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Flux Growth and Characterization of Layered $K_4Nb_6O_{17}$ Crystals

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Well-formed crystals of potassium hexaniobate ($K_4Nb_6O_{17}$) were successfully grown from potassium molybdate and tungstate fluxes. The crystal growth of $K_4Nb_6O_{17}$ was conducted by heating a mixture of solute and flux at 1100 °C for 10 h, followed by cooling to 500 °C at a rate of 5 °C/h^{-1}. Colorless and transparent crystals having sizes up to 18 × 9.0 × 2.9 mm were grown from high-temperature solutions containing solute of 1−60 mol %. The crystal sizes were dependent on the solute concentration. The basic form was a plate bounded by the well-developed {010}, {110}, and {021} faces. Potassium, niobium, and oxygen were almost homogeneously distributed in the crystals. Furthermore, the grown $K_4Nb_6O_{17}$ crystals exhibited a high activity for the dye adsorption and degradation. The degradation occurred via the photocatalytic process under ultraviolet light irradiation.

Introduction

Semiconductor photocatalysts have attracted much attention due to their potential applications in various industrial fields. In particular, they have been studied for the conversion of photon energy into chemical energy because of their applications such as splitting of water, degradation of toxic substances, and several types of solar cells.[1−4] Among various semiconductor photocatalysts, titanium(IV) oxide (TiO_2) has been widely researched due to the high activity and stability of TiO_2 and high photoinduction under ultraviolet (UV) light.[4] In recent years, a variety of metal oxides such as titanates, niobates, tantalites, and multi oxides have also been found to exhibit photocatalytic activity. In general, these metal oxides are synthesized via a conventional solid-state reaction or melt growth at high temperatures in excess of their melting points. These methods are not environmentally friendly. Most products synthesized by these methods have good crystallinity but low surface areas.

Concerning potassium hexaniobate ($K_4Nb_6O_{17}$) prepared by solid-state reaction of a mixture of K_2CO_3 and Nb_2O_5 at 1200 °C, it was reported as an effective photocatalyst in 1986.[1a] The crystals of $K_4Nb_6O_{17}$ belong to the orthorhombic system (layered structure).[5] The congruent melting point of this compound is 1163 °C.[5] The single crystals of $K_4Nb_6O_{17}$ have been grown in the K_2CO_3−Nb_2O_5 system.[6] However, detailed results such as the optimal growth conditions, crystal structure, size, and photocatalytic activity have not been described.[6] In our previous studies, a tantalate was grown from a $Na_2Mo_2O_7$ flux.[7] In this work, K_2MoO_4 and K_2WO_4 were chosen as fluxes to grow $K_4Nb_6O_{17}$ crystals on the basis of our experiences in growing the tantalate. Potassium dimolybdates and tungstates have a common cation (K^+) with the solute and a low melting point with sufficient solubility in water. No report on the growth of $K_4Nb_6O_{17}$ crystals from the K_2MoO_4 and K_2WO_4 fluxes has been published. The present paper describes the growth of $K_4Nb_6O_{17}$ crystals from K_2MoO_4 and K_2WO_4 fluxes by a slow cooling method and the examination of their morphology. Furthermore, their photocatalytic and adsorption properties were also evaluated.

Experimental Section

Growth of $K_4Nb_6O_{17}$ Crystals. The reagent-grade K_2CO_3, Nb_2O_5, and MoO_3 were used for the growth of $K_4Nb_6O_{17}$ crystals. A stoichiometric mixture of reagent-grade K_2CO_3 (Wako Pure Chemical Industries, Ltd.) and Nb_2O_5 (Wako Pure Chemical Industries, Ltd.) powders was used as a solute. Mixtures of K_2CO_3 + MoO_3 (Allied Materials, Co., Ltd.) or K_2CO_3 + WO_3 (Allied Materials, Co., Ltd.) powders were chosen as the fluxes. The typical

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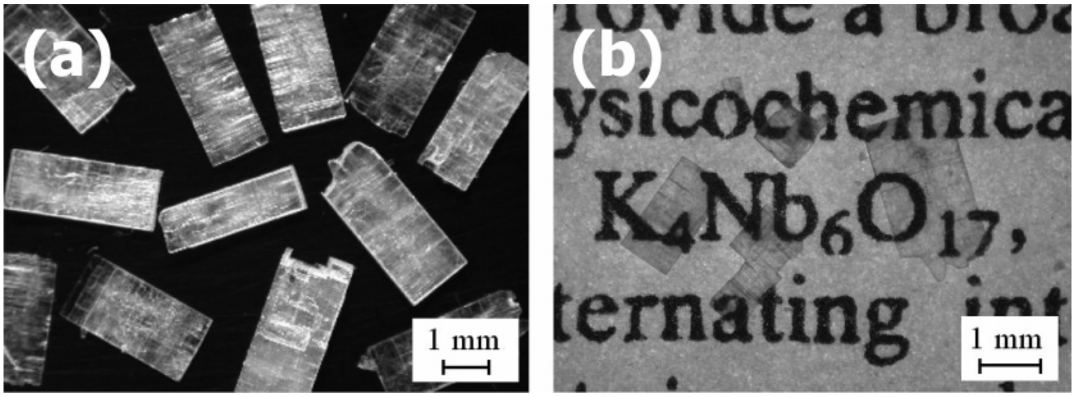

Figure 1. Optical micrographs showing $K_4Nb_6O_{17}$ crystals grown from K_2MoO_4 flux: (a) Platelike crystals and (b) thin platelike crystals.

Table 1. Typical Growth Conditions of the $K_4Nb_6O_{17}$ Crystals

run no.	solute concentration (mol %)	solute		flux		
		K_2CO_3/g	Nb_2O_5/g	K_2CO_3/g	MoO_3/g	WO_3/g
1	1	0.238	0.687	11.793	12.282	
2	3	0.678	1.955	10.957	11.411	
3	5	1.074	3.098	10.202	10.625	
4	7	1.433	4.134	9.519	9.914	
5	10	1.912	5.517	8.606	8.963	
6	20	3.138	9.052	6.275	6.535	
7	30	3.989	11.509	4.654	4.847	
8	60	5.476	15.798	1.825	1.901	
9	2	0.360	1.038	8.815		14.787
10	3	0.530	1.529	8.568		14.373
11	4	0.694	2.003	8.330		13.973
12	5	0.853	2.460	8.100		13.588
13	7	1.154	3.328	7.663		12.855
14	10	1.569	4.526	7.061		11.844
15	12	1.824	5.263	6.690		11.222
16	30	3.567	10.290	4.162		6.981

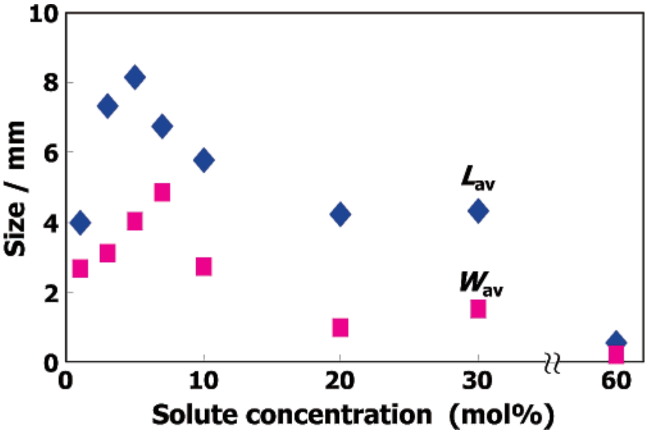

Figure 2. Relationship between solute concentration and grown crystal sizes (L_{av} and W_{av}).

growth conditions are given in Table 1. The concentrations of solute were respectively varied from 1 to 60 mol % (0.849−19.530 g) of the K_2MoO_4 flux and from 2 to 30 mol % (0.654−12.721 g) of the K_2WO_4 flux. These masses of the reagents were kept at approximately 25 g for all growth runs. The solute and flux powders were weighed out, mixed together, and put into platinum crucibles (36 mm diameter × 40 mm height) with loosely sealed lids. The crucibles were heated at a rate of about 45 °C/h to 1100 °C and held at this temperature for 10 h. Subsequently, the crucibles were cooled at a rate of 5 °C/h to 500 °C and taken out from the furnace and rapidly cooled at room temperature. The crystal products were separated from the remaining fluxes in warm water.

Evaluation of $K_4Nb_6O_{17}$ Crystals. The grown crystals were examined using an optical microscope and field emission scanning electron microscope (FE-SEM, Hitachi, S-4100). The crystal phases were identified by X-ray diffraction (XRD, Shimadzu, XRD-6000). A SEM equipped with an energy-dispersive X-ray spectrometer (EDS, Horiba, EMAX) was used to study variations in the concentration of the major constituents in the grown crystals. The presence of impurities from the K_2MoO_4 and K_2WO_4 fluxes and Pt crucible was also checked. The length (*L*, long side, perpendicular to the $\langle 010 \rangle$ direction), width (*W*, short side, perpendicular to the $\langle 010 \rangle$ direction), and thickness (*T*, parallel to the $\langle 010 \rangle$ direction) of the grown layered crystals were measured. The average length (L_{av}) and width (W_{av}) of the first 20 largest crystals were calculated for each growth run. The average size of the pulverized crystallites was measured by SEM observation. The morphology was investigated by the use of XRD and interfacial angle data.

Photocatalytic and adsorption properties were investigated in methylene blue (Chroma Gesellschaft Schmidt & Co.) and methyl orange (Wako Pure Chemical Industries, Ltd.) catalyst suspensions at around room temperatures. The pulverized $K_4Nb_6O_{17}$ crystals (ca. 0.2 g, average crystal size = 50−300 nm) and methylene blue (0.5 mg) or methyl orange (ca. 0.3 cm^3, 0.1% w/v) were placed in a glass beaker containing 100 cm^3 of distilled water and were kept in suspension by stirring continuously with a magnetic stirrer. The suspension (pH = 7) was irradiated with UV light at a center wavelength of 352 nm for 0−6 h under an atmosphere. The light source employed in this study was a commercial black light (15 W ×2). The suspension including the crystals and organic dyes were separated by centrifugation, and then the solution and the crystals were respectively analyzed by UV−visible (UV−vis) absorption spectroscopy and diffuse reflection spectroscopy. Methylene blue and methyl orange degradation were respectively detected by measuring the absorption at the center wavelength of 550−700 and 400−500 nm.

Results and Discussion

Flux Growth of $K_4Nb_6O_{17}$ Crystals. Well-developed platelike layered crystals of $K_4Nb_6O_{17}$ were grown from the K_2MoO_4 and K_2WO_4 fluxes. Colorless and transparent crystals up to 15 (length) × 5.0 (width) × 7.4 (thickness) mm (K_2MoO_4 flux) and 18 × 9.0 × 2.9 mm (K_2WO_4 flux) were obtained, their sizes depending on the solute concentration. Figure 1 shows the typical grown crystals of $K_4Nb_6O_{17}$. As shown in Figure 1b, printed characters beneath the crystals are clearly readable.

Figure 2 shows the variation in the average length (L_{av}) and width (W_{av}) of the $K_4Nb_6O_{17}$ crystals grown from the K_2MoO_4 flux with the solute concentration. Relatively large crystals of L_{av} = 8.2 mm and W_{av} = 4.0 mm were grown

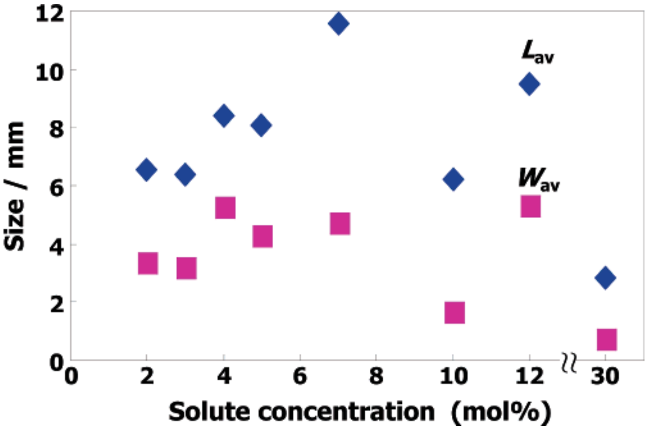

Figure 3. Relationship between solute concentration and grown crystal sizes (L_{av} and W_{av}).

from flux with 5 mol % of solute (run 3). The crystal sizes decreased gradually with decreasing or increasing solute content. When the solute amount was 60 mol %, small crystals of L_{av} = 0.5 mm and W_{av} = 0.2 mm were grown. The basic form of grown crystals was not related to the growth conditions. Byproduct crystals ($K_{5.75}Nb_{10.85}O_{30}$, tetragonal system[8]) of 10−150 μm in length and 0.5−5 μm in width were also grown from mixtures containing solute of 20−60 mol % (yield; much smaller than 20 mass %). Typical $K_{5.75}Nb_{10.85}O_{30}$ crystals were colorless and transparent, and their form was a cylindrical whisker.

In the case of the K_2WO_4 flux, a mixture containing 7 mol % solute produced large crystals with L_{av} = 11.6 mm and W_{av} = 4.8 mm (Figure 3). Any further increase or decrease in the solute concentration resulted in a decrease in the size of platelike layered crystals. The optimum solute concentration for the growth of $K_4Nb_6O_{17}$ crystals was 7 mol %. When the solute concentration was 2−4 mol %, typical bulk (rectangular) crystals of $KNbO_3$ (orthorhombic system[9]) were also grown as a byproduct, besides $K_4Nb_6O_{17}$ crystals. The obtained $KNbO_3$ crystals were up to 5.6 × 4.2 × 2.9 mm in size and black (yield, much smaller than 20 mass %). The color of $KNbO_3$ crystals is thought to be attributed to poor homogenization, oxygen vacancies, or Nb oxidation states.[10] The kind of byproduct differed depending on the fluxes.

During these growth runs, evaporation losses of the K_2MoO_4 and K_2WO_4 were respectively ∼5 and <5 mass %. In general, flux evaporation had a considerable influence on crystal growth. The flux evaporation, however, is insignificant of the $K_4Nb_6O_{17}$ crystal growth. The platinum crucibles were found to be undamaged after use. The K_2MoO_4 and K_2WO_4 fluxes did not attack the crucibles. The resulting crystals could be easily separated from the fluxes in warm water because K_2MoO_4 and K_2WO_4 were readily soluble.

Characteristics of the $K_4Nb_6O_{17}$ Crystals. Layered platelike crystals of $K_4Nb_6O_{17}$ were grown to a size of 18 × 9.0 × 2.9 mm, which were colorless and transparent. As byproducts, $K_{5.75}Nb_{10.85}O_{30}$ (whisker) and $KNbO_3$ (rectangular) crystals were obtained with $K_4Nb_6O_{17}$ crystals. The grown $K_4Nb_6O_{17}$ crystals were investigated by XRD in order to identify the colorless and transparent crystals and to determine the Miller indices of the crystal faces. Figure 4 shows XRD profiles of data for the layered platelike crystals, pulverized crystallites, and $K_4Nb_6O_{17}$ ICDD-PDF.[5] The pulverized crystallites pattern (Figure 4b) was the same as that of ICDD-PDF[5] (Figure 4c). Additionally, the EDS data showed that potassium and niobium atoms were homogeneously distributed in the crystals. Molybdenum and tungsten atoms from the fluxes were not detected in the crystals. $K_{5.75}Nb_{10.85}O_{30}$ and $KNbO_3$ crystals were also identified by powder XRD patterns.[8,9]

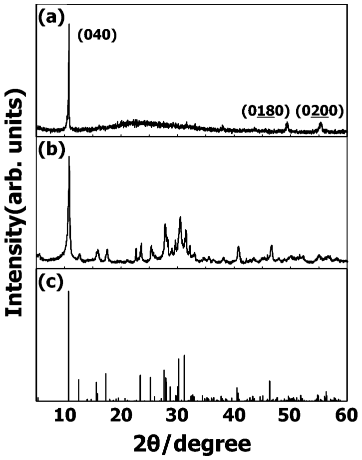

Figure 4. X-ray diffraction patterns (Cu Kα) of $K_4Nb_6O_{17}$ crystals: (a) Platelike crystals of which well-developed faces were laid in parallel with the holder plate, (b) pulverized crystallites, (c) $K_4Nb_6O_{17}$ JCPDS data.[5]

The grown crystals of $K_4Nb_6O_{17}$ crystals were bounded by two basal and eight sided faces (Figure 5). The XRD patterns of oriented platelike crystals showed that the diffraction intensities of the (040), $(0\underline{18}0)$, and $(0\underline{20}0)$ planes were predominant. The indices of well-developed basal faces were {010}, and the basal faces were very flat. As clearly shown in Figures 5a and 5c, they consisted of thin platelike (trapezium) crystals and are a layered structure. The interfacial angles between basal−side (1) faces, basal−side (2) faces, side (1)−side (1) faces and side (2)−side (2) faces were respectively 76 ± 1, 68 ± 2, 27 ± 1, and 42 ± 1°. These values are in good agreement with the calculated interfacial angle of 76.7° between the (010) and (110) faces, 68.7° between the (010) and (021) faces, 26.5° between (110) and $(1\bar{1}0)$ faces, and 42.5° between (021) and $(0\bar{2}1)$ faces, respectively. On the basis of the XRD data and interfacial angle measurements, the crystals were found to be bounded by the {010}, {110}, and {021} faces (Figures 5b and 5d).

The adsorption of methylene blue from aqueous solution onto $K_4Nb_6O_{17}$ crystals was investigated using a batch adsorption technique. The adsorption experiments (Figure 6) indicated that the grown $K_4Nb_6O_{17}$ crystals were effective in removing methylene blue from aqueous solution. Figure 7 shows the UV−vis diffuse reflectance spectra of $K_4Nb_6O_{17}$ crystals (before or after adsorption). After 1 min of stirring, the color of dispersed $K_4Nb_6O_{17}$ crystals was changed from colorless and transparent into blue (absorption at around 550−650 nm). Ion-exchange capability of $K_4Nb_6O_{17}$ has been

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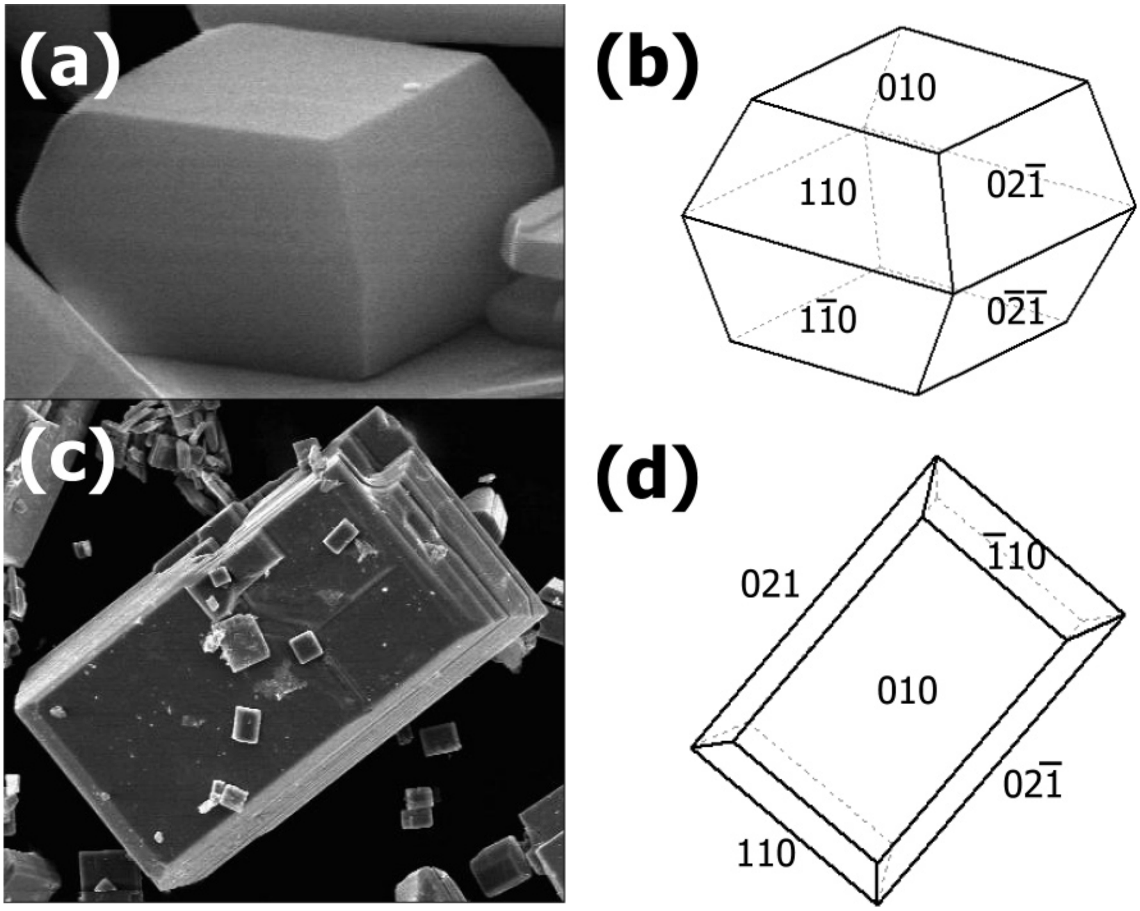

Figure 5. Typical $K_4Nb_6O_{17}$ crystals and schematic drawings of a crystal bounded by the {010}, {110}, and {021} faces.

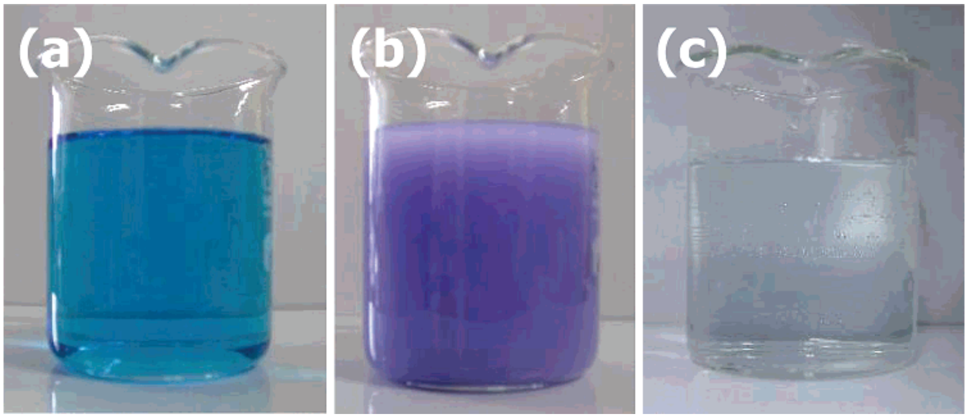

Figure 6. Adsorption experiments of methylene blue from aqueous solution onto $K_4Nb_6O_{17}$ crystals: (a) Methylene blue solution, (b) methylene blue/$K_4Nb_6O_{17}$ crystals suspension, and (c) solution after centrifugation.

well-known in the literature.[1] Methylene blue is cationic dye, and $K_4Nb_6O_{17}$ single crystal has an anisotropic surface with highly ordered NbO^- groups which act as cation-exchangeable sites.[1] Consequently, the removal of methylene blue is due to the adsorption of dye molecules on the layered $K_4Nb_6O_{17}$ crystals from the liquid phase. In the case of anionic dyes, they are hardly thought to exchange with potassium ions in the crystals.

Photocatalytic properties of the layered $K_4Nb_6O_{17}$ crystals were examined by the photodecolorization of aqueous methylene blue. The crystal-dye suspension was irradiated under the UV light. The color of the suspension faded gradually with an increase in irradiation time (Figure 8) and finally changed from blue (Figure 8a) to colorless (Figure 8d). The color of the suspension irradiated with UV light for 6 h was unchanged by the addition of acidic or basic

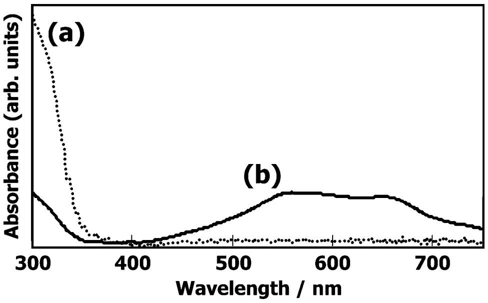

Figure 7. UV−vis diffuse reflection spectra of $K_4Nb_6O_{17}$ crystals (a) before and (b) after methylene blue adsorption.

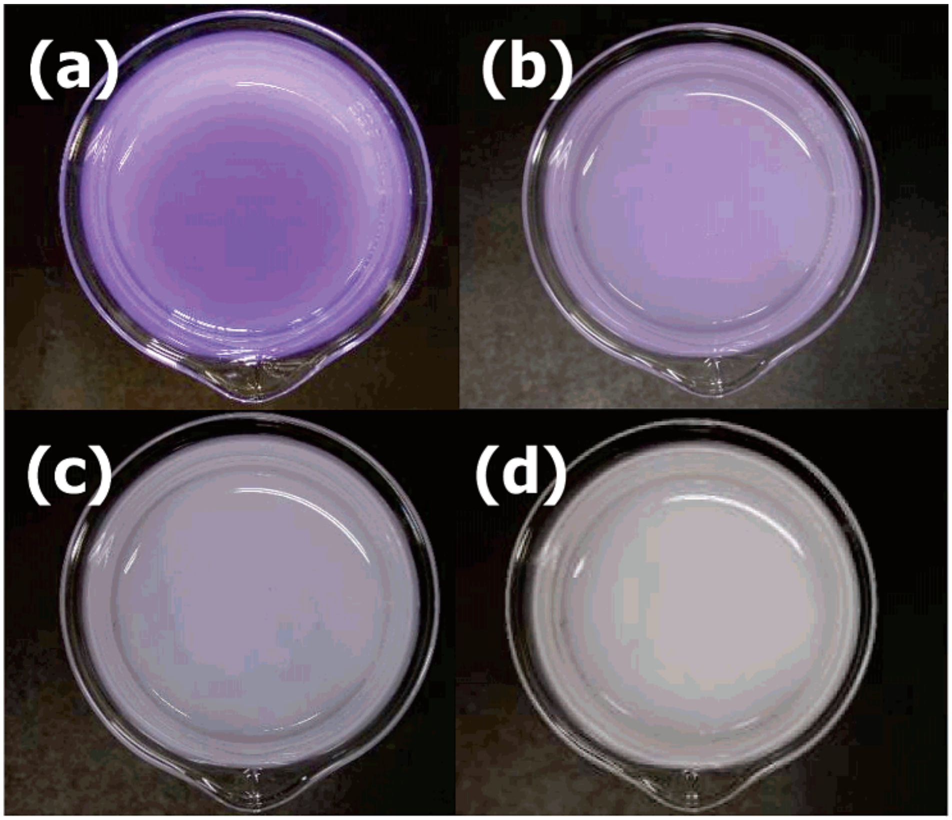

Figure 8. Photodecolorization of $K_4Nb_6O_{17}$ crystals/methylene blue suspension: UV irradiation time = (a) 0 h, (b) 1.5 h, (c) 3 h, and (d) 6 h.

media. On the other hand, the color of methylene blue solution remained unchanged when no $K_4Nb_6O_{17}$ crystal was added there. In the case of methyl orange suspension, the absorption spectra (center wavelength = 352 nm) corresponded to the UV light irradiation times. The color of the suspension decolorized gradually with an increase in irradiation time. Finally, the suspension changed from orange to colorless. Furthermore, $K_4Nb_6O_{17}$ crystals grown by our flux method decomposed methylene blue molecules faster than those synthesized by solid-state reaction. The difference is thought to be attributable to crystallinity and size of $K_4Nb_6O_{17}$ crystals. Under UV light irradiation, the grown $K_4Nb_6O_{17}$ crystals, therefore, act efficiently as photocatalysts.

Conclusions

Layered $K_4Nb_6O_{17}$ crystals were successfully grown by the slow cooling of K_2MoO_4 and K_2WO_4 fluxes. The $K_4Nb_6O_{17}$ crystals, which were transparent and colorless, were up to 18 × 9.0 × 2.9 mm in size. Their basic form was a platelike habit bounded by well-developed {010}, {110}, and {021} faces. The crystal generation and size of $K_4Nb_6O_{17}$ were dependent on the solute concentration of starting mixtures. In addition, $K_{5.75}Nb_{10.85}O_{30}$ and $KNbO_3$ crystals as byproducts also formed with mixtures containing solute of 20−60 mol % (K_2MoO_4) and 2−4 mol % (K_2WO_4), respectively. $K_4Nb_6O_{17}$ crystals exhibited high activity for the methylene blue adsorption and degradation. Its degradation occurs mainly via the photocatalytic process. Since the layered $K_4Nb_6O_{17}$ crystals grown by our process are relatively large and have high crystallinity and their characteristic properties, they will be favorable materials for various technological applications such as novel photocatalysts and adsorbents.

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