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Photocatalytic Activity of $NaNbO_3$ Thin Films

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Titanium dioxide (TiO_2) is a well-known photocatalyst material.[1] UV irradiation of TiO_2 generates electron−hole pairs, which reduce and oxidize adsorbates on the surface, respectively, thereby producing radical species, such as OH radicals and O_2^-. These radicals can decompose most organic compounds and bacteria.[2]

Photoinduced hydrophilicity was discovered in 1995,[3] soon after the time that conventional applications of TiO_2 as a photocatalyst began to be developed. Upon UV irradiation, a TiO_2 surface becomes highly hydrophilic. In addition to the TiO_2 photocatalyst, perovskite-type (ABO_3) oxides have been studied to determine their photocatalytic oxidation properties.[4] However, few have been determined to be capable of photoinduced hydorophilicity. Miyauchi et al.[5] have reported that films of $SrTiO_3$, which is a perovskite-type oxide, did not become hydrophilic under UV irradiation, even though it rapidly decomposed methylene blue adsorbed on its surface. Interestingly, the photocatalytic properties of perovskite-type oxides have been found to be different from those for TiO_2.

In this study, we focused on the well-known perovskite-type oxide $NaNbO_3$ and investigated the photocataytic activity of $NaNbO_3$ films. A coating solution was prepared by the sol−gel method. First, sodium acetylacetonate *n*-hydrate ($C_5H_7NaO_2 \cdot nH_2O$, 0.488 g) was dissolved in ethanol (C_2H_5OH, 35 mL), and acetylacetone (C_5H_8O, 0.821 mL) was added into it. After the solution was stirred for 30 min, niobium ethoxide [$Nb(OC_2H_5)_5$, 1.00 mL] was added to the solution, which was then vigorously stirred for an additional 30 min. These compounds were all reagent-grade; the molar ratio was $C_5H_7NaO_2 \cdot nH_2O/C_5H_8O/Nb(OC_2H_5)_5 = 1:2:1$. Next, the mixed solution was hydrolyzed by adding a drop of hydrochloric acid solution (5.00 mL, pH 1) with stirring at room temperature. Finally, reagent-grade polyethylene glycol 200 [$H(OCH_2CH_2)nOH$, 5.00 mL] was added into the solution to facilitate the coating of the glass substrates. Stirring for 15 min yielded a coating solution. Films were prepared by spin-coating this solution onto quartz glass followed by heating at 500 °C for 1 h.

Figure 1 shows the X-ray diffraction pattern of the prepared film, which exhibited a crystalline phase assigned as $NaNbO_3$, which is an orthorhombic pseudoperovskite structure with a space group of *Pbcm*. An scanning electron microscopy (SEM) image of the film surface microstructure is shown in Figure 2. A homogeneous microstructure with an average grain size of 15−25 nm was obtained.

The band gap of the film was calculated according to a general procedure from the absorption spectrum obtained using a UV−vis scanning spectrophotometer.[6] The band gap of the film was found to be 3.49 eV, which is nearly equivalent to the photon energy of 355 nm light; thus, it is possible that a blacklight blue (BLB) lamp may be incapable of completely exciting the film. The photocatalytic activity of the film was evaluated using two types of UV lamp chosen on the basis of this result: UV-A and UV-B lamps, with peaks in the emission spectra near 360 and 306 nm, respectively.

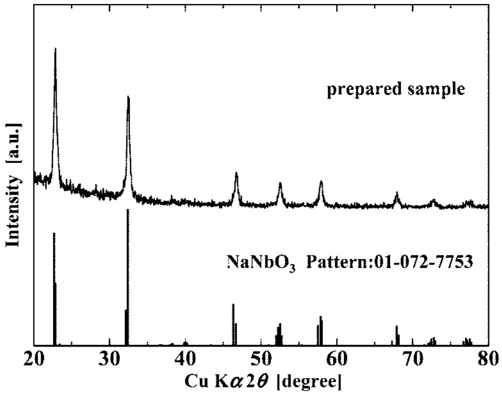

Figure 1. X-ray diffraction pattern of the prepared film. The film was measured by detector scan ($\omega = 0.2°$). As a reference, the standard pattern for $NaNbO_3$ is shown at the bottom.

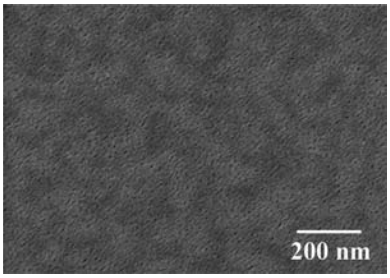

Figure 2. SEM image of the prepared $NaNbO_3$ film surface. The electron acceleration voltage was 1.5 kV.

Figure 3 shows the variation in water contact angle on the film under exposure to UV-A or UV-B irradiation. Before UV irradiation, the initial water contact angle on the film was more than 40°. When the film was irradiated with UV-A or UV-B, the water contact angle of the film started to decrease. The film under UV-B light exhibited a higher photoinduced hydrophilic conversion rate than that under UV-A. It is appropriate to consider that this result is due to the difference in the overall hydrophilic conversion behavior of these UV light sources. Sakai et al.[7] reported that the diffusion of photogenerated holes to the TiO_2 surface was an important process for hydrophilic conversion, suggesting that one of the reasons for different hydrophilic conversion rates is that the diffusion of photogenerated holes to the film surface is insufficient, as the film may not be completely excited by UV-A irradiation. This is first report that $NaNbO_3$ exhibits photoinduced hydrophilicity under UV irradiation.

Figure 4 shows the fraction of methylene blue decomposed via photocatalytic oxidation on the film under UV-A or UV-B irradiation. After 24 h, methylene blue was decomposed to a degree of ~10% on the $NaNbO_3$ film under UV-A irradiation and ~15% under UV-B irradiation. In contrast, methylene blue was decom-

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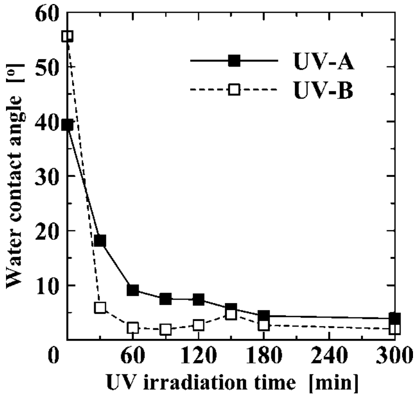

Figure 3. Variation of water contact angle on the film under UV-A or UV-B irradiation. The light intensity was 1.0 mW/cm^2. Values of the water contact angle were averages of three measurements.

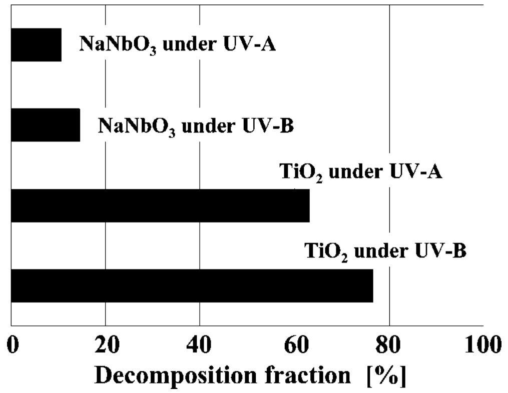

Figure 4. Fraction of methylene blue decomposed on photocatalytic films under UV-A or UV-B light irradiation after 24 h. The light intensity was 1.0 mW/cm^2.

posed to a degree of more than 60% on a similarly prepared TiO_2 film under the same conditions.

The band gap of the TiO_2 film calculated from the UV−vis spectrum (3.19 eV) was smaller than that of the $NaNbO_3$ film, and therefore, TiO_2 has the advantage of absorbing additional photons at longer wavelengths. However, the amounts of radiation absorbed from the UV-B lamp in the wavelength region from 275 to 350 nm should be nearly equivalent for the $NaNbO_3$ and TiO_2 films. As the $NaNbO_3$ film clearly exhibited photoinduced hydrophilic conversion under UV-A and UV-B light irradiation, it can be considered that it does absorb sufficient radiation for active photocatalytic oxidation. These results indicate there is very little photocatalytic oxidation activity on the $NaNbO_3$ film prepared here.

TiO_2 has two photocatalytic effects under UV light irradiation: photocatalytic oxidation and photoinduced hydrophilicity. The photoinduced hydrophilicity of TiO_2 is conjectured to be due to either (1) organic compounds on the film surface being decomposed by photocatalytic oxidation[8] or (2) hydrophilicity being induced by photoinduced modification of the surface structure, causing an increase in the number of hydroxyl groups.[9] In the event the surface is coated with organic material, photocatalytic decomposition of organic compounds regenerates first a hydrophilic surface and then a highly hydrophilic surface by increasing the number of hydroxyl groups. In the case of $SrTiO_3$, even though photocatalytic oxidation was prevalent, it did not become hydrophilic under UV light irradiation.[5] This result indicates that photoinduced hydrophilicity is not caused solely by photocatalytic oxidation.

In this study, the $NaNbO_3$ film exhibited photoinduced hydrophilic conversion under UV irradiation but little photocatalytic oxidation activity. These results confirm that photoinduced hydrophilicity was caused without photocatalytic oxidation, in contrast to the properties observed for TiO_2 and $SrTiO_3$. This is a valuable finding in the study of photoinduced hydrophilicity. Further investigation is required to clarify the cause of this phenomenon.

In summary, the photocatalytic activity of a $NaNbO_3$ film prepared by the sol−gel method was investigated. The film exhibited photoinduced hydrophilicity under irradiation with UV light, even though very little photocatalytic oxidation occurred. These results are interesting because this is the first observation that $NaNbO_3$ undergoes photoinduced hydrophilicity under UV irradiation. $NaNbO_3$ has thus proven itself to be an important material for elucidating the mechanism of photoinduced hydrophilicity on metal oxide surfaces.

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Supporting Information Available: Estimation of the optical band gap from the UV−vis spectrum. This material is available free of charge via the Internet at http://pubs.acs.org.

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