Development of Super-Hydrophilicity on Nitrogen-Doped TiO₂ Thin Film Surface by Photoelectrochemical Method under Visible Light

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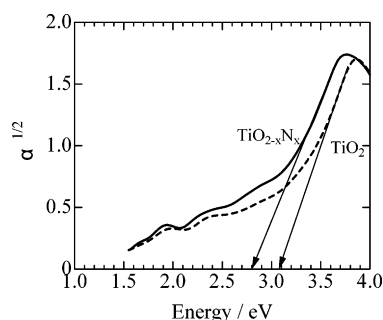*Research Center for Advanced Science and Technology, The University of Tokyo 4-6-1 Komaba, Meguro-ku, Tokyo 153-8904, Japan*

Titanium dioxide (TiO_2) has been a well-known photocatalytic material[1-4] for the past few decades. When UV light is irradiated on TiO_2, electron and hole pairs are generated and they will produce powerful radical species, and they are capable of decomposing most organic compounds.[5,6] In 1997, the behavior of the super-hydrophilicity on TiO_2 film surface was discovered,[7] and there have been plans to use this technology in many practical applications such as self-cleaning, water and air purifications, etc. For this achievement, such super-hydrophilic state of TiO_2 surface needs UV light with the intensity of natural sunlight, so the development of a photocatalyst sensitive in visible light irradiation condition is important for indoor use. Several approaches have been used to modify the semiconducting-natured TiO_2 for use in visible light. The main approaches were doping transition metal into TiO_2,[8] fabricating reduced TiO_{2-x} photocatalyst,[9] and substitutional doping[10] of nitrogen in TiO_2. The substitutional doping of nitrogen is effective because its p states contribute to the formation of narrow band by not mixing with O 2p states or to the band-gap narrowing by mixing with O 2p states. Since the nitrogen-doped TiO_2 film ($TiO_{2-x}N_x$) absorbs visible light, we have decided to use the visible light active $TiO_{2-x}N_x$ film for the development of super-hydrophilicity under different potential controlled condition with visible light irradiation.

The polycrystalline thin films were prepared on SnO_2-coated glass plates using sputtering method (Ti metal target under a N_2O(80SCCM)/Ar(20SCCM) gas mixture, annealing temperature 400 °C). Pure anatase phase was confirmed by XRD and nitrogen substitution at oxygen

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Figure 1. Transformed plot of (a) TiO_2 and (b) $TiO_{2-x}N_x$ films coated on conductive glass substrate.

sites by XPS, showing the peak at 396 eV.[11] The nitrogen concentration was estimated to be 6 atm%. The thin film thickness (200 nm) and its roughness (R_a, 24 nm) were measured. A Xe–Hg lamp was used as light source with proper optical filters to cut the UV light. The hydrophilicity of the sample was measured (at 25 °C, 50% RH) by the water contact angle with a commercial contact angle meter (FACE CA-X).

The TiO_2 and $TiO_{2-x}N_x$ were transparent and showed whitish and yellowish color, respectively. An absorbance spectrum of the $TiO_{2-x}N_x$ revealed that both the shift of absorption edge (approximately 20 nm) to the visible light region and the new absorption shoulder at around 400–550 nm were observed and that they were related to the nitrogen doping, since TiO_2 does not absorb such visible light regions. Assuming the $TiO_{2-x}N_x$ to be an indirect semiconductor, as is TiO_2, a plot of the square root of the absorbance coefficient versus the energy of light affords the band gap energy as shown in Figure 1. The band gaps optically obtained in such a way were approximately 3.1 and 2.8 eV for the TiO_2 and $TiO_{2-x}N_x$, respectively.

Since TiO_2 and $TiO_{2-x}N_x$ films were optically transparent, we used the spectroelectrochemical method[12,13] for determining the flatband potential (E_{fb}). Figure 2 shows the absorbance measured at 700 nm at each applied potential versus −0.20 V as reference. The potential for the $TiO_{2-x}N_x$ where the increase in absorption started (approximately −0.55 V) slightly shifted to the positive direction (anodic shift), compared with the TiO_2 (approximately −0.70 V, which is consistent with the value reported by Fitzmaurice et al.[13]). Therefore, the E_{fb} for the $TiO_{2-x}N_x$ electrode was a little more positive (approximately 0.15 V) than that for the TiO_2 electrode.

As Iimura et al. reported that the introducing oxygen vacancies leads to the anodic shift of the E_{fb},[14] the increase in the oxygen vacancies could be considered accompanied by nitrogen doping. As the assumption can be made that the difference between E_{fb} and the bottom edge of the conduction band is negligible,[14] the electro-

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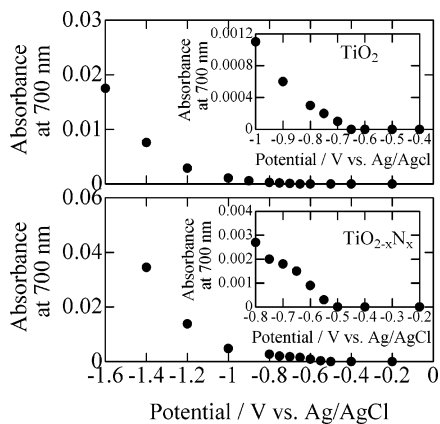
Figure 2. Changes in absorbance at 700 nm between those measured at each potential and those measured at -0.20 V for (a) TiO_2 and (b) $TiO_{2-x}N_x$ film electrodes.
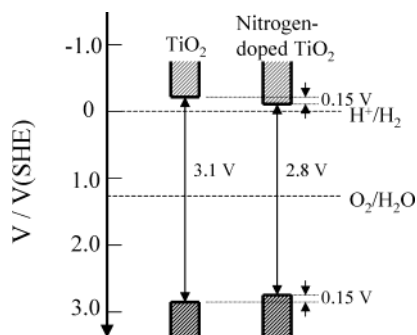
**Figure 3.** Schematic explanations of band gap narrowing for $TiO_{2-x}N_x$ thin film.

chemical potentials for the $TiO_{2-x}N_x$ could be estimated as shown in Figure 3; that is, the band gap of $TiO_{2-x}N_x$ was narrowed by shifting of the top edge of the valance band to the negative direction due to the mixture of N2p and O2p states and of the bottom edge of the conduction band to the positive direction (anodic shift) due to the generation of oxygen vacancies. The nitrogen doping in TiO_2 did not lead to the change in the position of the valence band edge and did lead to the generation of a manifold of surface states that were located close to the valence band edge.

The cyclic voltammograms of the TiO_2 and $TiO_{2-x}N_x$ thin film electrodes in 0.01 M sodium sulfate solution were obtained in the dark and light irradiation (UV and visible light separately) conditions (not shown here). Anodic currents were not observed in the dark in either of the films. No anodic photocurrent was observed in TiO_2 thin film under visible light irradiation, however the anodic photocurrent was observed in $TiO_{2-x}N_x$ thin film under visible light irradiation condition. Anodic photocurrents were observed under UV light irradiation in both films. In the $TiO_{2-x}N_x$ thin film, the anodic photocurrent was observed under visible light irradiation and increased with increasing the incident visible light intensity as shown in Figure 4. This type of light intensity dependence on photocurrent shows the characteristic of the n-type semiconductor electrodes.[15]

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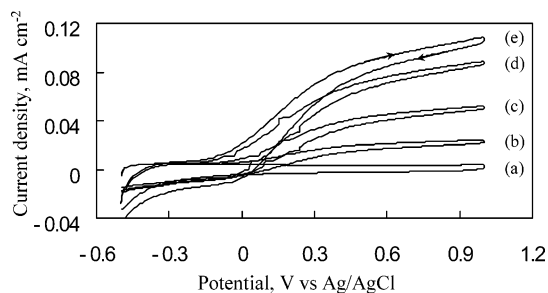
Figure 4. Cyclic voltammogram of $TiO_{2-x}N_x$ film electrode in 0.01 M sodium sulfate solution (a) in dark, and under visible light with intensity of (b) 1.1, (c) 2.1, (d) 4.1, and (e) 5.2 mW/cm². Scan rate is 100 mV/sec.
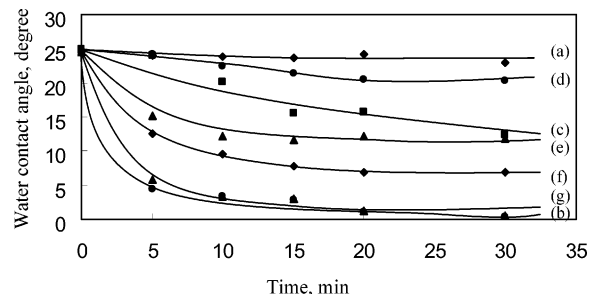
Figure 5. Changes of water contact angle of the $TiO_{2-x}N_x$ film electrode at various conditions: (a) in the dark at 1.0 V; under visible light irradiation at (b) 1.0 V, (c) without bias, (d) -0.8 V, (e) -0.5 V, (f) 0.0 V, and (g) $+0.5$ V. Visible light intensity was 5.2 mW/cm².

Figure 5 shows the changes of hydrophilicity on the $TiO_{2-x}N_x$ thin film by applying different anodic oxidation potentials under visible light irradiation and dark conditions. In the dark condition even applying an anodic oxidation potential (1.0 V), there was no change in the hydrophilic conversion (Figure 5a). However, in the presence of visible light and applying anodic oxidation potential (1.0 V) led to super-hydrophilicity on the $TiO_{2-x}N_x$ film within thirty minutes as shown in Figure 5b. The change of hydrophilicity on the $TiO_{2-x}N_x$ film was studied only in the presence of visible light and is shown in Figure 5c. Visible light alone could decrease the water contact angle at a certain level about $15\pm1°$, however, it could not make super-hydrophilicity on the film. The change of water contact angle measured in the negative potential region (-0.8 and -0.5 V) in the presence of visible light condition is shown in Figure 5d and e, respectively. Less decrease of water contact angle was observed in -0.5 V, due to the lower charge separation. Figure 5f and g show the decrease of water contact angle on the $TiO_{2-x}N_x$ film by applying different anodic oxidation potentials under visible light conditions. The super-hydrophilic conversion was enhanced by applying higher anodic potentials. This could be due to the efficient charge separation by the anodic potentials and it led to the better transformation of holes to the $TiO_{2-x}N_x$ surface. The detailed investigations are underway.