Preparation Carbonate species-doped TiO_2 and its photocatalytic activity under visible light irradiation

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Abstract Carbonate (CO_3^{2-}) species-doped titanium dioxide (TiO_2) photocatalysts were prepared. By doping carbonate species into a TiO_2 lattice, the absorption edge of TiO_2 was largely shifted from 400 nm to 700 nm. Furthermore, methylene blue was photocatalytically decomposed at high efficiency on carbonate species-doped TiO_2 photocatalysts under visible light at a wavelength longer than 550 nm.

Experimental Carbonate species-doped TiO_2 powders having an anatase phase were prepared as follows. Thiourea and urea were mixed with an anatase TiO_2 powder in an agate mortar. The mixed powder was packed in a lidded double alumina crucible and calcined at 400 and 500 °C under aerated conditions for 5 h. The resulting samples were dark orange in color and were found by using an X-ray diffractometer (XRD) to have a homogenous anatase phase. The surface areas of the resulting powders calcined at 400 and 500 °C are 180, and 87.0 m^2/g, respectively.

Results and discussion In order to investigate the chemical states of C, N and S atoms incorporated into TiO_2, C 1s, N 1s, and S 2p binding energies were

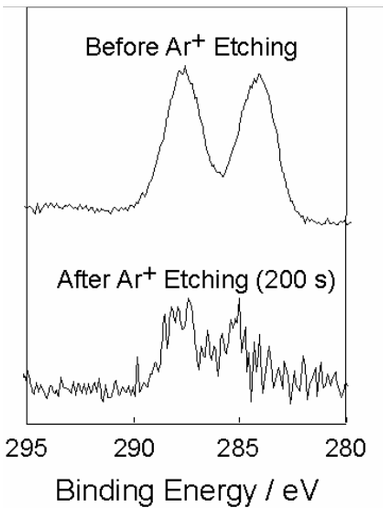

Figure 1. XPS spectra (C1s) of carbonate species-doped TiO_2 calcined at 400°C.

measured by X-ray photoemission spectroscopy (XPS). The results are shown in Fig. 1. Peaks at 284 and 288 eV were observed by XPS measurements of the C 1s binding energy of the resulting powders calcined at 400 and 500 °C. The peak around 284 eV was assigned to carbon adsorbed on the surface of TiO_2 as a contaminant. The latter peak around 288 eV suggests the presence of a carbonate species. The atomic contents of C atoms on the surface of the carbonate species-doped TiO_2 powders calcined at 400 and 500°C are about 0.4 and 0.2%, respectively. A XPS peak assigned to the carbonate species was also observed after Ar^+ ion etching of the sample for 200s. Etching depth is about 1.5nm. With increase in the depth from the surface of TiO_2 calcined at 400°C, the concentration of carbonate species decreases

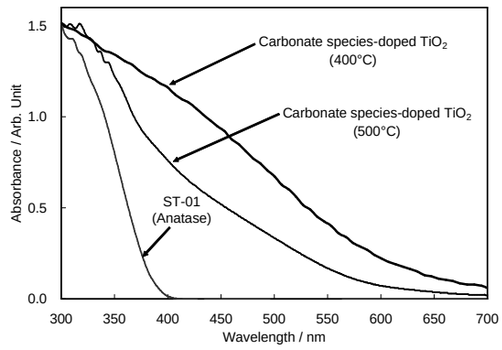

Figure 2. Optical absorbance spectra of carbonate species-doped TiO_2 calcined at 400 and 500 °C and a pure TiO_2 (ST-01; anatase).

gradually to about 0.15% in the bulk. These results strongly indicate that carbonate species are incorporated into the bulk phase of TiO_2.

The diffuse reflectance spectra of carbonate species-doped TiO_2 calcined at 400 and 500 °C, together with a pure anatase powder (ST-01), are shown in Figure 2. The photoabosorption in the visible region is much stronger than that of N-, C- or S-doped TiO_2 powders. The absorption in the visible region of the TiO_2 powder calcined at 400°C is stronger than that of the TiO_2 powder calcined at 500 °C.

Photocatalytic activity of the carbonate species-doped TiO_2 powder was evaluated by measuring the decomposition rate of methylene blue in an aqueous solution containing the TiO_2 photocatalyst. Figure 3 shows the activities of carbonate species-doped TiO_2 (calcined at 400 and 500 °C for 5 h) and pure TiO_2 (ST-01) as a function of the cutoff wavelengths of the glass filters. The activity of carbonate species-doped TiO_2 was about four-times higher than that of pure TiO_2 powder under photoirradiation at a wavelength longer than 350 nm. Furthermore, under visible light irradiation at wavelengths longer than 440 nm, only carbonate species-doped TiO_2 powder showed activity.

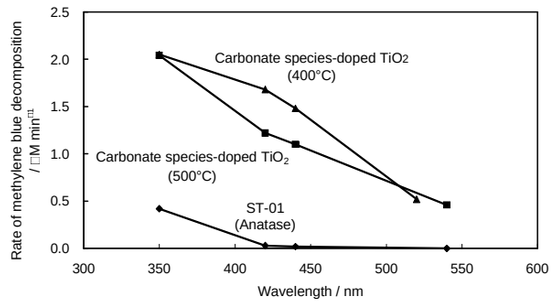

Figure 3. Decomposition of methylene blue using carbonate species-doped TiO_2 calcined at 400 and 500 °C and a pure TiO_2 (ST-01; anatase).

Summery It is of importance that we obtained a new class of TiO_2 powders. The activity of a carbonate species-doped TiO_2 photocatalyst for decomposition of methylene blue is much stronger than that of a fine anatase TiO_2 photocatalyst (ST-01) under a wide range of light including the visible region. Further development in carbonate species-doped TiO_2, such as pursuing the most suitable carbonate species content, is desired and currently being investigated.