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# Synthesis and Characterization of S-Doped $TiO_2$ Made by Anodic Oxidation of Titanium in Sulfuric Acid

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$TiO_2$ coating doped with S ions was made by the anodic oxidation process of the titanium sheet in sulfuric acid. $TiO_2$ coating on titanium plate prepared by the anodic oxidation possessed many nanohole-like pores. XPS results showed that $S^{6+}$ and $S^{2-}$ were incorporated in $TiO_2$ coating after anodic oxidation. These S-doped $TiO_2$ coatings showed the high photocatalytic activity.

Many studies have been carried out to improve the photocatalytic activity of $TiO_2$. Especially, the syntheses of $TiO_2$ with high photocatalytic activities under visible light were attempted by doping ions (N, S, C, P ions, etc.) into $TiO_2$.[1–6] Asahi et al. reported that N-doped $TiO_2$ prepared by sputtering possessed high activity under visible light.[1] Two types of S-doped $TiO_2$ were reported by Umebayashi et al.[2] and Ohno et al.[3,4] by chemical and thermal treatments for improving photocatalytic activities under visible light. Umebayashi et al. synthesized S-doped $TiO_2$ by oxidative annealing of $TiS_2$ and $S^{2-}$ ions as an anion were incorporated into $TiO_2$.[2] However, in case of Ohno et al.,[3,4] the calcinations of $TiO_2$ from hydrolysis of titanium alkoxide with thiourea resulted in S-doped $TiO_2$, in which $S^{6+}$ ions are incorporated as a cation in $TiO_2$.

Here, S-doped $TiO_2$ coatings were successfully made by simple anodic oxidation process of titanium for short time. Anodic oxidation process is an old technique for a surface modification of metal like Al and Ti.[7,8] Recently, Nakahira et al. reported that N-doped $TiO_2$ powders with high surface area were prepared by anodic oxidation of titanium.[9] In this study, the microstructure and photocatalytic properties for S-doped $TiO_2$ coating on titanium sheet made by anodic oxidation were evaluated.

Especially, the structure information of S-doped $TiO_2$ coatings was investigated by XPS and XANES measurements. The decomposition of formic aldehyde was measured.

Titanium sheet ($10 \times 10 \times 0.4\,mm^3$) was polished using abrasive paper and subsequently chemically etched with aqueous $HNO_3$:HF (=3:1) solution. A carbon rod (diameter: 5 mm) was used as a cathode. Electric source was applied with direct-current power in the range of 20 to 150 V. Samples were prepared by anodic oxidation for 3 min at room temperature in 0.5 M $H_2SO_4$. Samples were analyzed by thin film XRD. The microstructures were observed with SEM (Hitachi-S4500). The chemical states of S in $TiO_2$ coating were studied by X-ray photoelectron spectrum (XPS, ULVAC-PHI 5500MT) and X-ray absorption fine structure (XAFS, BL01, UVSOR). Photocatalytic activity for a piece of sample of titanium sheet with $TiO_2$ coatings was investigated by decomposition of formic aldehyde in a transparent glass apparatus under fluorescent lamp (40 W) irradiation. The concentration of formic aldehyde (initial concentration of 20 ppm) was usually measured in glass apparatus.

$TiO_2$ coating (approximately 10 μm in thickness) attached to the surface of titanium sheet for samples made by anodic oxidation at the voltage over 50 V. From SEM observation, the oxidation coating on titanium sheet has many one-dimensional pores with 20 to 50 nm in diameter, nanohole-like pores.[6,9] These nanopores in $TiO_2$ coatings were generated for samples anodized at the voltage over 100 V. With the applied voltage less than 120 V, no nanopores existed. XRD results show that the $TiO_2$ formed on titanium sheet was anatase for samples anodized at 80 to 120 V and a mixture of anatase and rutile for samples anodized at 150 V. In case of anodic oxidation at 50 V, no crystalline $TiO_2$ was detected.

Figure 1 shows XPS spectra of $TiO_2$ coatings prepared by anodic oxidation in a condition of electrolytic solution in $H_2SO_4$ with 150 V. Before etching, signal occurred around 168 eV, which is attributed to $S^{6+}$ state and diminished after Xe etching treatment. Ohno et al. reported that the signal detected around 170 eV was caused by both the adsorbent of $S^{6+}$ species, such as $H_2SO_4$, and the interstitial or substitutional incorporation into $TiO_2$.[3,4] Therefore, in this study, it is speculated that the peak of 168 eV is caused by Ti–$SO_4$ bond or structure of $SO_4{}^{2-}$ remaining in near-surface $TiO_2$ coating.

After etching, small signal around 161 eV was detected instead of 170 eV from $S^{6+}$ state. According to Umebayashi

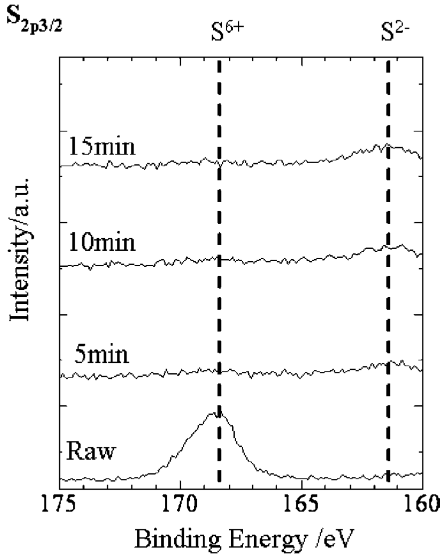

**Figure 1.** XPS depth profile spectra of samples by anodic oxidation process in 0.5 M $H_2SO_4$ at 150 V with various etching times. Raw denotes samples before etching.

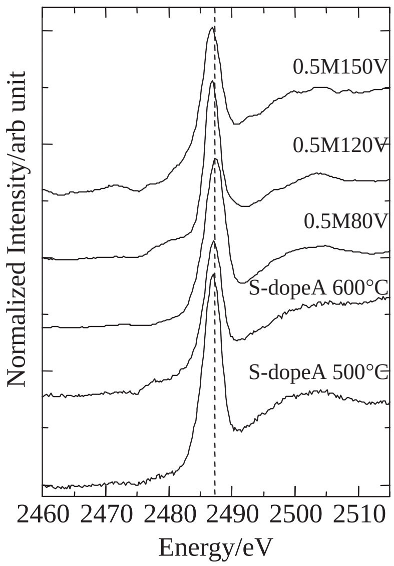

**Figure 2.** S K-edge XANES spectra of various samples prepared by anodic oxidation process. S-Doped A was a reference material.

et al.,[2] $S^{2-}$ signal around 160 eV was associated with S forming Ti–S bond in $TiO_2$, and a trace of amount of S ions remains in the annealed sample as substituted atoms at O sites. In our case, it is speculated that $S^{2-}$ as an anion existed in the $TiO_2$ on titanium sheet without heat treatment for samples after the anodic oxidation treatment, although its peak intensity was weak. Therefore, a small amount of $S^{2-}$ ion was substituted as an anion for oxygen in $TiO_2$ coating through the anodic oxidation process at room temperature. It is thought that $S^{2-}$ resulted from the reduction of $S^{6+}$ species such as $SO_4{}^{2-}$ during the anodic oxidation reaction and consequently $S^{2-}$ ions were doped into $TiO_2$ coating.

Figure 2 shows XANES spectra of $TiO_2$ coatings on titanium sheet by anodic oxidation at 150 V in 0.5 M $H_2SO_4$. For a comparison, S-doped $TiO_2$ (denoted by S-doped A) was prepared by Ohno's method. The peaks for both our samples and S-doped A were conformed. Therefore, samples prepared by anodic oxidation process show the same local structure of S-K edge as S-doped A. These results suggest that S ions were doped in $TiO_2$ coatings made by anodic oxidation.

Figure 3 shows decomposition results of formic aldehyde for S-doped $TiO_2$ coatings prepared by anodic oxidation at 150 V. Concentration of formic aldehyde decreased with time. Although $TiO_2$ was approximately 0.015 g for $TiO_2$ coatings on titanium sheet, these S-doped $TiO_2$ coatings possessed the high photocatalytic activity as well as P-25 $TiO_2$.[6,9]

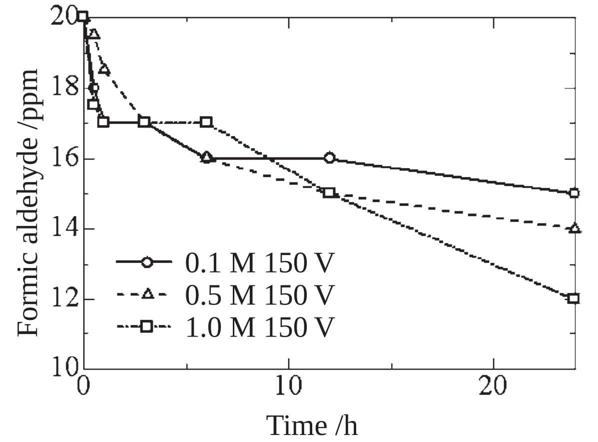

**Figure 3.** Photocatalytic decomposition of formic aldehyde for samples by anodic oxidation at 150 V with $H_2SO_4$ (0.1 to 1.0 M).

In this study, S-doped $TiO_2$ coating on titanium sheet was easily prepared by anodic oxidation process in $H_2SO_4$ for short time and had many nanohole-like pores.

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