# Degradation of Methylene Blue on Carbonate Species-doped $TiO_2$ Photocatalysts under Visible Light

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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 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.

Semiconductor photocatalysis is an efficient method for chemical utilization of solar energy. Although titanium dioxide, the most promising photocatalyst, is now used in various practical applications,[1] only a small UV fraction of solar light, about 2–3%, can be utilized because of its large band gap of 3.2 eV. Therefore, the development of a $TiO_2$ photocatalyst that shows a high activity under visible light is needed. For this purpose, doping of $TiO_2$ with transition metals[2–5] and reduced forms of $TiO_x$ photocatalysts[6–8] have been investigated. However, most of these catalysts do not show long-term stability or do not have sufficiently high levels of activities for a wide range of applications. Nitrogen-doped $TiO_2$ having an anatase form that shows a relatively high activity under visible light irradiation was reported in 2001.[9–11] Umebayashi et al. succeeded in synthesizing $TiO_2$ doped with S anions.[12] Kahn et al.[13] reported the synthesis of C-doped $TiO_2$ having a rutile phase. Irie et al. also reported the synthesis of C-doped $TiO_2$ having an anatase phase and its photocatalytic activity under visible light irradiation.[14] Sakthivel et al. succeeded in preparing $TiO_2$ photocatalysts containing some carbon species that show photocatalytic activity under visible light.[15] However, the absorption spectra of all of these photocatalysts in the visible region are relatively small.[9–15] It should be noted that all of the dopants, such as N-, C-, or S-, described above occupied O site in the lattice of $TiO_2$. We have also reported the preparation of an S cation-doped $TiO_2$ and its photocatalytic activity.[16,17] The absorbance of an S cation-doped $TiO_2$ in the visible region is larger than that of N-, C-, or S anion-doped $TiO_2$. In addition to an increase in absorbance, photocatalytic activity of an S cation-doped $TiO_2$ is relatively high under visible light compared to that of N-, C-, or S anion-doped $TiO_2$. It is noted that S atoms were incorporated into the lattice of $TiO_2$ as cations and were considered to be replaced with Ti ions in the case of S-cation doped $TiO_2$.

We have developed a carbonate-modified $TiO_2$ photocatalyst in order to increase absorbance in the visible region, resulting in improvement of photocatalytic activity under visible light irradiation. There has been no report on fabrication of a pure carbonate species-doped $TiO_2$ having an anatase phase and its photocatalytic activity under visible light irradiation. In this paper, we describe carbonate species-doped $TiO_2$ having an anatase phase as a photocatalyst for the decomposition of an organic compound under visible light irradiation.

Carbonate species-doped $TiO_2$ powders having an anatase phase were prepared as follows. Thiourea (7.6 g) and urea (6.0 g) were mixed with 4.0 g of an anatase $TiO_2$ powder (ST-01 from Ishihara Sangyo; 100% anatase; surface area, 330 m$^2$/g) 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. After calcination, the powder was washed with distilled water. 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 relative surface area of each powder was determined by using a surface area analyzer. The surface areas of the resulting powders calcined at 400 and 500 °C are 180, and 87.0 m$^2$/g, respectively. The relative surface area reduced with increasing the calcined temperature.

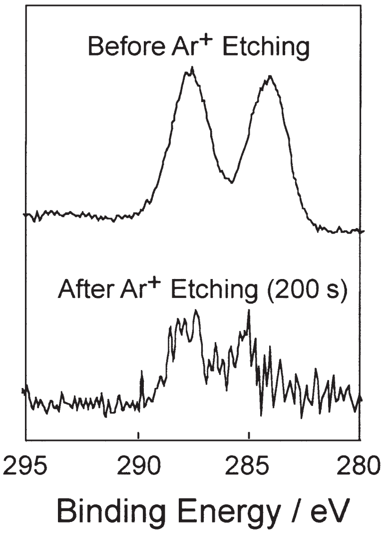

**Figure 1.** XPS spectra (Cls) of carbonate species-doped $TiO_2$ calcined at 400 °C.

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 measured by X-ray photoemission spectroscopy (XPS). The results are shown in Figure 1. The peaks assigned to N and S atoms were not observed from XPS analyses. Consequently, the resulting powders contained C atoms instead of N and S atoms. 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 (contamination of organic residues on their surfaces).[18] The latter peak around 288 eV suggests the presence of a carbonate species.[19] The peak around 281 eV, which was previously found to result from Ti-C bonds,[14,18] was not observed for the carbonate species-doped $TiO_2$ powders. A XPS peak assigned to the carbonate species was also observed after $Ar^+$ ion etching of the sample for 200s. Etching depth is about 1.5 nm. 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. With increase in the depth from the surface of $TiO_2$ calcined at 400 °C, the concentration of carbonate species decreases gradually to about 0.15% in the bulk. These results strongly indicate that carbonate species are incorporated into the bulk phase of $TiO_2$. Furthermore, the XRD measurements of the powders observed the only anatase phase of $TiO_2$. No peaks assigned to TiC were fund by XRD measurements.

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. Photoabsorption in the visible region of carbonate species-doped $TiO_2$ is very large. The photoabosorption in the visible region is much stronger than that of N-, C-, or S-doped $TiO_2$ powder reported previously.[9,10,12–14] 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.

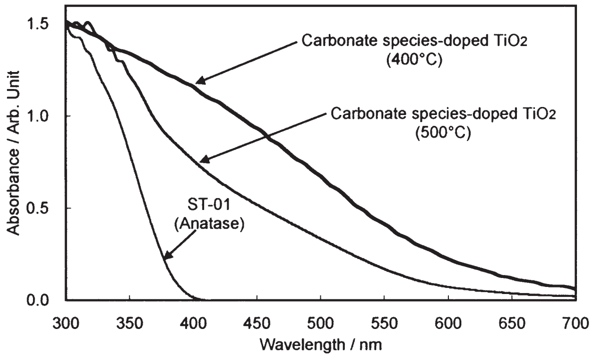

**Figure 2.** Optical absorbance spectra of carbonate species-doped $TiO_2$ calcined at 400 and 500 °C and a pure $TiO_2$ (ST-01; anatase).

Photocatalytic activity of the carbonate species-doped $TiO_2$ powder was evaluated by measuring the decomposition rate of methylene blue (50 mmol $dm^{-3}$) in an aqueous solution (5 mL) containing 100 mg of the $TiO_2$ photocatalyst. As the photocatalyst, a carbonate species-doped $TiO_2$ or a fine $TiO_2$ powder (anatase: ST-01) was used. A 500-W Xe lamp was used as the light source, and the short-wavelength components of the light were removed using cutoff glass filters with different cutoff wavelengths. 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 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. No degradation of methylene blue was observed in the absence of $TiO_2$ powder or without irradiation.

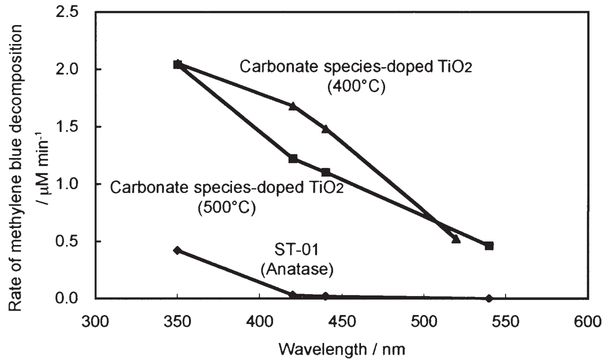

**Figure 3.** Decomposition of methylene blue using carbonate species-doped $TiO_2$ calcined at 400 and 500 °C and a pure $TiO_2$ (ST-01; anatase).

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.

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