

A Novel Aqueous Process for Preparation of Crystal Form-Controlled and Highly Crystalline BiVO₄ Powder from Layered Vanadates at Room Temperature and Its Photocatalytic and Photophysical Properties

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Received July 19, 1999

Abstract: BiVO₄ photocatalysts for O₂ evolution, which work under visible light irradiation, were prepared by an aqueous process. The BiVO₄ photocatalysts were obtained by the reaction of layered potassium vanadate powder (KV₃O₈ and K₃V₅O₁₄) with Bi(NO₃)₃ for 3 days in aqueous media at room temperature. Highly crystalline monoclinic and tetragonal BiVO₄ were selectively synthesized by changing the ratio of vanadium to bismuth in the starting materials. X-ray diffraction and scanning electron microscopy measurements showed that the monoclinic BiVO₄ was formed via a tetragonal BiVO₄ intermediate. Tetragonal BiVO₄ with a 2.9 eV band gap mainly possessed an ultraviolet absorption band while monoclinic BiVO₄ with a 2.4 eV band gap had a characteristic visible light absorption band in addition to the UV band. The UV bands observed in the tetragonal and monoclinic BiVO₄ were assigned to the band transition from O_{2p} to V_{3d} whereas the visible light absorption was due to the transition from a valence band formed by Bi_{6s} or a hybrid orbital of Bi_{6s} and O_{2p} to a conduction band of V_{3d}. The photocatalytic activity for O₂ evolution from an aqueous silver nitrate solution under UV irradiation (300 < λ < 380 nm) on the tetragonal BiVO₄ was comparable to that on the monoclinic BiVO₄. The monoclinic BiVO₄ also showed the high photocatalytic activity for the O₂ evolution under visible light irradiation (λ > 420 nm). When the monoclinic BiVO₄ was calcined at 700–800 K the activity was increased. The activity of this monoclinic BiVO₄ was much higher than that of BiVO₄ prepared by a conventional solid-state reaction. The quantum yield at 450 nm for the O₂ evolution on the monoclinic BiVO₄ was 9%.

Introduction

Water splitting by photocatalysts is important from the viewpoint of artificial photosynthesis. When semiconductor photocatalysts are used, it is thermodynamically indispensable that the conduction band level be more negative than the reduction potential of H₂O to form H₂ and that the valence band level is more positive than the oxidation potential of H₂O to form O₂ as shown in Figure 1a. The following wide band gap photocatalysts have been reported to be highly active for splitting water into H₂ and O₂ in stoichiometric amounts under UV irradiation: TiO₂ loaded with Pt,^{1–3} Rh,⁴ and NiO,⁵ SrTiO₃ loaded with Rh⁶ and NiO,⁷ ZrO₂,⁸ NiO/K₄Nb₆O₁₇,⁹ NiO/K₂-

La₂Ti₃O₁₀,¹⁰ NiO/Ta₂O₅,¹¹ RuO₂/Na₂Ti₆O₁₃,¹² RuO₂/BaTi₄O₉,¹³ NiO/K₃Ta₃Si₂O₁₃,¹⁴ some tantalates (NiO/BaTa₂O₆,^{15a} NiO/NaTaO₃,^{15b} NiO/SrTa₂O₆,^{15c} NiO/Sr₂Ta₂O₇,^{15d} etc.), and NiO/

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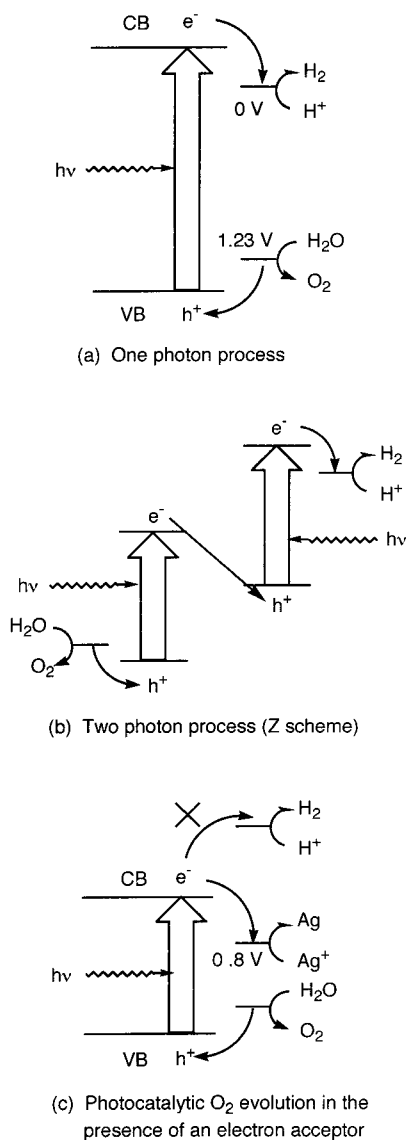


Figure 1. Schemes of water splitting on semiconductor photocatalysts: (a) one-photon process, (b); two-photon process (Z scheme), (c); and O₂ evolution in the presence of electron acceptors.

Sr₂Nb₂O₇.^{15d,16} Among them, about 30% quantum yields have been obtained for the water splitting on pretreated NiO/K₂La₂-Ti₃O₁₀ photocatalysts in an aqueous KOH solution (0.1 mol/L)^{10c} and on nontreated NiO/NaTaO₃ photocatalysts in pure water.^{15b} ZrO₂ also shows very high activities in aqueous NaHCO₃ solutions.⁸ However, these photocatalysts are active only under UV irradiation. Photocatalysts which work under visible light irradiation have to be developed to use solar light. Photocatalysts which can efficiently split water into H₂ and O₂ under visible light irradiation by the one-photon excitation process as shown in Figure 1a have not been found so far. Water-splitting systems by the two-photon excitation process (Z scheme) as shown in Figure 1b have also been studied¹⁷ but have not been successful using only visible-light-driven photocatalysts. To construct the Z scheme, first of all, new visible-light-driven photocatalysts, which may possess the ability for either H₂ or O₂ production from aqueous solutions, have to be developed. Aqueous solutions containing reducing reagents such

as alcohol and sulfide ions (electron donors) are often used as test reactions for the photocatalytic H₂ evolution while those containing oxidizing reagents such as Ag⁺ (electron acceptors) are employed for testing the photocatalytic O₂ evolution reaction. For example, the photocatalytic O₂ evolution is thermodynamically possible if the valence band level is more positive than the oxidation potential of H₂O to form O₂, and the conduction band level is more negative than the reduction potential of not H⁺ but Ag⁺ as shown in Figure 1c. It can be checked by the reaction in the presence of electron acceptors if a photocatalyst possesses an activity for O₂ evolution. Even in the presence of such a sacrificial reagent, the only well-known photocatalyst that is active for H₂ evolution under visible light irradiation is Pt/CdS.^{18,19} One of the authors has reported that CuS–ZnS solid solution photocatalysts are also active for H₂ evolution under visible light irradiation in aqueous K₂SO₃ solutions.²⁰ On the other hand, WO₃^{18,19,21–23} is a well-known photocatalyst that is active for O₂ evolution under visible light irradiation in the presence of electron acceptors such as Ag⁺ and Fe³⁺. The authors have reported that BiVO₄ prepared by the solid-state reaction of NH₄VO₃ with Bi₂O₃ showed photocatalytic activity for O₂ evolution from an aqueous silver nitrate solution under visible light irradiation.²⁴ The quantum yield at 450 nm was 0.5%. The band gap of the BiVO₄ photocatalyst is 2.3–2.4 eV, which is smaller than that of the WO₃ photocatalysts (2.8 eV). This indicates that BiVO₄ can absorb visible light more widely than WO₃. Therefore, BiVO₄ is a candidate for an O₂ evolution photocatalyst to construct the Z scheme.

BiVO₄ has attracted attention as a ferroelastic material.^{25–39} Its acoustooptical^{27,28} and ion conductive²⁹ properties have also

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been studied. These properties strongly depend on the crystal form. The main crystal forms of BiVO₄ are monoclinic (distorted sheelite structure, fergusonite structure) (1), tetragonal (zircon type structure) (2), and tetragonal (sheelite structure) (3).^{26,30} The phase transition from (2) to (1) irreversibly occurs at 670–770 K. The phase transition is also observed at room temperature by crushing the powder.³⁴ The phase transition between (1) and (3) reversibly occurs at 528 K. The transition between ferroelastic and paraelastic is induced by the phase transition. The transition has extensively been studied in detail by EPR, NMR, Raman, XRD, neutron diffraction, etc.^{37–39} Thus, BiVO₄ is an interesting material and is expected to be applied for uses such as catalysts. Moreover, studying the relationship of some of the properties between monoclinic and tetragonal BiVO₄ is of interest.

Some synthesis methods for BiVO₄ have been reported. Monoclinic BiVO₄ is obtained by solid state and melting reactions at high temperature.^{26,40,41} Tetragonal BiVO₄ (2) is prepared by a precipitation method from a Bi(NO₃)₃ nitric acid solution and an aqueous NH₄VO₃ solution at room temperature.^{34,42} Thus, monoclinic BiVO₄ is usually obtained by the high-temperature process while tetragonal BiVO₄ with a zircon-type structure is prepared in aqueous media by the low-temperature process. Monoclinic BiVO₄ is also prepared by an alkoxide method at 400 K.²⁹ Thus, the obtained crystal form depends on the preparation method. It will be of interest if the preparation method controlling the crystal forms under mild conditions is developed.

Environmentally friendly aqueous processes have received much attention.⁴³ This is the process in which materials are synthesized under mild conditions in nonharmful solvents such as water. Biocomposites such as bone and shells are produced by this process.⁴⁴ This process is applied to the syntheses of metastable compounds in aqueous solutions and the fabrication of thin films of various single-crystal compounds.^{45–47} Layered compounds can produce various host–guest compounds by intercalation reactions.^{48,49} Such a host–guest compound is obtained under mild conditions in aqueous media when ion-exchangeable layered compounds are employed. For example, the epitaxial growth of thin films of layered compounds has been studied.^{50,51} Thus, layered compounds are expected to be important starting materials for the aqueous process.

In the present paper, the preparation of visible-light-driven BiVO₄ photocatalysts with high activities by the aqueous process using layered compounds was explored. The photophysical and photocatalytic properties of tetragonal and monoclinic BiVO₄ prepared by the aqueous process were discussed based on the band structure.

Experimental Section

Preparation of Layered Alkali Vanadates.^{52–56} Layered alkali vanadates used as starting materials were prepared by solid-state

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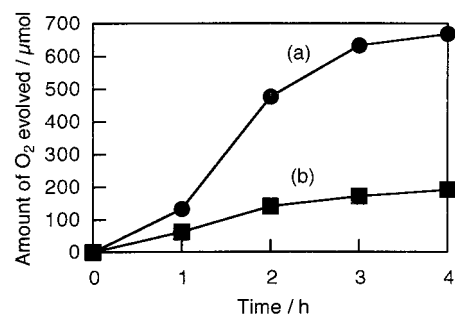


Figure 2. Photocatalytic O₂ evolution from aqueous AgNO₃ solutions (0.05 mol/L, 300 mL) under visible light irradiation ($\lambda > 420$ nm) on (a) BiVO₄ synthesized from K₃V₅O₁₄ and (b) WO₃.

reactions. KV₃O₈ and K₃V₅O₁₄ were obtained by the calcination of K₂CO₃ (Kanto Chemical, purity; 99.5%) and V₂O₅ (Wako Pure Chemical, purity; 99.0%) in air at 730 K for 10 h and 720 K for 5 h, respectively. CsV₃O₈ and Cs₂V₄O₁₁ were prepared by the calcination of Cs₂CO₃ (Kanto Chemical, purity; 99.99%) and V₂O₅ in air at 600 K for 10 h.

BiVO₄ Syntheses by Aqueous Processes. BiVO₄ powder was synthesized by merely stirring vanadate powder and Bi(NO₃)₃·5H₂O powder (Kanto Chemical, purity; 99.9%, Bi(NO₃)₃·5H₂O reacts with water to form slightly soluble BiONO₃) as a dispersion in water (ca. 50 mL) at room temperature for 3 days. The ratio of vanadium to bismuth in the starting materials was varied and the samples were calcined in air at various temperatures for 10 h.

Characterization. Products were identified by X-ray diffraction (Rigaku, RINT-1400) and scanning electron microscopy (Hitachi, S-5000). Surface areas were determined by BET measurement (Coulter, SA3100). Diffuse reflection spectra were obtained using a UV–vis–NIR spectrometer (JASCO, Ubest-570) and were converted from reflection to absorbance by the Kubelka–Munk method. Luminescence spectra were measured using a fluorospectrometer (Spex, Fluoromax).

Photocatalytic Reactions. The photocatalytic O₂ evolution from an aqueous silver nitrate solution was carried out in a closed gas circulation system. The photocatalytic activity of BiVO₄ was compared with that of WO₃ powder (Nacalai tesque, purity; 99.5%) which is a well-known photocatalyst working under visible light irradiation. The catalyst powder (1 g) was dispersed by a magnetic stirrer in an aqueous AgNO₃ solution (0.05 mol/L, 300 mL) in a reaction cell made of a Pyrex glass. The light source was an ozone-free 300 W Xe illuminator (CERMAX, LX300). Cutoff and band pass filters (Kenko, L42 ($\lambda > 420$ nm) and U34 ($280 < \lambda < 380$ nm)) were employed for the visible and UV irradiations, respectively. The quantum yield at 450 nm was determined using a band pass filter (half width: 11.5 nm) by chemical actinometry employing ammonium ferrioxalate.

$$\text{quantum yield (\%)} = \frac{\text{number of O}_2 \text{ molecules evolved} \times 4}{100 / (\text{amount of incident photons})} \quad (1)$$

The amount of evolved O₂ was determined using a gas chromatograph (Shimadzu, GC-8A, TCD, Ar carrier).

Results and Discussion

Crystal Forms and Photocatalytic Activities of BiVO₄ Prepared from Various Vanadates at Different Ratios of Vanadium to Bismuth in the Starting Material. Figure 2 shows typical time courses for the photocatalytic O₂ evolution from aqueous silver nitrate solutions under visible light irradiation on monoclinic BiVO₄ and commercial WO₃. In this

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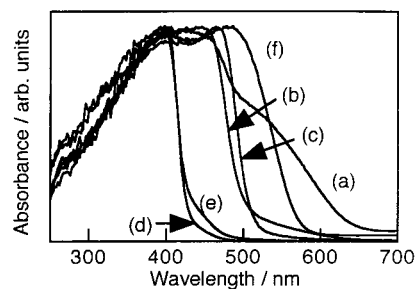
Table 1. Photocatalytic O₂ Evolution from Aqueous AgNO₃ Solutions (0.05 mol/L, 300 mL) under Visible Light Irradiation ($\lambda > 420$ nm) and the Crystal Form of BiVO₄ Synthesized by the Aqueous Process at Room Temperature from Vanadates

starting materials of V	V:Bi in preparation	crystal form	rate of O ₂ evol, $\mu\text{mol/h}$
K ₃ V ₅ O ₁₄	3:3	monoclinic	421
K ₃ V ₅ O ₁₄	3:4	tetragonal	8.4
KV ₃ O ₈	3:1	monoclinic + tetragonal + KV ₃ O ₈	10
KV ₃ O ₈	3:2	monoclinic	46
KV ₃ O ₈	3:3	monoclinic	382
KV ₃ O ₈	3:4	tetragonal	17
KV ₃ O ₈	3:5	tetragonal	2.5
CsV ₃ O ₈	3:3	monoclinic	145
Cs ₂ V ₄ O ₁₁	3:3	tetragonal	16
V ₂ O ₅	3:3	monoclinic	97

reaction, the rate of O₂ evolution decreased with the reaction time because metallic silver was deposited on the surface to shield incident light by the reaction, although induction periods were observed during the initial stage. Therefore, the fastest O₂ evolution rate was regarded as the activity. The activity of the monoclinic BiVO₄ was much higher than that of the commercial WO₃, which is a well-known photocatalyst for the O₂ evolution reaction under visible light irradiation. This is due to the smaller band gap of monoclinic BiVO₄ and the high quantum yield as mentioned below. Table 1 shows the photocatalytic activities for O₂ evolution from aqueous silver nitrate solutions under visible light irradiation and the crystal forms of BiVO₄ prepared by the reactions of some vanadates with Bi(NO₃)₃ at different ratios of vanadium to bismuth in the starting material in aqueous media at room temperature. BiVO₄ powder was formed from the dispersion of the starting materials by such a simple procedure. When the ratio of vanadium to bismuth in the starting material was 3:3, only BiVO₄ prepared from Cs₂V₄O₁₁ was tetragonal (hereafter, tetragonal represents a tetragonal phase (2) with a zircon-type structure). Other prepared BiVO₄ had monoclinic forms.

Next, the BiVO₄ powders prepared from KV₃O₈ and K₃V₅O₁₄ were examined in detail. When the ratio was 3:3, monoclinic phases were formed in both cases. The monoclinic BiVO₄ possessed a high photocatalytic activity under visible light irradiation as shown in Table 1. Although the monoclinic BiVO₄ was also obtained at a 3:2 ratio for KV₃O₈, the activity was not very high. On the other hand, tetragonal phases were obtained when excess amounts of bismuth (3:4 and 3:5) were used. The photocatalytic activity of the tetragonal BiVO₄ was low. When the amount of bismuth was too small (3:1 for KV₃O₈), the reaction was not completed and the mixture was obtained.

Diffuse reflectance spectra of BiVO₄ prepared from KV₃O₈ at different ratios of vanadium to bismuth in the starting material are shown in Figure 3. Tetragonal BiVO₄ was pale yellow and the band gap was estimated to be 2.9 eV from the absorption edge (Figures 3d and 3e). The band gap of monoclinic BiVO₄ was 2.4 eV and the color was vivid yellow (Figures 3b and 3c). In the spectrum of monoclinic BiVO₄, a characteristic absorption band was observed in a visible light region in addition to the UV band observed in tetragonal BiVO₄. The absorption edge of monoclinic BiVO₄ prepared at a 3:3 ratio of vanadium to bismuth was more distinct than that at 3:2. Although KV₃O₈ also possessed an absorption band in the visible region, it did not show any photocatalytic activity. The high photocatalytic activity of monoclinic BiVO₄ as shown in Table 1 was attributed to the characteristic absorption band in the visible light region. When K₃V₅O₁₄ was used as a starting material, similar results on the effects of the V:Bi ratio were obtained.

**Figure 3.** Diffuse reflectance spectra of BiVO₄ synthesized from KV₃O₈ at different ratios of vanadium to bismuth in the starting materials: V:Bi = 3:1 (a), 3:2 (b), 3:3 (c), 3:4 (d), 3:5 (e), and KV₃O₈ (f).

The same UV bands were observed in tetragonal and monoclinic BiVO₄. Therefore, the photocatalytic activities for the O₂ evolution under UV irradiation (300 < λ < 380 nm) were tested. The activity of tetragonal BiVO₄ was similar to that of monoclinic BiVO₄ (ca. 50 $\mu\text{mol/h}$), suggesting that their UV bands are due to the same transition.

Scanning electron microscope photographs of BiVO₄ prepared from KV₃O₈ at different ratios of vanadium to bismuth in the starting material are shown in Figure 4. KV₃O₈ of the starting material was a layered crystal with more than a 10 μm particle size (Figure 4a). When BiVO₄ was prepared at a 3:3 ratio, highly crystalline monoclinic BiVO₄ powder with a plate form was obtained (Figure 4b). The high crystallinity was also confirmed by the XRD measurements. The particle size (ca. 1–2 μm) was much smaller than that of the starting material. Crystal growth in which a small plate dug in a base plate was also observed. On the other hand, highly crystalline tetragonal BiVO₄ powder (ca. 500 nm) was formed (Figure 4c) when the ratio was 3:4. Similar SEM images were also observed when tetragonal and monoclinic BiVO₄ were prepared from K₃V₅O₁₄. These particles seemed to be close to single crystals. Although monoclinic BiVO₄ with a plate form was formed even from V₂O₅, the photocatalytic activity was lower than that from KV₃O₈ and K₃V₅O₁₄ as shown in Table 1. Many defect cracks which can be recombination centers between photogenerated electrons and holes were observed on the BiVO₄ particles prepared from V₂O₅ by SEM and seemed to decrease the photocatalytic activity.

As mentioned above, it was found that tetragonal and monoclinic BiVO₄ were selectively prepared by changing the ratio of vanadium to bismuth in the starting material in the present aqueous process at room temperature. The high crystallinity of the BiVO₄ powder was confirmed by SEM and XRD. Monoclinic BiVO₄ prepared at a 3:3 ratio possessed a steep absorption edge and showed a high photocatalytic activity under visible light irradiation.

The Formation Process of Monoclinic BiVO₄ with a High Photocatalytic Activity. The X-ray diffraction of products obtained after different reaction times was measured as shown in Figure 5 to investigate the formation process. KV₃O₈ was used as the starting material. An XRD pattern of Bi(NO₃)₃·5H₂O treated with water was also shown because Bi(NO₃)₃·5H₂O was hydrolyzed to form slightly soluble BiO(NO₃). Only patterns of KV₃O₈ and Bi(NO₃)₃·5H₂O treated with water of the starting materials were observed after 5 h. The pattern of tetragonal BiVO₄ became visible after 15 h. The pattern had grown after 24 h. The intensities of the patterns of the starting materials began to decrease and monoclinic BiVO₄ was observed in addition to tetragonal BiVO₄ after 36 h. The pattern of monoclinic BiVO₄ became predominant and the patterns of the starting materials disappeared after 40 h. Only the pattern of

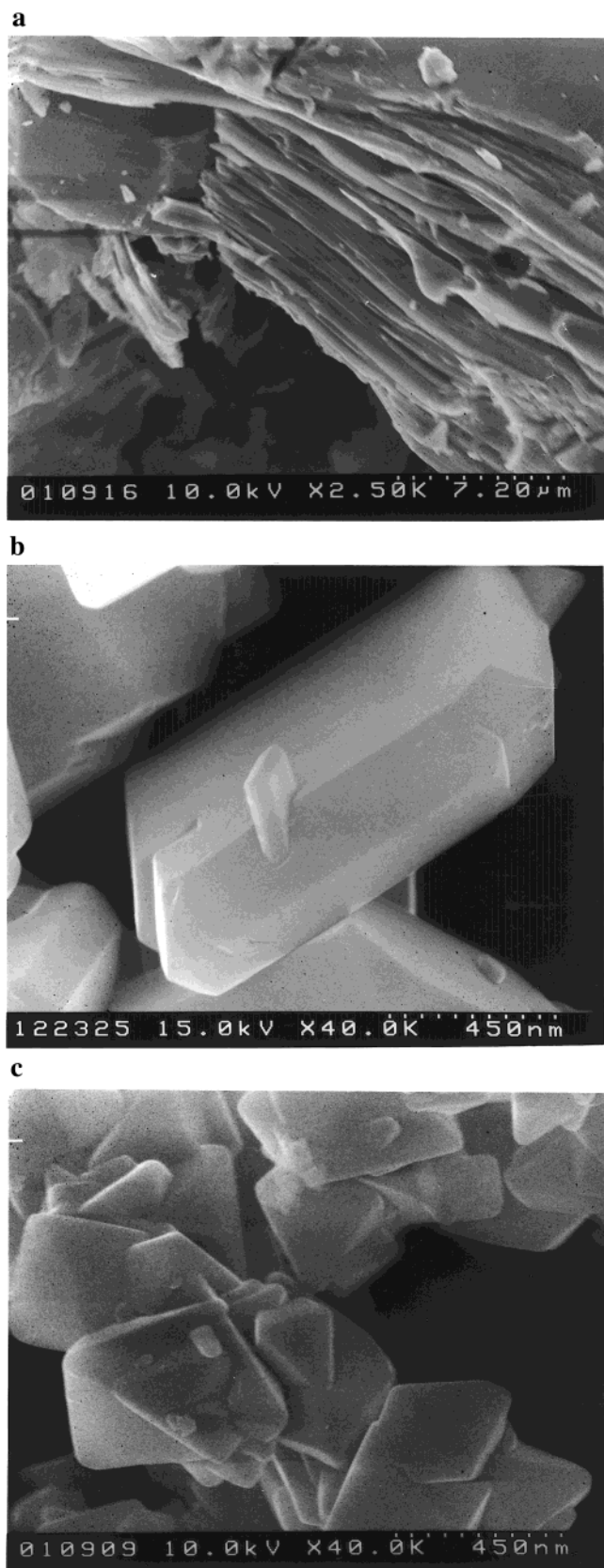


Figure 4. SEM photographs of (a) KV_3O_8 and (b) monoclinic and (c) tetragonal BiVO_4 synthesized at different ratios of vanadium to bismuth in the starting materials: V:Bi = 3:3 (b) and 3:4 (c).

monoclinic BiVO_4 was finally obtained after 72 h. Thus, tetragonal BiVO_4 was unexpectedly formed during the first stage and then it was converted to the monoclinic phase. Next, this process was investigated by SEM as shown in Figure 6. The

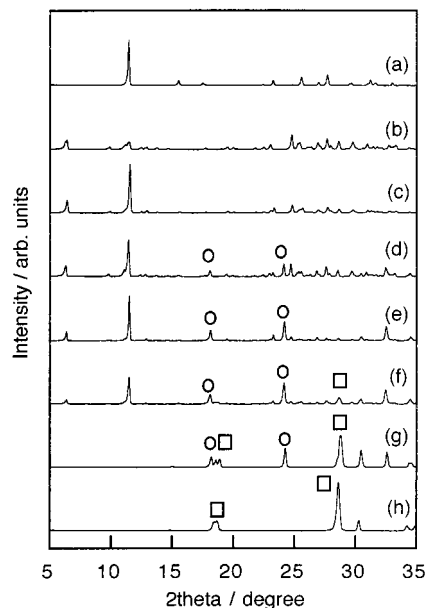


Figure 5. XRD patterns of products prepared from KV_3O_8 and $\text{Bi}(\text{NO}_3)_3$ at different preparation times under preparation conditions of the monoclinic BiVO_4 (V:Bi = 1:1): (a) KV_3O_8 , (b) $\text{Bi}(\text{NO}_3)_3$ treated with water, (c) after 5, (d) 15, (e) 24, (f) 36, (g) 40, and (h) 72 h. Circles and squares indicate the representative peaks of the tetragonal and monoclinic forms of BiVO_4 , respectively.

starting material was the layered crystal as shown in Figure 4a. KV_3O_8 crystals with the large particle size of the starting material and fine crystals were observed after 24 h (Figure 6a). Fine crystals attached on the external surface of the layered crystal were observed after 36 h (Figure 6b). The reaction of KV_3O_8 with $\text{Bi}(\text{NO}_3)_3$ (or BiO^+) seemed to also proceed at the interlayers because the layers of KV_3O_8 were divided into sections. The shapes of the fine crystals observed in Figures 6a and 6b were the same as that of tetragonal BiVO_4 as shown in Figure 4c. Only fine crystals were observed after 40 h (Figure 6c). Most fine crystals were monoclinic with a plate structure. A small amount of tetragonal BiVO_4 was observed in addition to the monoclinic BiVO_4 crystals in the aggregations. The aggregations finally came apart to form the grown monoclinic BiVO_4 crystals as shown in Figure 4b. These SEM observations agreed well with the results of the XRD measurements.

Next, let us consider the factors affecting the selectivity of the tetragonal and monoclinic BiVO_4 formation. The XRD and SEM results raise the question that tetragonal BiVO_4 prepared at a 3:4 ratio may also be converted to the monoclinic form if the preparation time was prolonged. Moreover, the phase transition from tetragonal to monoclinic occurs by mechanical stirring as has been previously reported.³⁴ However, the tetragonal BiVO_4 did not convert to monoclinic even after two weeks, indicating that the effects of the preparation time and stirring were neglected for the monoclinic BiVO_4 formation. Under the condition in which the tetragonal BiVO_4 was formed, insufficient vanadium was provided for the stoichiometric conversion to BiVO_4 . The insufficient amount of layered potassium vanadate was added to the reactant in which tetragonal BiVO_4 and excess $\text{Bi}(\text{NO}_3)_3$ were present. However, the reaction did not lead to the monoclinic BiVO_4 formation. Thus, layered potassium vanadates and $\text{Bi}(\text{NO}_3)_3$ have to be added at the beginning in a 1:1 ratio to obtain the monoclinic BiVO_4 powder. The effects of the preparation temperature of BiVO_4 on the crystal form and the preparation time were also examined. When the preparation was carried out at 340 K for

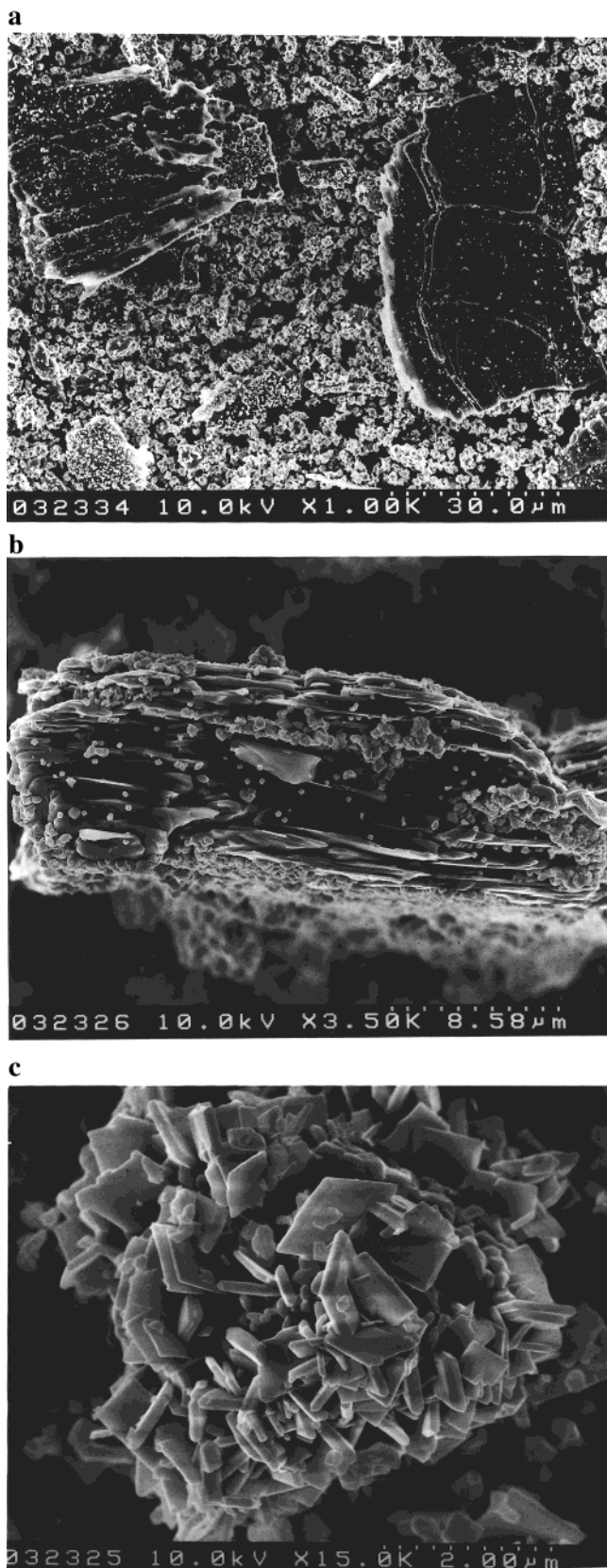


Figure 6. SEM photographs of products prepared from KV_3O_8 and $\text{Bi}(\text{NO}_3)_3$ at different preparation times under preparation conditions of the monoclinic BiVO_4 (V:Bi = 1:1): (a) 24, (b) 36, and (c) 40 h.

4 days under the conditions of the monoclinic formation, a pure monoclinic phase was not obtained. Moreover, the preparation time for the BiVO_4 formation was not shortened by increasing the temperature. Thus, the selectivity was sensitive to the

Table 2. Effects of Calcination Temperature on the BET Surface Areas, the Crystal Forms, and the Photocatalytic Activities of Originally Tetragonal and Monoclinic BiVO_4 Synthesized from $\text{K}_3\text{V}_5\text{O}_{14}$

calcination temp, K	surface area, m^2/g		crystal form mon./ (tetr. + mon.) ^a	rate of O_2 evol. ^b $\mu\text{mol}/\text{h}$	
	tetr.	mon.	tetr.	tetr.	mon.
298	6.3	2.4	0	4.4	344
373		2.2			350
473		2.3			288
623	4.5	1.9	0.02	9.7	397
673	3.2	1.9	0.02	7.6	478
723	2.4	1.7	0.92	25	471
748	2.0		1.00	31	
773	1.6	1.4	1.00	21	461
873		1.0			250
973		0.5			56

^a Determined from the intensity of XRD patterns. ^b From aqueous AgNO_3 solutions (0.05 mol/L, 300 mL) under visible light irradiation ($\lambda > 420$ nm).

temperature. The monoclinic formation seems to be suppressed by an increase in the BiO^+ concentration with an increase in temperature. The highly crystalline monoclinic BiVO_4 is produced under a low concentration of BiO^+ . These effects of temperature and the ratio of starting material suggest that the concentration of BiO^+ is an important factor for the selectivity. The excess BiO^+ might suppress the conversion to monoclinic by the adsorption on the tetragonal BiVO_4 crystals. On the other hand, the pH of the solution for the tetragonal and monoclinic BiVO_4 preparation was 0.7–0.8 due to the hydrolyses of $\text{Bi}(\text{NO}_3)_3$ in both cases, suggesting that pH was not a major factor for the selectivity in the present system.

It is considered as a formation process that vanadate layers with negative charges react with BiO^+ slightly dissolved in water to form BiVO_4 . The interaction of the BiO^+ cation with vanadate sheets of KV_3O_8 and $\text{K}_3\text{V}_5\text{O}_{14}$ must be stronger than that with V_2O_5 because of the electrostatic force. This is probably the reason the crystallinity of BiVO_4 prepared from the layered vanadates was higher than that from V_2O_5 .

Effects of Calcination Temperature on the Photocatalytic Activity, Crystal Form, and Surface Area of BiVO_4 Prepared from $\text{K}_3\text{V}_5\text{O}_{14}$. Table 2 shows the effect of calcination temperature on the BET surface areas, the crystal forms, and photocatalytic activities of the tetragonal and monoclinic BiVO_4 prepared from $\text{K}_3\text{V}_5\text{O}_{14}$. The surface areas were monotonically decreased with an increase in the calcination temperature. The surface area of monoclinic BiVO_4 dried at 330 K was lower than that of the tetragonal BiVO_4 . This is reasonable because the particle size of the tetragonal BiVO_4 was smaller than that of the monoclinic BiVO_4 as shown in Figure 4. The surface area of the tetragonal BiVO_4 suddenly decreased near phase transition temperature (around 700 K) and became similar to that of the monoclinic BiVO_4 . This suggests that the particles of the tetragonal BiVO_4 were sintered and grown during the phase transition from the tetragonal to monoclinic forms.

The phase transition of the tetragonal BiVO_4 was also confirmed by the diffuse reflection spectra as shown in Figure 7, as well as the XRD measurements. The absorption spectra of the originally tetragonal BiVO_4 calcined at 770 and 1170 K consisted of a characteristic absorption band in the visible light region indicating the monoclinic formation. The spectrum of monoclinic BiVO_4 calcined at the high temperature of 1170 K had a tail at the absorption edge. This tailing was also observed for BiVO_4 prepared by a solid-state reaction at 970 K.²⁴ It suggests the formation of surface states and impurity levels.

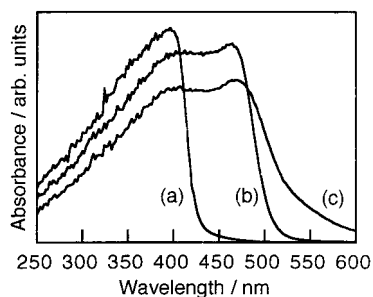


Figure 7. Diffuse reflectance spectra of BiVO_4 (originally tetragonal form synthesized from $\text{K}_3\text{V}_5\text{O}_{14}$) calcined at different temperatures: (a) 330, (b) 770, and (c) 1170 K.

The photocatalytic activity of the tetragonal BiVO_4 was drastically increased with the phase transition. The temperature dependence on the photocatalytic activity of the tetragonal BiVO_4 was different from that on the surface area. It indicated that the crystal phase predominantly affects the photocatalytic activity rather than the surface area. However, the activity of the monoclinic BiVO_4 obtained by the phase transition from the tetragonal form was low (20–30 $\mu\text{mol/h}$) and almost the same as that of the monoclinic BiVO_4 obtained by a solid-state reaction.²⁴

Although the monoclinic BiVO_4 showed a high photocatalytic activity even without calcination, the activity was slightly increased by the calcination around 670–770 K as shown in Table 2. This is probably due to a decrease in the defects by the annealing. This monoclinic BiVO_4 efficiently produced O_2 from an aqueous silver nitrate solution even using monochromatic light at 450 nm (ca. 100 $\mu\text{mol/h}$). The quantum yield was 9% which was much higher than that of BiVO_4 prepared by a solid-state reaction (0.5%).²⁴ The activity was drastically decreased by the calcination at temperatures higher than 870 K. The melting point of BiVO_4 is around 1213 K.⁴⁰ Moreover, the vanadium and bismuth oxides are easily volatilized at high temperatures resulting in the formation of defects. The defect formation suggested by the tailing in the diffuse reflectance spectra as shown in Figure 7 decreased the photocatalytic activity because the defects work as recombination sites of photogenerated electrons with holes. The decrease in the surface area was another factor decreasing the photocatalytic activity. The calcination temperature dependence of the photocatalytic activity of the tetragonal and monoclinic BiVO_4 prepared from KV_3O_8 was similar to that from $\text{K}_3\text{V}_5\text{O}_{14}$.

The activity of the monoclinic BiVO_4 obtained from the monoclinic form by calcination at 770 K was 1 order of magnitude higher than that obtained from similar calcination of the tetragonal BiVO_4 . SEM measurements were carried out to clarify the factor as shown in Figure 8. In the monoclinic BiVO_4 obtained from the tetragonal form by calcination, although the primary particles still had small sizes, they were significantly sintered to each other (Figure 8a). This was also suggested by a sharp decrease in the BET surface area as shown in Table 2. In contrast, the crystallinity of the monoclinic BiVO_4 calcined at 770 K (Figure 8b) was still as high as that of the noncalcined monoclinic BiVO_4 (Figure 4b). Significant sintering was not observed. In general, the higher the crystallinity, the higher the photocatalytic activity, because recombination between photogenerated electrons and holes is suppressed in highly crystalline photocatalysts. The low crystallinity of the monoclinic BiVO_4 obtained from the tetragonal form by calcination is the reason its photocatalytic activity was low.

It is noteworthy that obtaining the highly crystalline powder without the significant formation of defects and decreasing the

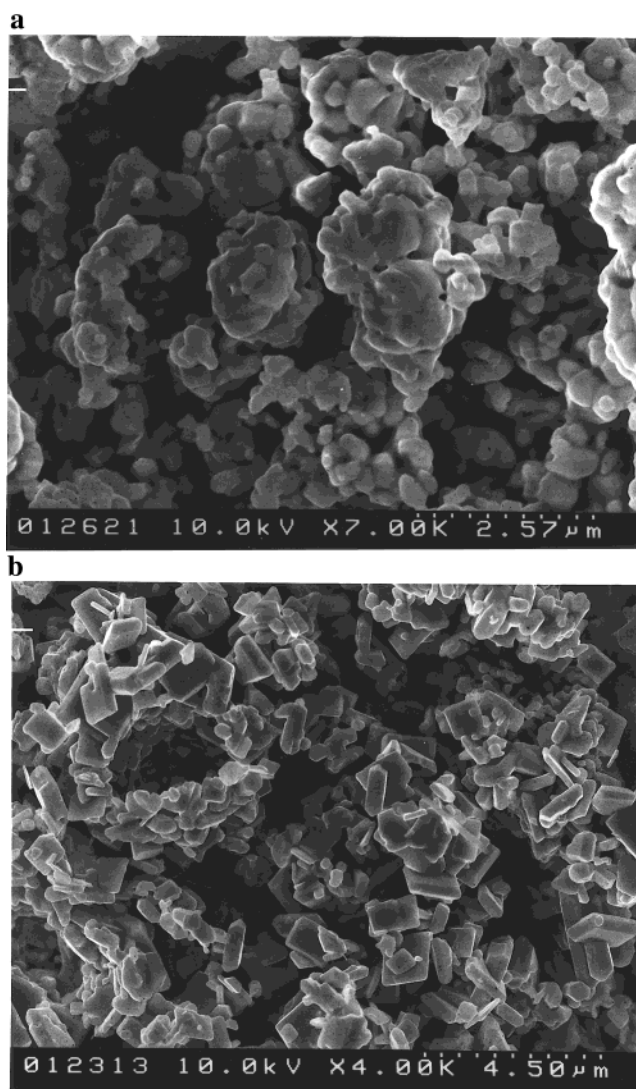


Figure 8. SEM photographs of monoclinic BiVO_4 obtained from (a) tetragonal and (b) monoclinic BiVO_4 (from $\text{K}_3\text{V}_5\text{O}_{14}$) by calcination at 770 K.

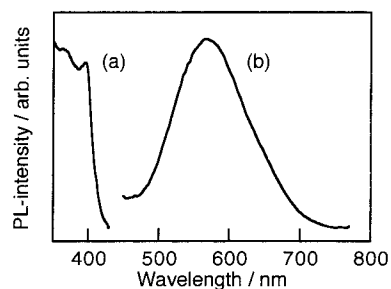


Figure 9. (a) Excitation and (b) emission spectra at 77 K of tetragonal BiVO_4 synthesized from $\text{K}_3\text{V}_5\text{O}_{14}$ at room temperature.

surface area by the aqueous process at room temperature led to the development of a highly active photocatalyst working under visible light irradiation. It was shown that the aqueous process is especially advantageous for the preparation of materials in which defects are easily formed by volatilization at high temperatures.

Energy Structure of Tetragonal and Monoclinic BiVO_4

Tetragonal BiVO_4 showed photoluminescence at 77 K as shown in Figure 9. The excitation spectrum agreed with the diffuse reflectance spectrum. In contrast, monoclinic BiVO_4 did not show luminescence at 77 K even if the UV and VIS bands were

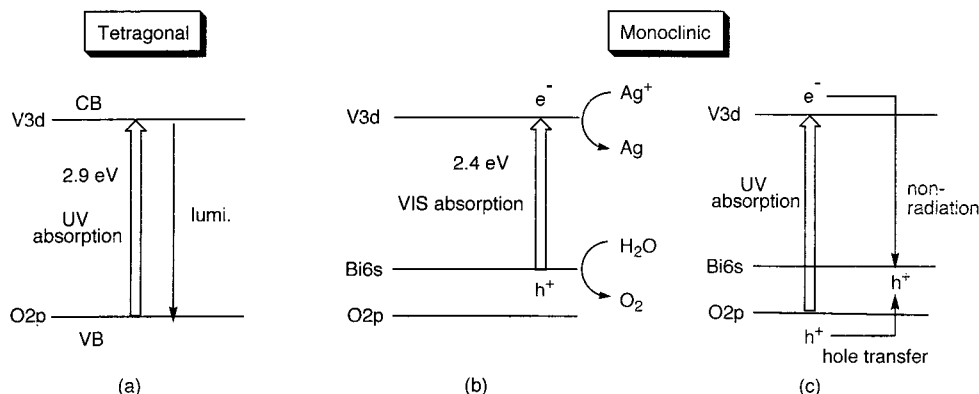


Figure 10. Band structures of the tetragonal and monoclinic BiVO_4 .

excited. It was concluded from the photocatalytic activity that the transition of the UV band of the tetragonal BiVO_4 should be the same as that of the monoclinic BiVO_4 . Despite this, the emission property of the monoclinic BiVO_4 was different from that of the tetragonal BiVO_4 .

The transition of 6s electrons of Bi^{3+} often contributes to luminescence of the phosphor consisting of bismuth.^{57–59} Ghamri and co-workers have investigated the absorption spectra of $\text{Bi}_x\text{Ln}_{1-x}\text{VO}_4$ ($\text{Ln} = \text{Eu}$ and Gd) in detail.⁶⁰ $\text{Bi}_x\text{Ln}_{1-x}\text{VO}_4$ possesses a tetragonal form in the case of $0 < x < 0.60$ while it is monoclinic for $0.94 < x < 1$. In this system, the absorption of the monoclinic form is observed at longer wavelengths than that of the tetragonal one as well as in the present BiVO_4 system. The absorption of the tetragonal one is due to the charge-transfer transition between vanadium and oxygen in VO_4^{3-} . In the monoclinic phase, the transition of the 6s electrons of Bi^{3+} to the empty 3d orbitals of V^{5+} becomes possible. Such a transition has been also observed in the BiNbO_4 and BiTaO_4 phosphors.⁵⁹ This transition due to the 6s electrons usually occurs at a lower energy than the charge-transfer transition in VO_4^{3-} . Therefore, the characteristic absorption band observed for the monoclinic BiVO_4 is assigned to the band transition from a 6s valence band of bismuth to a 3d conduction band of vanadium. Based on the facts mentioned above, the band structures of the tetragonal and monoclinic BiVO_4 are described as shown in Figure 10. The valence bands may be formed by not only Bi_{6s} but also O_{2p} , namely a hybrid orbital of Bi_{6s} and O_{2p} . In the tetragonal BiVO_4 , only the UV absorption band due to the V–O transition was observed, and it contributed to the photoluminescence at 77 K and the photocatalytic property (Figure 10a). In contrast, monoclinic BiVO_4 possesses at least two absorption bands in the UV and VIS regions. The absorption band in the visible light region contributed to the photocatalytic activity (Figure 10b). However, photoluminescence was not observed by the VIS band excitation even at 77 K. On the other hand, the UV band transition in the monoclinic BiVO_4 is similar to that in the tetragonal BiVO_4 because the shape of the diffuse reflectance spectra in the UV region (Figures 3 and 7) and photocatalytic activity under UV irradiation of the monoclinic BiVO_4 are similar to those of the tetragonal BiVO_4 (Figures 10a and 10c). If the relaxation process of the excitation state formed by the

UV band excitation in the monoclinic BiVO_4 is the same as that in the tetragonal BiVO_4 , a photoluminescence similar to the tetragonal BiVO_4 would be observed for the monoclinic BiVO_4 . However, it was not observed. This result suggests that the excitation energy (electron–hole pairs) transfers to the quenching centers. The energy transfer process probably occurs as follows: the hole formed in the O_{2p} band by photoexcitation transfers to the Bi_{6s} valence band in which recombination between electrons and holes does not give luminescence at 77 K (Figure 10c).

In oxide semiconductors, the conduction band levels of small band gap semiconductors are usually low because the deep valence bands are formed by O_{2p} .⁶¹ This is a major problem for developing visible-light-driven and stable oxide photocatalysts. To find a breakthrough, it is indispensable to control the valence band with orbitals of some elements instead of O_{2p} . Bismuth is a candidate for such a valence-band-control element. Bismuth usually exists as Bi^{3+} in BiVO_4 . When the Bi^{3+} ions form a valence band, holes formed by photoexcitation are regarded as Bi^{5+} (or Bi^{4+}). Although a redox potential in an aqueous solution is different from that in solids, a standard redox potential of $\text{Bi}_2\text{O}_3/\text{BiO}^+$ ($\text{Bi}^{\text{V}}/\text{Bi}^{\text{III}}$) ($E^\circ = +1.59$ V at pH 0)⁶² could make sense for a rough estimation of the oxidation potential of holes (Bi^{5+}) photogenerated in the BiVO_4 photocatalyst. In monoclinic BiVO_4 , the potential of the valence band of Bi_{6s} is more negative than that of O_{2p} and, moreover, is sufficient to oxidize water to form O_2 judging from the experimental results. It is reasonable because the standard redox potential of $\text{Bi}^{\text{V}}/\text{Bi}^{\text{III}}$ is more positive than that of $\text{O}_2/\text{H}_2\text{O}$ (+1.23 V at pH 0). The valence band control by the Bi_{6s} or hybrid $\text{Bi}_{6s}\text{--O}_{2p}$ orbitals is expected to provide information for the development of visible-light-driven photocatalysts.

Conclusion

A simple aqueous process at room temperature was developed for the BiVO_4 synthesis. Tetragonal and monoclinic BiVO_4 were selectively obtained only by changing the ratio of vanadium to bismuth in the starting materials. It was shown by the results of the calcination temperature dependence on the photocatalytic activity and the comparison with BiVO_4 prepared by a solid state reaction at high temperature that the aqueous process is especially advantageous for the preparation of materials which consist of easily volatilized components at high temperature. By the present method, the calcination temperature dependence of the properties of monoclinic BiVO_4 , which was usually

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obtained by high-temperature processes, was able to be examined from room temperature to high temperature. This examination led us to the development of photocatalysts which showed a high activity for the O₂ evolution reaction under visible light irradiation. This fact makes us expect the possibility that other visible-light-driven photocatalysts may be found by developing new synthesis methods. The visible light absorption band was attributed to the band transition from the Bi_{6s} or hybrid Bi_{6s}–O_{2p} orbitals to V_{3d} based on the reports of the photophysical properties of other compounds consisting of bismuth. One of the ways for the valence band control to develop visible-light-

driven photocatalysts seems to be indicated by applying the Bi_{6s} transition.

Acknowledgment. This work was supported by New Energy and Industrial Technology Development Organization (NEDO)/Research Institute of Innovative Technology for the Earth (RITE), Core Research for Evolutional Science and Technology (CREST), and a Grant-in-Aid (No. 11640601) from the Ministry of Education, Science, Sports, and Culture, Japan.

JA992541Y