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Hydrothermal Synthesis and Photocatalytic Property of 2-Dimensional Bismuth Molybdate Nanoplates

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Bi_2MoO_6 nanoplates with an Aurivillius structure and a uniform thickness of 15–30 nm were fabricated by a hydrothermal process at 413 K for 48 h with the assistance of the surfactant cetyltrimethylammonium bromide (CTAB). The nanoplate structure was favorable to the photocatalytic O_2-evolution performance under visible light irradiation.

In recent years, nanoscale materials, especially low-dimensional inorganic semiconductor materials have attracted great interest because of their size-dependent optical and electronic properties and potential applications in nanoscale electronics and photonics.[1] The preparation of nanoscale photocatalysts is also of great interest, because nanomaterials offer a high surface-to-volume ratio and short distance from bulk to surface, which are favored for the migration of electrons and holes, and this property reduces the probability of recombination of photogenerated electrons and holes.[2] However, nanomaterials of ternary compounds have not been extensively reported.

Bismuth molybdates are interesting, not only as materials for their catalytic applications on selective oxidation and ammoxidation of lower olefins,[3–6] but also because of their unique physical properties with other potential technological applications, e.g., as ionic conductors,[7,8] acousto-optical materials,[9–11] photoconductors,[12] and gas sensors.[13] Bismuth molybdate was also developed to be a visible-light responsive photocatalyst.[14,15] Thus, if nanoscale bismuth molybdate can be fabricated successfully, it will provide an attractive candidate for these potential applications.

Bismuth molybdates exist in three different crystallographic phases: α-$Bi_2Mo_3O_{12}$, β-$Bi_2Mo_2O_9$, and γ-Bi_2MoO_6,[16] and each phase exhibits different properties. The phase that shows a highly selective oxidation property is generally α-$Bi_2Mo_3O_{12}$, while γ-Bi_2MoO_6, with an Aurivillius structure, shows photocatalytic activity for O_2 evolution under visible-light irradiation.[15] Various processes have been developed to prepare bismuth molybdates. However, hydrothermal synthesis of γ-Bi_2MoO_6 with the Aurivillius structure is limited.[17] In this paper, we report the successful fabrication of uniform Bi_2MoO_6 nanoplates with an Aurivillius structure via a hydrothermal process with the assistance of the surfactant CTAB. Their photophysical and photocatalytic properties were studied.

All chemicals were analytical grade and were used as received, without further purification. In a typical procedure, CTAB was added into 17.9 mL of 0.1 mol L^{-1} aqueous $(NH_4)_6Mo_7O_{24}$ (Kanto, 99.0%) solution and magnetically stirred until a homogeneous gel was formed. To control the shape of the products, the concentrations of CTAB were adjusted to 0, 0.25, and 0.5 mol L^{-1}. Subsequently, 16.6 mL of 1.5 mol L^{-1} of $Bi(NO_3)_3{\cdot}5H_2O$ (Kanto, 99.0%) in a 2.0 mol L^{-1} HNO_3 solution was added dropwise into the molybdate solution under stirring. The pH of the mixture was adjusted to 8.0 with an aqueous ammonia solution. After further stirring for half an hour, the mixture was transferred into a Teflon-lined stainless autoclave and maintained at 413 K for 48 h. The products were filtered off, washed several times with distilled water and absolute ethanol, and finally dried at room temperature.

X-ray powder diffraction (XRD) patterns were measured with an X-ray diffractometer with Cu Kα radiation (Rigaku; MiniFlex). Field-emission scanning electron microscopic (FE-SEM) images were obtained with a JEOL JSM-6700F electron microscope. Diffuse reflection spectra were obtained with a UV–vis–NIR spectrometer (JASCO: Ubest V-570) and were converted from reflection to absorption by the Kubelka–Munk method. The photocatalytic properties were investigated by O_2 evolution from an aqueous $AgNO_3$ solution (0.05 mol L^{-1}) under visible light irradiation (Kenko, L-42 ($\lambda > 420$ nm)). The amount of evolved O_2 was determined by gas chromatography (Shimadzu GC-8A, TCD, Ar carrier). After the samples were calcined at 823 K for 5 h in air, they were used as photocatalysts.

The XRD patterns of samples synthesized hydrothermally and by a solid-state process are shown in Figure 1. The positions of all diffraction peaks in the four samples agreed well and were indexed to γ-Bi_2MoO_6 with the Aurivillius structure. This result indicates that the present hydrothermal conditions used in the synthesis (pH 8, 413 K) are favorable for the crystallization of Bi_2MoO_6 in this structure. However, differences in the intensities and peak widths of several diffraction peaks among the sam-

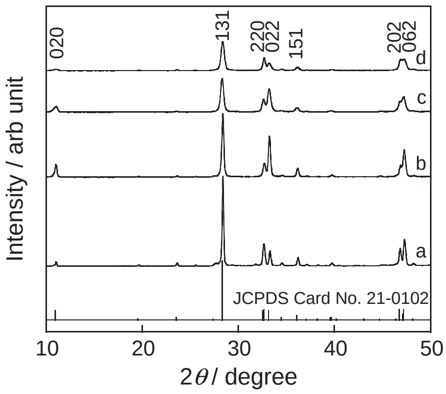

Figure 1. X-ray diffraction patterns of JCPDS Card No. 21-0102; (a) Bi_2MoO_6 prepared by a solid-state reaction at 823 K for 5 h; (b)–(d) hydrothermally synthesized Bi_2MoO_6 with the presence of 0, 0.25, and 0.5 mol L^{-1} of CTAB, respectively.

ples were observed. The solid-state-prepared sample showed the narrowest, most intense peak for the (131) plane among the samples, while the hydrothermally synthesized samples showed broad, low intensity peaks. This observation suggests that the crystallinity and microstructure of the materials were different from one another.

Figure 2 shows typical FE-SEM images of Bi_2MoO_6 samples prepared by the solid-state reaction and the hydrothermal process. The solid-state-prepared Bi_2MoO_6 consisted of large irregular particles up to 500 nm (Figure 2a). The hydrothermally synthesized Bi_2MoO_6 exhibited platelet-shaped particles, even in the absence of CTAB. Bi_2MoO_6 samples hydrothermally synthesized by Beale et al.[17] also showed platelet-like particles. In the absence of CTAB, the particles obtained were not uniform, and the thickness of most particles was larger than 100 nm. However, the presence of CTAB in the synthesis significantly improved the uniformity of the plate structure and decreased the plate thickness. As shown in Figure 2c, the presence of a low concentration CTAB led to the formation of nanoplate-structured Bi_2MoO_6. As the concentration of CTAB was increased to 0.5 mol L^{-1}, the uniformity of the nanoplates was further improved, and a great number of platelet-type crystals with uniform thickness, particle size, and high aspect ratio were observed, as shown in Figure 2d. The typical thickness of the plate was in the range of 15–30 nm. Thus, it can be concluded that uniform Bi_2MoO_6 nanoplates were able to be synthesized hydrothermally with the assistance of the CTAB surfactant. The surfactant would form lamellar micelles at a certain concentration, and the bismuth and molybdate species were intercalated between the lamellar structures. Under hydrothermal conditions, the inorganic species would form bismuth molybdate nanoplates with a high aspect ratio.

Table 1 lists the band gaps, surface areas, and photocatalytic activities of the calcined Bi_2MoO_6 samples. An increase in the bandgap with the formation of platelet structure was observed. The nanoplate-structured catalyst prepared in the absence of CTAB (HT-0) gave a higher activity than that of bulk Bi_2MoO_6 prepared by the solid-state method (SS), indicating that the nanoplate-structured Bi_2MoO_6 was more active than the bulk sample, because of the short migration distance of electrons and holes to the surface, resulting in the low probability of recombination. Furthermore, the highly uniform nanoplates (HT-0.5) exhibited a higher activity than the less-uniform Bi_2MoO_6 (HT-0.25). However, the samples synthesized in the presence of CTAB gave lower activities than that synthesized in the absence of CTAB. This observation might be explained by the low crystallinity and the wide band gap of the former sample.

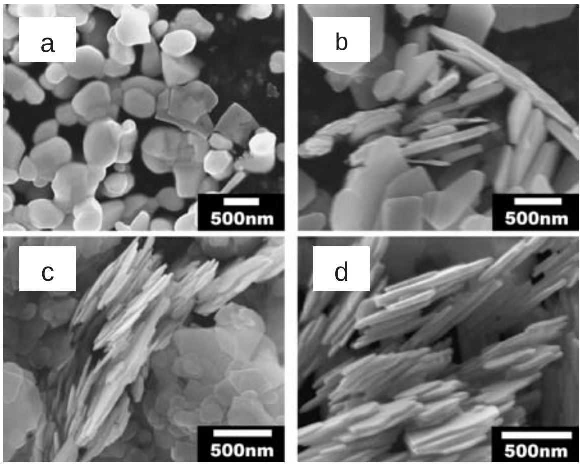

Figure 2. FE-SEM images of (a) Bi_2MoO_6 prepared by a solid-state reaction at 823 K for 5 h; (b)–(d) hydrothermally synthesized Bi_2MoO_6 with the presence of 0, 0.25, and 0.5 mol L^{-1} of CTAB, respectively.

Table 1. The physical parameters of Bi_2MoO_6 and the photocatalytic activities for oxygen evolution from an aqueous $AgNO_3$ solution under visible light irradiation

Samples[a]	Band gap/ eV	Surface area/ $m^2\,g^{-1}$	Activity[b]/ $\mu mol\cdot h^{-1}$
SS	2.64	2.3	11
HT–0	2.70	3.5	15
HT–0.25	2.74	4.2	2
HT–0.5	2.80	5.4	6

[a] SS: Bi_2MoO_6 prepared by a solid-state reaction; HT: Hydrothermally synthesized Bi_2MoO_6, the followed numbers denoted the concentration of CTAB used. [b] Catalyst: 0.2 g, light $\geq$ 420 nm, 0.05 mol L^{-1} $AgNO_3$: 150 mL.

In summary, bismuth molybdate nanoplates were synthesized successfully via a hydrothermal process with the assistance of a surfactant. The synthesized nanoplates were active for photocatalytic O_2 evolution.

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