Flux Growth and Characterization of Photocatalytic $Na_2Ti_6O_{13}$ Whiskers

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High quality, hexagonal prismatic $Na_2Ti_6O_{13}$ whiskers were easily grown by the slow-cooling of a NaCl flux. Whisker growth was conducted by heating a mixture of solute ($Na_2CO_3 + TiO_2$) and flux (NaCl) at 1100 °C and held at this temperature for 10 h, and then the mixture was cooled at a rate of 5 °C h^{-1} to 500 °C. The $Na_2Ti_6O_{13}$ whiskers had average lengths of up to 100 µm and widths of up to 2.0 µm and were transparent and colorless. The whiskers were hexagonal prisms bounded by well-developed {010}, {100}, {001}, and {20$\bar{1}$} faces. The whiskers exhibited good photocatalytic activity under UV light irradiation. Sodium chloride was found to be a very suitable flux for environmental friendly growth of photocatalytic whiskers.

Micro- and nanostructural materials have attracted much interest for their novel properties that differ from those of bulk materials. One-dimensional materials, such as whisker, tube, and fiber, are of importance for various applications in electronic, mechanical and chemical engineering because they exhibit unique properties.[1] In particular, whiskers of hexatitanate series materials, such as $Na_2Ti_6O_{13}$ and $K_2Ti_6O_{13}$, which have thermal durability, chemical resistivity and dispersibility, have been widely used in industry. Furthermore, many kinds of alkali metal titanates including $Na_2Ti_6O_{13}$ have been studied for potential use as photocatalysts for the degradation of toxic substances and decomposition of pure water and for oxygen electrodes in potentiometric sensors for O_2 and CO_2.[2]

The crystals of sodium hexatitanate, $Na_2Ti_6O_{13}$, are monoclinic with the space group $C2/m$. $Na_2Ti_6O_{13}$ has been reported to have lattice parameters of $a = 15.12$, $b = 3.74$, and $c = 9.16$ Å, $\beta = 99.3°$, and a density of 3.51 g cm^{-3}.[3] Sodium hexatitanate has a melting point of 1300 °C. In a viewpoint of crystal structure, $Na_2Ti_6O_{13}$ has a unique structure, which is a tunnel structure (Fig. 1) consisting of three vacant spaces where one vacant space corresponds to removal of a TiO_6 unit (perovskite-type unit).[4] Several properties of the $Na_2Ti_6O_{13}$ whiskers are attributed to their unique crystal structure (tunnel structure). There have been many studies on alkali hexatitanate crystallite syntheses including calcination, solid-state reaction, hydrothermal synthesis, sol–gel method and flux growth.[2,4,5] Among these syntheses, flux growth by use of NaCl is the most promising because NaCl is abundant in nature and harmless to human beings and the environment. Moreover, it has advantages in an extensive synthesis since it is very convenient and $Na_2Ti_6O_{13}$ whiskers can be produced at temperatures well below the melting point of the solute. The present paper describes the growth of high-quality $Na_2Ti_6O_{13}$ whiskers from a NaCl flux and evaluation of their photocatalytic properties. The effect of the solute concentration on the whisker morphology was also examined.

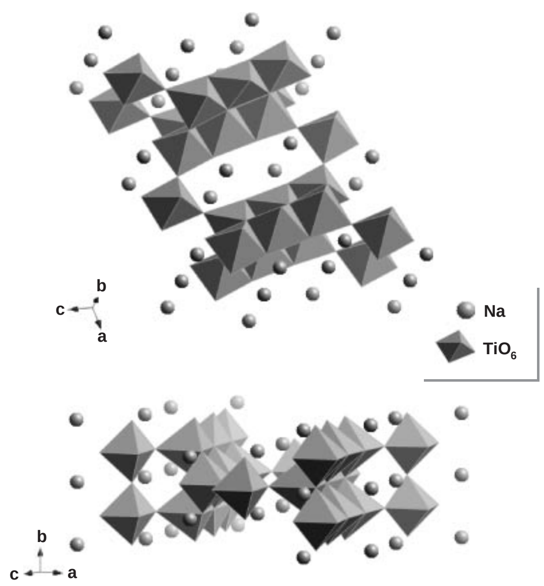

Fig. 1. Schematic representation of tunnel structure of $Na_2Ti_6O_{13}$.

Experimental

Sodium hexatitanate whiskers were grown by slow-cooling of a NaCl flux. A stoichiometric mixture of reagent-grade Na_2CO_3 (Wako Pure Chemical Industries, Ltd.) and TiO_2 (anatase, Wako Pure Chemical Industries, Ltd.) powders was used as the solute, and reagent-grade NaCl (Wako Pure Chemical Industries, Ltd.) was chosen as the flux. The concentration of the solute was varied from 0.5 to 20 mol % of the flux. The masses of the mixtures were about 30 g. The mixtures were put into 30 cm^3 platinum crucibles.

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The lids were fitted loosely, and the crucibles were placed in an electric furnace with silicon carbide heating elements. They were heated at a rate of about 45 °C h^{-1} to 1100 °C and held at this temperature for 10 h, and then, they cooled at a rate of 5 °C h^{-1} to 500 °C. When the cooling program was completed, the crucibles were allowed to cool down to room temperature. The crystalline products were then separated by dissolving the flux in warm water. The whiskers were examined by using an optical microscope (NIKON, SMZ800) and a scanning electron microscope (SEM, HITACHI, S-4100). The crystal phases were identified by X-ray diffraction (XRD, SHIMADZU, XRD-6000). An energy dispersive X-ray spectrometer (EDS, HORIBA, EMAX) was used to study variations in the concentration of the major constituents in the grown whiskers. Electron diffraction measurements were carried out on JEM-2000EXII (JEOL) instrument operated at 200 kV to determine the direction of elongations of the crystals. The presence of impurities from the NaCl flux and Pt crucible was also checked. The length (parallel to the *b* axis) and width (perpendicular to the *b* axis) of the whiskers were measured, and their averages were calculated. The morphology was investigated by use of XRD and interfacial angle data. Ultraviolet (UV)–visible (vis) light diffuse reflectance spectra of the whiskers grown from a mixture containing 20 mol % solute were obtained on spectrophotometer (SHIMADZU, UV3150).

Photocatalytic reactions were performed at room temperature in methyl orange (Wako Pure Chemical Industries, Ltd.) catalyst suspensions. The whiskers (ca. 0.5 g, aspect ratio = 13) grown from a mixture containing 20 mol % solute and methyl orange (ca. 0.5 cm^3, 0.1 w/v %) were placed in the glass beaker containing 100 cm^3 distilled water and was kept in suspension by stirring continuously with a magnetic stirrer. Before stirring, the whiskers were pulverized by using a dry milling method (whisker sizes: ca. 50–300 nm). The suspension (pH = 7.5) was irradiated with UV light at an average 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 whiskers and methyl orange were separated by centrifugation, and then, the solution was analyzed by UV–vis spectrophotometer. Methyl orange degradation was detected by measuring the absorption at the center wavelength of 400–500 nm.

Results and Discussion

Idiomorphic whiskers of $Na_2Ti_6O_{13}$ having an average aspect ratio of up to 50 were selectively grown by using a NaCl flux slow-cooling method. Typical $Na_2Ti_6O_{13}$ whiskers are shown in Fig. 2. Only $Na_2Ti_6O_{13}$ whiskers were grown from all growth runs. The whiskers were identified as $Na_2Ti_6O_{13}$ by their powder XRD patterns, using data reported in the literatures.[3] The whiskers were colorless and transparent. Figure 3 shows the variation in the average length (L_{av}) and width (W_{av}) of the $Na_2Ti_6O_{13}$ whiskers with solute concentration. Long whiskers of $L_{av} = 100\,\mu m$ and $W_{av} = 2.0\,\mu m$ (aspect ratio: ca. 50) were grown from a mixture containing 0.5 mol % solute. As the solute concentration was increased, L_{av} and W_{av} values decreased drastically and very slightly, respectively. The mixture containing a solute of 20 mol % produced whiskers with $L_{av} = 7.8\,\mu m$ and $W_{av} = 0.6\,\mu m$ (aspect ratio: ca. 13). As the solute concentrations increased, any undissolved solute particles in the solution were likely to act as nucleation centers when crystallization occurred. As a result, many small whiskers grew onto these nuclei.

Figure 4 shows a typical example of the grown $Na_2Ti_6O_{13}$ whiskers and a schematic drawing of the whisker habit. The $Na_2Ti_6O_{13}$ whiskers were hexagonal rods, and the surfaces

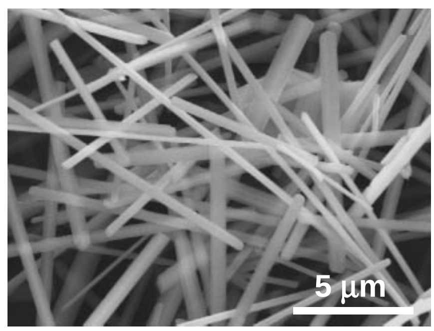

Fig. 2. Optical micrograph showing typical $Na_2Ti_6O_{13}$ whiskers grown from the NaCl flux.

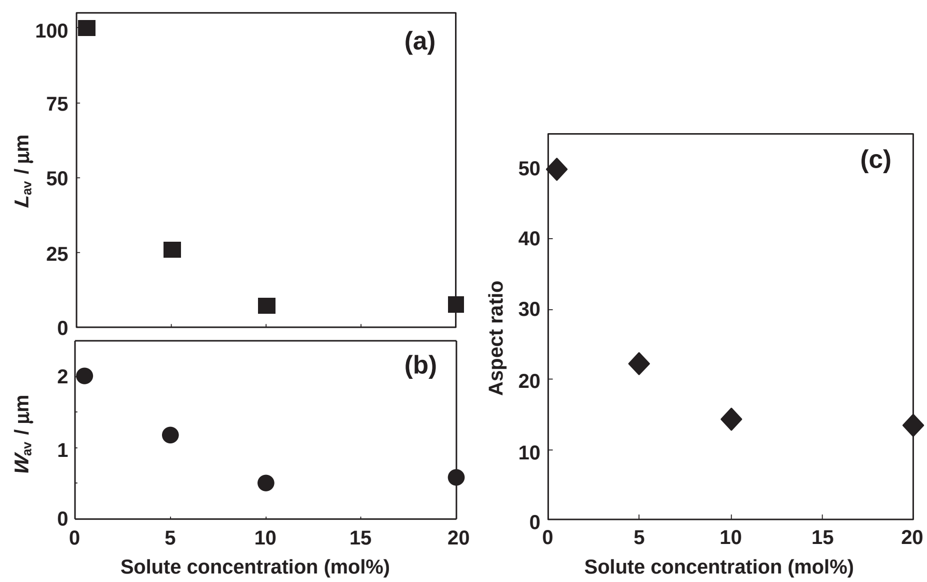

Fig. 3. Relationship between solute concentration and grown whisker sizes [(a) L_{av}, (b) W_{av}, and (c) aspect ratio].

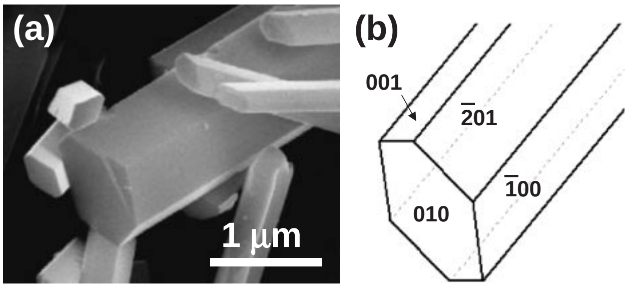

Fig. 4. Typical $Na_2Ti_6O_{13}$ whisker (a) and drawing of whisker habit (b).

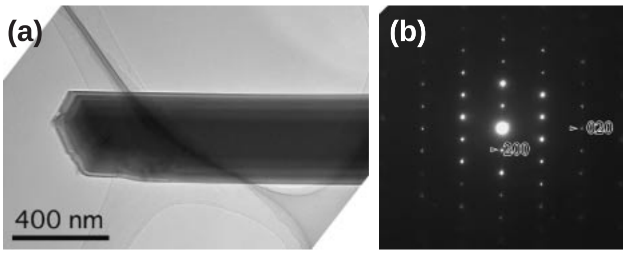

Fig. 5. TEM micrograph of $Na_2Ti_6O_{13}$ whisker grown from a mixture containing 0.5 mol % solute (a) and its diffraction pattern (b).

of these whiskers were very flat as shown in Fig. 4a. The XRD pattern for oriented whiskers indicated that the diffraction intensities of the (200), (600), and $(\bar{2}01)$ planes were dominant. The TEM micrograph (Fig. 5a) and the corresponding diffraction pattern (Fig. 5b) of a typical whisker grown from a mixture containing 0.5 mol % solute are shown in Fig. 5. The elongated direction corresponded to the ⟨010⟩ direction. In addition, the whisker had good crystallinity. The measured interfacial angles were $90 \pm 1°$, $81 \pm 2°$, $41 \pm 2°$, and $58 \pm 2°$. These values were in good agreement with the calculated interfacial angle of 90° between (010) and (001), 90° between (010) and $(\bar{1}00)$, 90° between (010) and $(\bar{2}01)$, 80.7° between $(\bar{1}00)$ and (001), 43.2° between $(\bar{1}00)$ and $(\bar{2}01)$, and 56.1° between (001) and $(\bar{2}01)$, respectively. On the basis of the XRD data and interfacial angle measurements, the whiskers were found to be bounded by {010}, {100}, {001}, and $\{\bar{2}01\}$ (Fig. 4b).

The UV–vis diffuse reflectance spectrum of $Na_2Ti_6O_{13}$ whiskers is shown in Fig. 6. The spectrum shows the onset wavelength of absorption at around 380 nm (ca. 3.26 eV) and a maximum at around 315 nm (ca. 3.94 eV). Furthermore, the whiskers also had a small shoulder absorption at 400–420 nm. Typical absorption of TiO_2 (anatase) powders shifts to longer wavelength by approximately 20 nm at the onset. Figure 7 shows the decay of absorbance with time (0–6 h) during the progress of the reaction upon stirring the suspension. The absorption spectra corresponded to the UV-light irradiation times. The color of the suspension faded gradually with an increase in irradiation time. Finally, the suspension changed from orange (Fig. 7a) to colorless (Fig. 7g). Before irradiation, the suspension color changed from orange to light-pink by the addition of oxalic acid. On the other hand, the color of the suspension irradiated with UV light for 6 h was unchanged by the addition of oxalic acid. When no $Na_2Ti_6O_{13}$ whisker was added, the color of the methyl orange solution remained

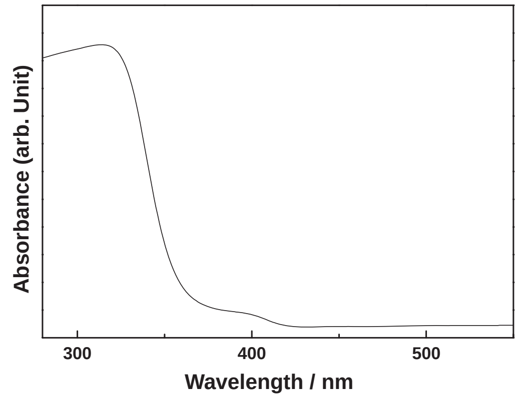

Fig. 6. UV–vis light diffuse reflectance spectrum of $Na_2Ti_6O_{13}$ whiskers.

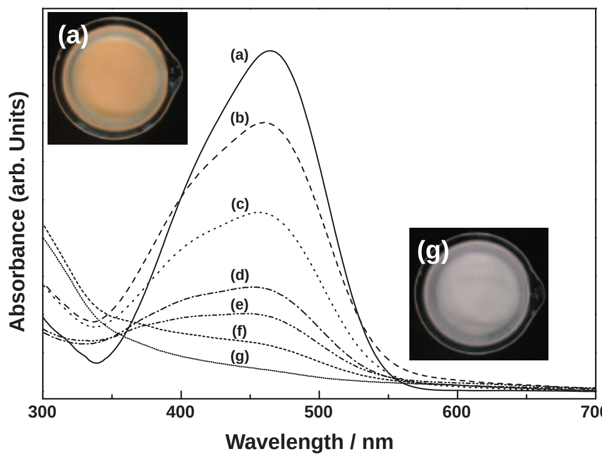

Fig. 7. Absorbance of methyl orange solution before and after photocatalytic reaction [UV irradiation time: (a) 0 h, (b) 1 h, (c) 2 h, (d) 3 h, (e) 4 h, (f) 5 h, and (g) 6 h].

unchanged. Under UV irradiation, the $Na_2Ti_6O_{13}$ whiskers, therefore, act efficiently as a photocatalyst and break methyl orange molecules into several different smaller molecules. Furthermore, the photocatalytic capabilities were found to be better when the surface area of the whiskers was larger, that is, the sizes of the whiskers were smaller.

Conclusion

Highly crystalline $Na_2Ti_6O_{13}$ whiskers were readily grown by slow-cooling of a NaCl flux. The $Na_2Ti_6O_{13}$ whiskers, which were transparent and colorless, were up to 100×2.0 μm in average size (aspect ratio = 50). The whiskers were hexagonal prisms bounded by well developed {010}, {100}, {001}, and $\{\bar{2}01\}$ faces, and they elongated in the ⟨010⟩ directions. Furthermore, they exhibited photocatalytic activity for decomposition of organic materials. From these results, it should be possible to prepare highly active photocatalysts because the crystallinity of photocatalysts appears to be important for high activity.

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