Fabrication of Rutile TiO_2 Foils with High Specific Surface Area via Heterogeneous Nucleation in Aqueous Solutions

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Rutile TiO_2 foils with high specific surface area were fabricated through heterogeneous nucleation on substrates in acidic aqueous solutions of titanyl sulfate. Rutile crystals were directly deposited even at a near room temperature in the solutions at the conditions around the boundary between the Ti(IV) soluble species and the TiO_2 crystal in the phase stability diagram of the Ti(IV)-H_2O system.

Since Fujishima and Honda[1] discovered an electrochemical photolysis of water on the rutile crystal surface under irradiation with light, many workers have been investigating the photocatalysis and the applications of TiO_2. The anatase structure is generally known to be more active in photocatalysis than the rutile structure.[2,3] Recently, however, Sopyan et al. [4] reported that synthesized rutile powder showed higher photocatalytic performance than commercial anatase powder with almost the same specific surface area. The high specific surface area is one of the factors for the superiority of anatase to rutile as a photocatalyst. A wider range of wavelength is expected to be effective for the photocatalytic activity of rutile because of its smaller bandgap. The relatively low specific surface area is attributable to sintering behavior during preparation of rutile at high temperatures. Thus, a low-temperature processing is required for the synthesis of rutile with high specific surface area.

Film preparation is important for applying TiO_2 as a photocatalyst in the various fields. The thin films have been fabricated by numerous methods such as chemical vapor deposition (CVD),[5,6] sputtering,[7] and sol–gel processes.[2,8] In general, temperatures above 500 °C[5,7,9] are applied for formation of the rutile phase. On the other hand, anatase thin films were fabricated at low temperatures by direct-deposition techniques with aqueous solutions of ammonium hexafluorotitanate ($(NH_4)_2TiF_6$)[10] or titanium tetrafluoride (TiF_4).[11] A biomimetic process for inorganic materials such as the direct-deposition techniques via heterogeneous nucleation by controlling the supersaturation in the aqueous solution is notable as a low energy process. Moreover, the prepared anatase films exhibited excellent photocatalytic activity on account of the high crystallinity and the high specific surface area.[11,12]

This letter describes low-temperature preparation of rutile foils having high specific surface area using a direct-deposition technique via heterogeneous nucleation in acidic aqueous solutions of titanyl sulfate ($TiOSO_4$). Although rutile fine powders have been reported to be synthesized from titanium tetrachloride ($TiCl_4$) solutions at low temperatures,[13–15] the morphological control of the crystalline TiO_2 was not sufficient. Furthermore, the conditions and the mechanism for the rutile formation have not been clarified theoretically. Here, we discuss the phase control of the deposited TiO_2 with the thermodynamic stability of the rutile structure in the Ti(IV)-H_2O system.

$TiOSO_4 \cdot xH_2O$ (Nacalai Tesque Inc., $x_{av} = 4.6$) was used as an inexpensive starting material having relatively low reactivity with water. Precursor solutions at the Ti concentration of 0.001–0.1 mol dm^{-3} prepared by adding $TiOSO_4 \cdot xH_2O$ into the aqueous solvent containing HCl or NH_4OH were stirred for approximately 1 h at room temperature. The pH values of resultant precursor solutions were varied between –1.00 and 1.70. Glass slides and a variety of polymer sheets washed ultrasonically with diluted nitric acid and ethanol or acetone for 1 h were immersed into the precursor solutions, and then kept at 60 °C. After appropriate reaction time (several hours to 10 days), TiO_2 was directly deposited on the substrates. The crystalline phase of the deposited TiO_2 depended on the Ti concentration (m_{Ti}) and pH of the solutions, as shown in Figure 1. The rutile phase was formed in a restricted range of the conditions. The solid line denotes the boundary between the Ti(IV) soluble species and the rutile phase estimated by the thermodynamic data of Lencka et al.[16] with the ideal solution approximation at 333.15 K. The conditions forming the rutile phase is found to lie beside the boundary in the phase stability diagram of the Ti(IV)-H_2O system. Considering the activity coefficients of the ionic species, the calculated boundary should move toward the condition area constructing the rutile phase. Therefore, the rutile phase is inferred to be deposited at the conditions near the thermodynamic equilibrium between the ionic species and the solid phase in aqueous solution. The stable Ti–O bonds are selectively formed with dissolving and condensing repeatedly near the boundary because of the small difference in the chemical potentials between the soluble species and the rutile structure. On the contrary, the metastable anatase structure was pro-

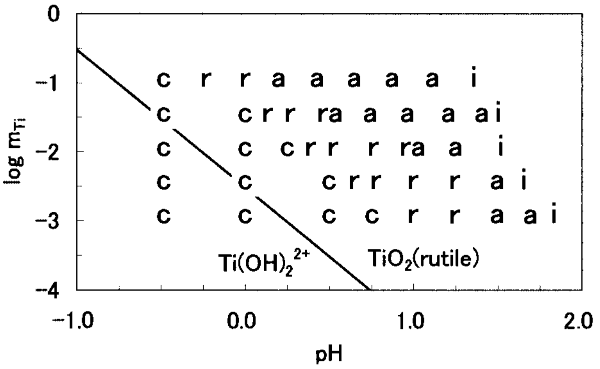

Figure 1. Crystalline phases of deposited TiO_2, identified by Rigaku X-ray diffraction spectrometer (XRD). c; clear solution without deposition for 30 days, r; rutile phase, ra; both rutile and anatase phases, a; anatase phase, i; insoluble. The boundary in Ti(IV)- H_2O system is also drawn.

duced at the region far from the equilibrium.

The existence of sulfate anions are also essential for this process because relatively strong coordination of sulfate anions to the Ti^{4+} cations plays a vital role for the film formation via heterogeneous nucleation with reducing the condensation rate of the hydrolyzed Ti^{4+} species,[17,18] Uniform and continuous rutile thin films were deposited through heterogeneous nucleation on the relatively hydrophobic surface such as polypropylene, polystyrene and polyethylene. On the other hand, the thin films formed on the relatively hydrophilic surface such as poly(vinyl chloride) and glass slide were discontinuous. These facts indicate that the heterogeneous nucleation of rutile is promoted on the hydrophobic surface rather than the hydrophilic one. Although these phenomena may be ascribed to the amphiphilicity of the rutile structure,[19] further detailed investigations are required to clarify the surface nature. Since the uniform rutile thin films were poorly adhesive in the absence of the covalent bonds between the films and the surfaces, self-standing foils with the rutile phase were easily obtained by peeling off the films from the substrates with the large difference in the thermal shrinkage coefficients of them. Field emission scanning electron microscope (FESEM; Hitachi S-4700) images in Figure 2 show that the foils consist of fine needle-like crystallites with diameters of ~20 nm vertically to the surface. Since the (101) and (002) planes provided relatively strong and sharp peaks as shown in Figure 3, the *c*-axis of the rutile crystal predominantly grew perpendicularly to the surface of the substrates. The specific surface area of the rutile foils was calculated to be ~140 m^2g^{-1} by the BET method with a Micromeritics TriStar 3000. The broaden XRD peaks are attributed to the rutile fine particles because the crystallite size estimated to be 7–25 nm with the Scherrer equation is almost the same as that obtained from the specific surface area. Thus, the rutile foils with high specific surface area by low-temperature processing are expected to be valuable as a new type of photocatalyst.

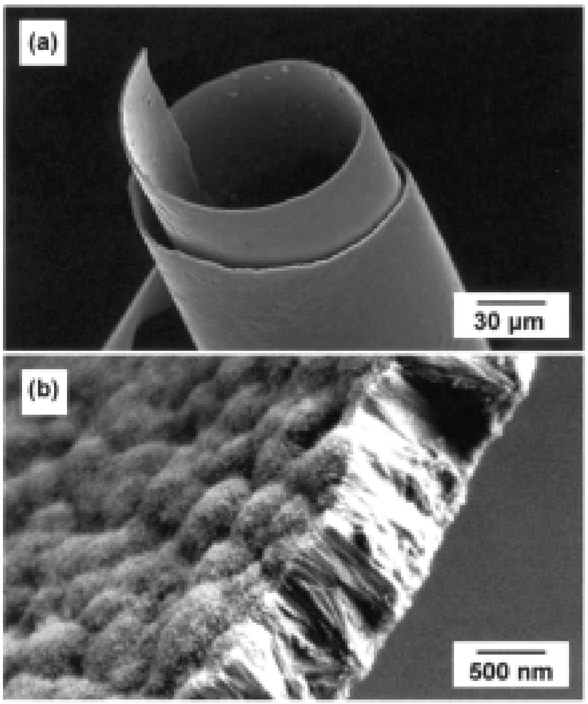

Figure 2. FESEM images of the rutile foil prepared at the $TiOSO_4$ concentration of 0.01 M and the initial pH value of 0.50, and kept at 60 °C for 5 days. The rutile foil rolled spontaneously during drying (a) and the cross section of the foil (b).

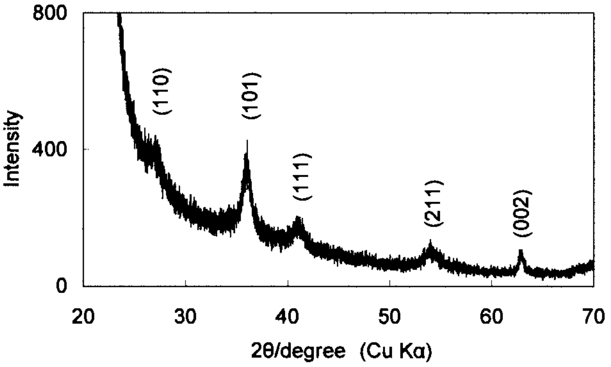

Figure 3. A representative XRD pattern for the rutile foil synthesized at the $TiOSO_4$ concentration of 0.01 M and the initial pH value of 0.50, and kept at 60 °C for 5 days. Broaden tail at the lower angle is attributed adhesive tape fixing a self-standing foil.

References and Notes

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