Photocatalytic Activity of S-doped TiO_2 Photocatalyst under Visible Light

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In order to effectively utilize visible light in photocatalytic reactions, we have developed S-doped TiO_2 particles. They show strong absorption for visible light and high activities for degradation of methylene blue in aqueous solution under irradiation at wavelengths longer than 440 nm. The oxidation state of the S atoms incorporated into the TiO_2 particles is determined to be S^{6+} from the XPS spectra.

After the discovery of photoinduced water splitting at titanium dioxide (TiO_2) electrodes,[1] the phenomena have been applied to TiO_2-mediated heterogeneous photocatalyses.[2–17] Because electrons and holes photogenerated in the TiO_2 photocatalysts have strong reduction and oxidation power, respectively, they can drive a variety of reactions. By utilizing this property, it has been reported that pollutants in air and water can be effectively decomposed.[2–6] It has also been reported that unique organic synthetic reactions occur on irradiated TiO_2.[7–17] Most of these investigations have been carried out under UV light, because TiO_2 absorbs light of wavelength 400 nm or shorter.

In order to utilize sunlight or rays from artificial sources more effectively in photocatalytic reactions, photocatalysts with strong absorption in the visible region should be developed. For this purpose, doping of TiO_2 with transition metals has been investigated.[18,19] Treatment of TiO_2 powder with hydrogen peroxide[20] or chelating agents[21] allows some kind of photocatalytic reactions to proceed under visible light. However, most of these catalysts do not show long term stability or do not have activities high enough for a wide range of applications. Asahi et al.[22] reported that N-doped TiO_2 shows photoabsorption at wavelengths longer than 400 nm. It has also been reported that the N-doped TiO_2 has photocatalytic activity under visible light. Recently, Umebayashi et al. have also succeeded in synthesizing TiO_2 doped with S atoms.[23] The compound absorb visible light. This result is supported by a theoretical calculation using full-potential linearized augmented plane wave formalism.[22] However, the absorption spectra of these compounds in the visible region are extremely small. It is noted that the dopants are incorporated as anions and take the place of oxygen in the lattice of TiO_2.

Here, we report synthesis of new S-doped TiO_2 powders. In contrast to the S-doped TiO_2 reported by Umebayashi et al., S atoms are incorporated as cations and are expected to be replaced with Ti ions. Furthermore, these powders absorb visible light more strongly than the N-doped TiO_2 and the S-doped TiO_2 powders, and show photocatalytic activity under visible light.

For synthesizing the S-doped TiO_2 powders, titanium isopropoxide (50 g, 0.175 mol) was mixed with thiourea (53.6 g, 0.70 mol) at a molar ratio of 1 to 4 in ethanol (500 mL). The solution was stirred at room temperature for 1 h and evaporated completely under reduced pressure. After evaporation of ethanol, white powder was obtained. We calcined the powder at different temperatures under aerated conditions, and obtained yellow powder. We call this powder S-doped TiO_2, because a small amount of S atoms, but no C and N atoms, are included in it, as shown later.

The density of the yellow color depends on the calcination temperatures. Some examples of diffuse reflectance spectra of these powders, together with pure rutile and anatase powders, are shown in Figure 1. Photoabsorption in the visible region is strongest when the powder was calcined at about 500 °C. The photoabosorption in the visible region is stronger than that of the N-doped TiO_2 powder, which was prepared according to the literature.[21] With the increase of the calcination temperature above 500 °C, the absorption in the visible region decreases gradually. When it reaches 700 °C, the absorption decreases drastically. Despite the drastic decrease of the absorption in the visible region, the S-doped TiO_2 powder calcined at temperatures higher than 700 °C keeps strong photoabsorption at wavelengths near 400 nm (see Figure 1).

The relative surface area of S-doped TiO_2 powders was determined by the BET method using a surface area analyzer (Micromeritics, FlowSorb II 2300). When the powder was calcined at 400 °C for 3 h, the surface area was 75.8 m^2/g. The surface area decreases with increasing calcination temperature (Table 1). Contents of the anatase and rutile phases in the S-doped TiO_2 powders were determined from the X-ray diffraction (XRD) patterns obtained by using an X-ray diffractometer (Philips, X'Pert-MRD) with a Cu target Kα-ray ($\lambda = 1.5405$ Å). The

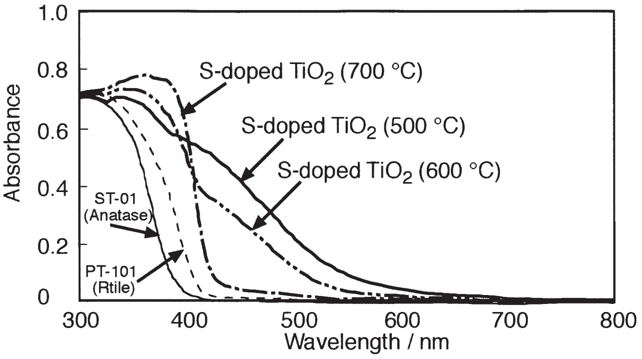

Figure 1. Diffuse reflectance spectra of S-doped and pure TiO_2 powders.

Table 1. Specific surface area and content of anatase phase of S-doped TiO_2 powders calcined under different conditions

Calcination temperature /time	Specific Surface area /m^2/g	Content of anatase /%
400 °C/3 h	75.8	100
400 °C/10 h	60.1	100
500 °C/3 h	17.7	99
500 °C/10 h	16.9	97
600 °C/3 h	9.3	43
600 °C/10 h	8.7	38
700 °C/3 h	5.3	0
700 °C/10 h	4.9	0

content of the anatase phase in the particles is also shown in Table 1. By comparing the changes of the diffuse reflectance spectra and the contents of the anatase phase, one can conclude that the anatase particles are strongly colored. However, it should also be noted that the rutile powder still shows weak photoabsorption in the visible region; see the spectrum of S-doped TiO_2 (700 °C) in Figure 1.

The chemical states of S atoms incorporated into TiO_2 were studied by measuring the XPS spectra of the S-doped TiO_2. From the results, it was found that S atoms are in the state of S^{2-} before the calcination of the sample. By calcination under aerated conditions at temperatures above 400 °C, the S2p(3/2) peak appears at 170 eV, which is attributed to S^{6+} state, as shown in Figure 2. By washing the powder with deionized water and HCl aqueous solution for several times, the XPS peak due to S^{6+} is lowered, suggesting that S^{6+} species such as sulfuric acid are adsorbed on the surface of TiO_2. However, it should be emphasized that a weak peak attributable to S^{6+} remains after complete washing. The peak was also observed after the Ar^+ ion etching of the sample. The atomic content of S atoms on the surface of the S-doped powder is about 1.6% after the washing treatment. With the increase of the depth from the surface of TiO_2, the concentration of S^{6+} decreases gradually to about 0.5% in the bulk. These results strongly indicate that S atoms are incorporated into the balk phase of TiO_2. It is important to note that no peak attributable to C and N atoms was observed after calcination of the S-doped TiO_2 powders.

By comparing the XRD patterns of the S-doped TiO_2 powders with those of pure anatase and rutile powders having nearly the same particle sizes, we found that the S-doped samples show broader peaks than those of pure TiO_2 samples. On the other hand, the peak positions are nearly the same. These results suggest that the crystal lattices of S-doped TiO_2 powders are locally distorted by incorporating S^{6+} species into TiO_2, while the averaged unit cell length is unchanged. Whether the S^{6+} species are introduced interstitially or at the lattice sites is to be clarified. However, the distortion of the local lattice is probably responsible to the absorption in the visible region and to the shift of the onset of their absorption edge near 400 nm.

Photocatalytic activity of the S-doped TiO_2 powders was evaluated by measuring the decomposition rates of methylene blue ($50\ \mathrm{mmol\ dm^{-3}}$) in aqueous solution (5 mL) containing 100 mg of the TiO_2 photocatalyst. As the photocatalyst S-doped TiO_2 or pure TiO_2 powder (Degussa, P-25) was used. As the light source a 1000 W Xe lamp was used, and the short-wavelength components of the light was removed using cutoff glass filters with different cutoff wavelengths. Under UV irradiation, the activity of S-doped TiO_2 was a little lower than that of pure TiO_2. However, under irradiation at wavelengths longer than 440 nm, only S-doped TiO_2 showed the activity. Figure 3 shows the activities of S-doped TiO_2 (calcined at 500 °C for 3 h) and pure TiO_2 (Degussa, P-25), as a function of the cutoff wavelengths of the glass filters. In addition, no degradation of methylene blue was observed in the absence of TiO_2 powders or without irradiation.

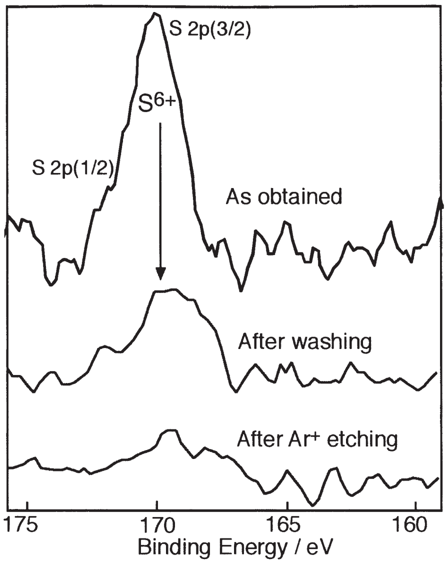

Figure 2. XPS spectra of S-doped TiO_2 powder (calcined at 500 °C).

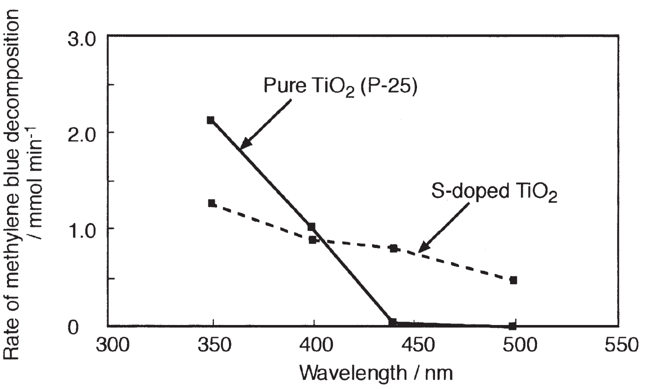

Figure 3. Photocatalytic decomposition of methylene blue using S-doped TiO_2 or pure TiO_2 as a function of the cutoff wavelength for irradiation from a 1000 W Xe lamp.

It is of importance that we obtained a new class of TiO_2 powder which shows photocatalytic activity under visible light. We expect that the activity will be much improved by optimizing the preparing conditions of the S-doped TiO_2 powders.

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