## Preparation of S-Doped TiO<sub>2</sub> and Their Photocatalytic Activity Under Visible Light

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**1.** Introduction In this paper, we report that preparation S-doped  $TiO_2$  and their photocatalytic activities under visible light. We have investigated the oxidation of adamantane and methylene blue dissolved in acetonitrile or water on pure  $TiO_2$  and S-doped  $TiO_2$  powder under UV or Visible light.

2. Methods *Preparation of S-doped TiO*<sub>2</sub> *powders* The S-doped TiO<sub>2</sub> powder can be obtained the following procedure. The TiO<sub>2</sub> colloids ethanol solution contained thiourea were prepared. After evaporating the solvent under reduced pressure, the white residues were obtained. After calcinations of the residues at 400 ~900°C, the yellow colored S-doped TiO<sub>2</sub> powders were obtained. Absorption spectra of these powders are as shown in Fig.1. The S-doped TiO<sub>2</sub> powder shows a large red shift of absorption (Fig. 1). Absorption edge of these photocatalysts was shifted to the wavelengths between 600 and 700 nm, while pure TiO<sub>2</sub> powders having anatase or rutile phase show their absorption edge between  $390 \sim 410$  nm.

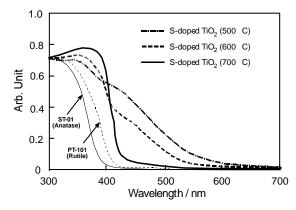


Fig. 1. Absorption Spectra of S-doped TiO<sub>2</sub> Powders

**3. Results** *Photocatalytic oxidation of adamantane using pure TiO*<sub>2</sub>. Photocatalyzed oxidation of adamantane has been investigated using several kinds of TiO<sub>2</sub> powders in mixed solvent of acetonitrile and butyronitrile under aerated conditions. Using any kinds of TiO<sub>2</sub> powders having anatase and rutile phases used as photocatalysts, 1-adamantanol, 2-adamantanol, and 2-adamantanone were obtained as main products after photoirradiation in which 1-adamantanol was produced at the highest yield. Among the TiO<sub>2</sub> powders investigated, an anatase powder (ST-41) having small surface area shows the highest activity as shown in Fig.2. These results suggested that the

developing the band vending in  $TiO_2$  particles needed to proceed this reaction effectively. The quantum efficiencies of the production of 1-adamananol, 2-adamantanone, and 2-adamantanol are 6.4%, 2.0%, and 1.0%, respectively.

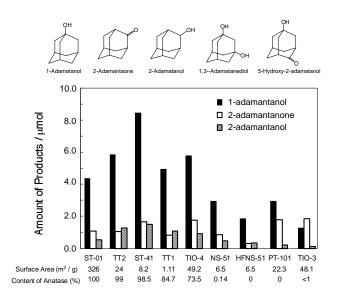


Fig. 2. Photocatalytic oxidation of adamantane using pure  $TiO_2$  Powders

S-doped TiO<sub>2</sub> photocatalyzed oxidation of organic compounds under visible ligh.t. We have been recently succeeded in preparing S-doped TiO<sub>2</sub> photocatalysts which show potocatalytic activity under visible light as described above. The oxidation of adamantine or methylene blue using the S-doped TiO<sub>2</sub> powders effectively proceeds under visible light at the wavelength longer than 500nm. The results for the oxidation of adamantine are as shown in Fig. 3. Under the same condition, no activity shows for the reaction using pure TiO<sub>2</sub> powders.

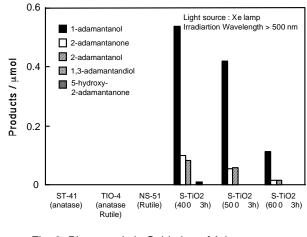


Fig. 3. Photocatalytic Oxidation of Adamantane Using TiO<sub>2</sub> Powders

## 4. Conclusions

These findings open the door to the utilization of visible light in the photocatalytic oxidation of organic compounds using  $TiO_2$  photocatalyts, and to the effective utilization of solar light.