

## Visible Light-Induced Degradation of Methylene Blue on S-doped TiO<sub>2</sub>

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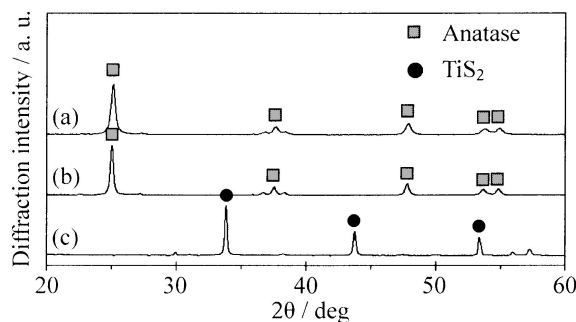
A sulfur (S)-doped titanium dioxide (TiO<sub>2</sub>) photocatalyst was synthesized by oxidative annealing of titanium disulfide (TiS<sub>2</sub>). TiS<sub>2</sub> turned into anatase TiO<sub>2</sub> when annealed in air. The residual S atoms occupied O-atom sites in the TiO<sub>2</sub> to form Ti-S bonds. The S doping caused the absorption edge of TiO<sub>2</sub> to be shifted into the lower energy region. Consequently, methylene blue adsorbed on the S-doped TiO<sub>2</sub> was photocatalytically decomposed by visible light irradiation.

The photocatalytic decomposition of pollutants in water and air has attracted much interest for several decades.<sup>1</sup> Although titanium dioxide (TiO<sub>2</sub>) is the most popular photocatalytic material,<sup>2</sup> it is active only in the ultraviolet (UV) region because of its wide band gap. Therefore, many researchers have attempted to modify the electronic properties of TiO<sub>2</sub> in order to extend its optical absorption edge into the visible light region and to improve the photocatalytic activity.<sup>3-9</sup> Recently, some groups have carried out the substitution of a nonmetal atom, such as nitrogen (N)<sup>4-6</sup> and fluorine (F),<sup>7</sup> for oxygen (O). For example, Asahi et al.<sup>4</sup> showed that N doping shifted the absorption edge to a lower energy, thereby increasing the photocatalytic activity in the visible light region. These studies demonstrated that the doping with a nonmetal can provide an effective modification of the electronic structures of TiO<sub>2</sub>.

Although the previous theoretical study showed that the S doping into TiO<sub>2</sub> contributed to the band gap narrowing, it was considered that the S-doping was difficult to carry out due to the large formation energy required for the substitution of S for O in TiO<sub>2</sub>.<sup>4</sup> Contrary to this expectation, the S-doped anatase TiO<sub>2</sub> polycrystalline powder, including S substituted for O, was synthesized by the oxidative heating of the titanium disulfide (TiS<sub>2</sub>) powder.<sup>8</sup> The S-doping caused the photon-to-carrier conversion in the energy region below the band gap of pure TiO<sub>2</sub>.<sup>9</sup> The photocatalyst applications of the S-doped TiO<sub>2</sub>, therefore, are of great importance. In this letter, we report the optical and photocatalytic properties of the S-doped TiO<sub>2</sub> synthesized by oxidative heating of the TiS<sub>2</sub> powder.

The TiO<sub>2</sub>-based polycrystalline powder samples, including S substituted for O, were prepared by heating the TiS<sub>2</sub> powder (High Purity Chemicals Laboratory Co., Ltd.) in air. The annealing was performed under different conditions, i.e., at 500 °C for 90 min or at 600 °C for 24 h. After the thermal treatments, the color of the powders changed from black to beige (500 °C) or white (600 °C).

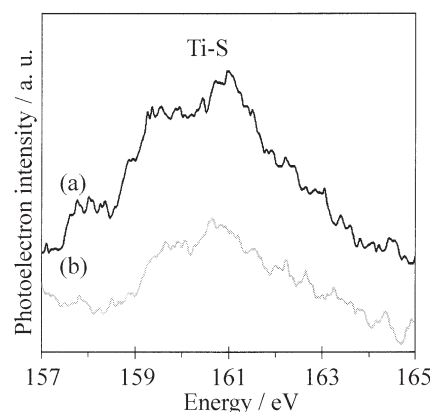
Figure 1 shows the X-ray diffraction (XRD) patterns (Cu K $\alpha$ ,  $\lambda = 1.542 \text{ \AA}$ ) of the annealed samples and standard pure TiS<sub>2</sub> powder. A single phase of anatase TiO<sub>2</sub> appeared in the patterns of the annealed samples, irrespective of the heating conditions. It



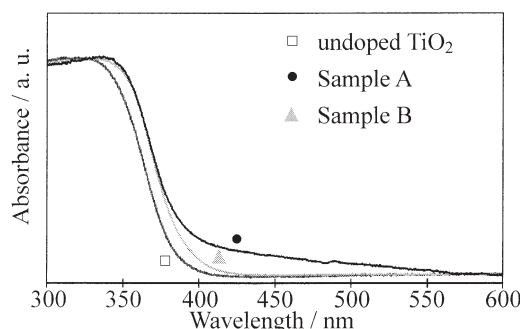
**Figure 1.** XRD patterns for the annealed TiS<sub>2</sub> (a) at 500 °C for 90 min or (b) at 600 °C for 24 h, compared to (c) pure TiS<sub>2</sub> as a reference.

is thus considered that the TiS<sub>2</sub> powder is completely transformed into the anatase TiO<sub>2</sub> powder.

Figure 2 shows the X-ray photoelectron spectroscopy (XPS) spectra (S 2p core level) after Ar<sup>+</sup> etching (1 Å/min) for 15 min of the anatase TiO<sub>2</sub> powders prepared by the annealing of TiS<sub>2</sub>. As seen in both the spectra, a signal occurred around 160 eV. This signal is associated with S forming Ti-S bonds in the TiO<sub>2</sub>.<sup>8</sup> Therefore, a trace amount of S atoms would remain in the annealed sample as homogeneously distributed substitutional atoms at the O sites. Compared to spectrum (a), the signal intensity was smaller for (b), indicating the decrease in the doping amount. Probably, there is an evaporation of S as a volatile



**Figure 2.** XPS spectra after the Ar<sup>+</sup> etching (1 Å/min) for 15 minutes of the anatase TiO<sub>2</sub>-based powders prepared by the annealing of TiS<sub>2</sub> (a) at 500 °C for 90 min or (b) at 600 °C for 24 h.

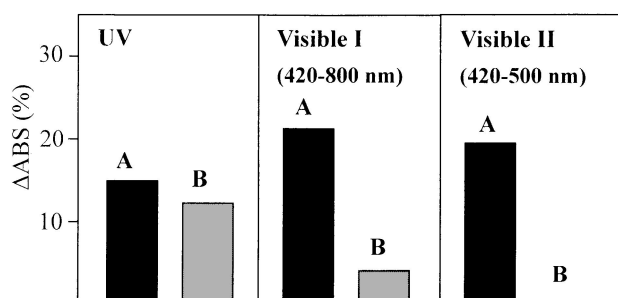


**Figure 3.** DRS spectra of undoped TiO<sub>2</sub> and S-doped TiO<sub>2</sub> prepared by the annealing of TiS<sub>2</sub> at 500 °C for 90 min (sample A) or at 600 °C for 24 h (sample B).

component from the TiO<sub>2</sub> surface during the annealing at 600 °C for 24 h.

We investigated the optical and photocatalytic properties of the S-doped anatase prepared by the annealing of TiS<sub>2</sub> at 500 °C for 90 min (sample A) or 600 °C for 24 h (sample B). Figure 3 shows the diffuse reflectance spectra (DRS) of these doped samples and undoped TiO<sub>2</sub> (as a reference). The optical absorption edge was shifted into the lower energy region in the spectra of the S-doped samples. The shift of the absorption edge for sample A was larger than that of sample B. The increase in the doping level would enhance the absorption of visible light. Based on the band calculation results, the mixing of the S 3p states with VB increases the width of the valence band itself and causes the lower energy shift in the optical absorption.<sup>8</sup>

The photocatalytic activities were evaluated in air by measuring the decomposition rates of methylene blue (MB) adsorbed on the surface of the pellets of S-doped samples (A and B). A black light fluorescent tube was used as the UV light source, while the light of a halogen lamp was cut by some color filters to produce two kinds of the visible light source, region I (420-800 nm) and II (420-500 nm). The absorbance of MB, ABS, was estimated by taking ratio of the intensities of the incident ( $I_0$ ) to reflected light ( $I_r$ ) of a He-Ne laser ( $\lambda = 633$  nm) on the surface:  $ABS = \log(I_0/I_r)$ . Figure 4 shows the change in the absorbance of MB after 10 min of UV or visible light irradiation. The



**Figure 4.** Change in the absorbance  $\Delta ABS = 100 \times (1 - A(10)/A(0))$  of MB on S-doped TiO<sub>2</sub> prepared by the annealing of TiS<sub>2</sub> at 500 °C for 90 min (sample A) or at 600 °C for 24 h (sample B), where A(0) and A(10) are absorbance of MB before and after UV or visible light irradiation for 10 min, respectively.

photocatalytic activity of sample A and B was comparable to that of the undoped anatase (not shown) during UV light irradiation. Under the irradiation of the region I light, the decomposition of MB on sample A and B was observed. In sample B, which does not absorb this region light, the electron injection from the photoexcited dye into the conduction band would contribute to the degradation of MB, so called self-photodegradation of a colored organic contaminant.<sup>10</sup> Because MB cannot be photoexcited by the region II light, this light did not decompose the dye on sample B as well as the undoped anatase. On the other hand, sample A, exhibiting the optical absorption at wavelengths of <550 nm, showed a large color decrease even in region II.

According to our preliminary experiments, the ABS of MB on the sample A decreased continuously during the irradiation of the region II light, along with a slight blue shift of the spectrum due to the *N*-demethylation.<sup>11</sup> Because this photobleaching process doesn't originate from the self-photodegradation, there are two possibilities for their mechanisms: photocatalytic decomposition of MB and production of the doubly reduced form of MB, *leuco*-MB, i.e. LBM.<sup>12</sup> The former reaction is irreversible, while the latter is reversible and causes recoloration because LBM easily return into MB. In our sample, actually, recovery in the blue coloration due to MB was observed after the visible light irradiation. However, such a recoloration was not significant, in other words, the reduced absorbance of MB did not reach the initial level. These results undoubtedly mean that the decomposition of MB on sample A under the visible light irradiation is due to the photocatalytic oxidative reactions.

In summary, S-doped anatase TiO<sub>2</sub> was prepared by the annealing of TiS<sub>2</sub>. The S-doped TiO<sub>2</sub> exhibited a red-shift in the optical absorption edge from the undoped TiO<sub>2</sub>, consequently, the photoexcited carriers in the S-doped TiO<sub>2</sub> induced the photocatalytic decomposition of MB under the visible light irradiation. This compound should be effective as a novel visible light photocatalyst.

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