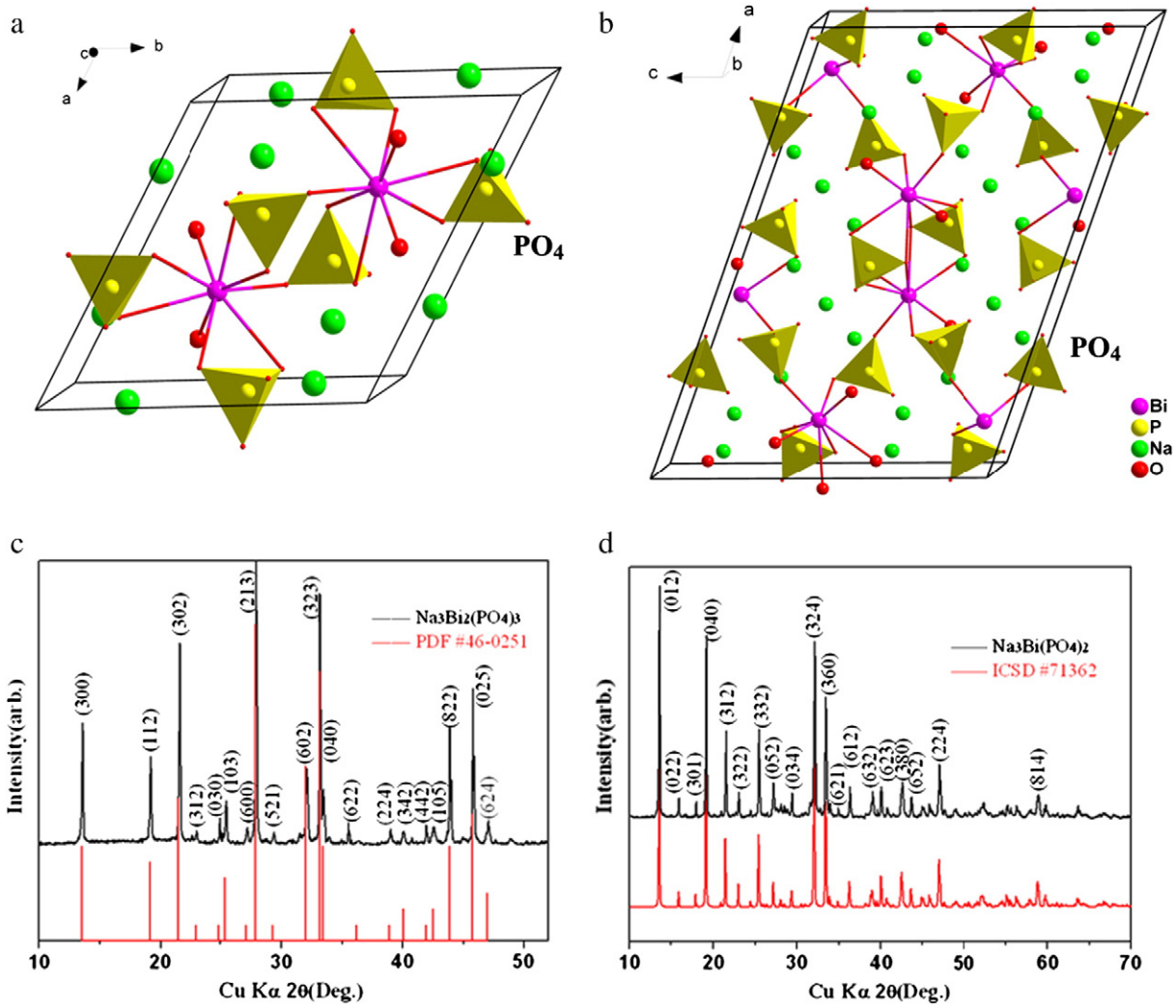

Fig. 1. Crystal structures of (a) $Na_3Bi_2(PO_4)_3$ and (b) $Na_3Bi(PO_4)_2$. XRD patterns of as-synthesized (c) $Na_3Bi_2(PO_4)_3$ and (d) $Na_3Bi(PO_4)_2$.

The surface morphologies and microstructures of $Na_3Bi_2(PO_4)_3$ and $Na_3Bi(PO_4)_2$ were studied by a S-4800 scanning electron microscope (SEM). Fig. 2a and c shows that the $Na_3Bi_2(PO_4)_3$ products were of block-like structures with particle size ranging from 1 μm to several micrometers. Different from the micro-cube morphologies of $Na_3Bi_2(PO_4)_3$, the samples of $Na_3Bi(PO_4)_2$ mainly consist of a large quantity of microsphere with average diameter of several hundreds nanometers as shown in Fig. 2b and d.

UV–vis diffuse reflectance spectra (DRS) of $Na_3Bi_2(PO_4)_3$ and $Na_3Bi(PO_4)_2$ samples were performed using a PerkinElmer Lambda 35 UV–vis spectrometer. It is found that the DRS spectra of $Na_3Bi_2(PO_4)_3$ and $Na_3Bi(PO_4)_2$ samples possessed steep edges in the profile, indicating that the visible light absorption was not caused by the transition from the impurity level but was due to the band gap transition [11] (see Fig. 3a). Data plots of absorption versus energy in the absorption edge region were shown in the inset of Fig. 3a. By extrapolating the straight line to the x-axis in this plot, the Eg of $Na_3Bi_2(PO_4)_3$ and $Na_3Bi(PO_4)_2$ were estimated to be 3.60 and 3.01 eV, respectively. Here, the design for Bi-based phosphate with narrow band gap was realized (Fig. 3b). Through the incorporation of Na_3PO_4 into $BiPO_4$, the band gap was gradually decreased from 3.77, 3.6 to 3.01 eV for $BiPO_4$, $Na_3Bi_2(PO_4)_3$ and $Na_3Bi(PO_4)_2$, respectively.

Photocatalytic activities were evaluated by degradation of MB solution (10^{-5} mol/L) under ultraviolet light (300 W high-pressure mercury lamp). Before illumination, the suspension was vigorously stirred in dark to achieve the adsorption–desorption equilibrium. At certain intervals of 10 min, about 2 mL of suspension was taken out, centrifuged and analyzed by a U-3010 spectrophotometer. It can be obviously seen that MB are almost photodecomposed catalyzed by $Na_3Bi(PO_4)_2$, $BiPO_4$ and $Na_3Bi_2(PO_4)_3$ in 40, 50 and 60 min, respectively (Fig. 4a). MB photolysis without the photocatalyst can almost be neglected. In order to compare the degradation rate quantitatively, the first order kinetics curves (Fig. 4b) were also plotted [12]. The experimental data show that the apparent rate constant k is 0.0596 min^{-1}, 0.0508 min^{-1} and 0.0361 min^{-1} for $Na_3Bi(PO_4)_2$, $BiPO_4$ and $Na_3Bi_2(PO_4)_3$ respectively. Thus, the photocatalytic activity of $Na_3Bi_2(PO_4)_3$ and $Na_3Bi(PO_4)_2$ is 1.17 and 0.71 times that of $BiPO_4$. Compared with $BiPO_4$, the relatively high photocatalytic activity of $Na_3Bi(PO_4)_2$ may be attributed to the more light absorption in the UV range.

In the current work, two Bi-based phosphate photocatalysts $Na_3Bi_2(PO_4)_3$ and $Na_3Bi(PO_4)_2$ were successfully developed by a solid-state reaction. The as-prepared products were of high purity and composed of a large number of micro-cubes and micro-spheres, respectively. Compared to $BiPO_4$ with band gap 3.77 eV, the band gaps of