

## Degradation of Methylene Blue on Carbonate Species-doped TiO<sub>2</sub> Photocatalysts under Visible Light

Teruhisa Ohno,\* Toshiki Tsubota, Kazumoto Nishijima, and Zenta Miyamoto  
Department of Applied Chemistry, Faculty of Engineering, Kyushu Institute of Technology,  
1-1 Sensuicho, Tobata, Kitakyushu 804-8550

(Received February 16, 2004; CL-040171)

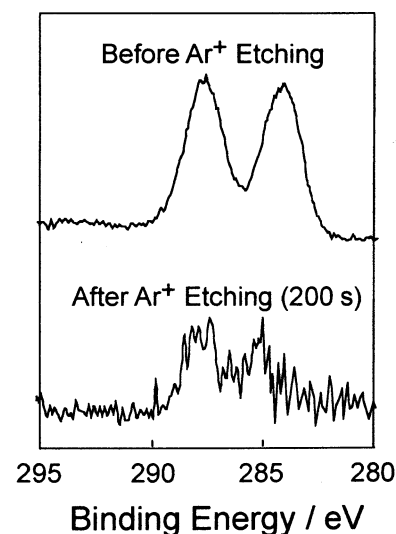
Carbonate (CO<sub>3</sub><sup>2-</sup>) species-doped titanium dioxide (TiO<sub>2</sub>) photocatalysts were prepared. By doping carbonate species into a TiO<sub>2</sub> lattice, the absorption edge of TiO<sub>2</sub> was largely shifted from 400 to 700 nm. Furthermore, methylene blue was photocatalytically decomposed at high efficiency on carbonate species-doped TiO<sub>2</sub> 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,<sup>1</sup> 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<sub>2</sub> photocatalyst that shows a high activity under visible light is needed. For this purpose, doping of TiO<sub>2</sub> with transition metals<sup>2–5</sup> and reduced forms of TiO<sub>x</sub> photocatalysts<sup>6–8</sup> 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<sub>2</sub> having an anatase form that shows a relatively high activity under visible light irradiation was reported in 2001.<sup>9–11</sup> Umebayashi et al. succeeded in synthesizing TiO<sub>2</sub> doped with S anions.<sup>12</sup> Kahn et al.<sup>13</sup> reported the synthesis of C-doped TiO<sub>2</sub> having a rutile phase. Irie et al. also reported the synthesis of C-doped TiO<sub>2</sub> having an anatase phase and its photocatalytic activity under visible light irradiation.<sup>14</sup> Sakthivel et al. succeeded in preparing TiO<sub>2</sub> photocatalysts containing some carbon species that show photocatalytic activity under visible light.<sup>15</sup> However, the absorption spectra of all of these photocatalysts in the visible region are relatively small.<sup>9–15</sup> 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<sub>2</sub>. We have also reported the preparation of an S cation-doped TiO<sub>2</sub> and its photocatalytic activity.<sup>16,17</sup> The absorbance of an S cation-doped TiO<sub>2</sub> in the visible region is larger than that of N-, C-, or S anion-doped TiO<sub>2</sub>. In addition to an increase in absorbance, photocatalytic activity of an S cation-doped TiO<sub>2</sub> is relatively high under visible light compared to that of N-, C-, or S anion-doped TiO<sub>2</sub>. It is noted that S atoms were incorporated into the lattice of TiO<sub>2</sub> as cations and were considered to be replaced with Ti ions in the case of S-cation doped TiO<sub>2</sub>.

We have developed a carbonate-modified TiO<sub>2</sub> 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<sub>2</sub> having an anatase phase and its photocatalytic activity under visible light irradiation. In this paper, we describe carbonate species-doped TiO<sub>2</sub> having an anatase

phase as a photocatalyst for the decomposition of an organic compound under visible light irradiation.

Carbonate species-doped TiO<sub>2</sub> 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<sub>2</sub> powder (ST-01 from Ishihara Sangyo; 100% anatase; surface area, 330 m<sup>2</sup>/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<sup>2</sup>/g, respectively. The relative surface area reduced with increasing the calcined temperature.

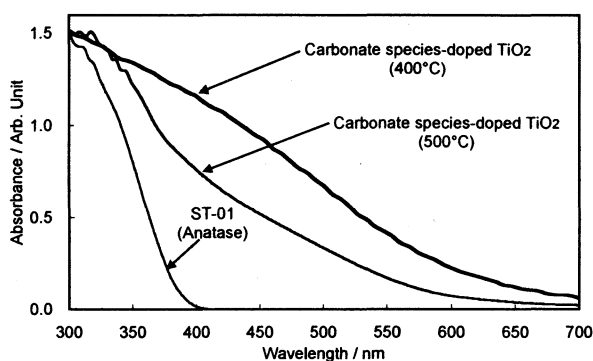


**Figure 1.** XPS spectra (Cl<sub>1s</sub>) of carbonate species-doped TiO<sub>2</sub> calcined at 400 °C.

In order to investigate the chemical states of C, N, and S atoms incorporated into TiO<sub>2</sub>, 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<sub>2</sub> as a contam-

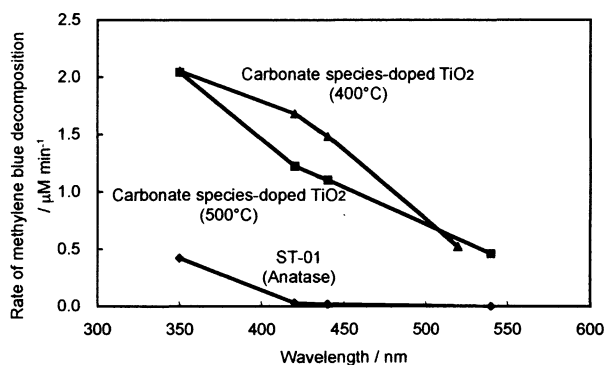
inant (contamination of organic residues on their surfaces).<sup>18</sup> The latter peak around 288 eV suggests the presence of a carbonate species.<sup>19</sup> The peak around 281 eV, which was previously found to result from Ti-C bonds,<sup>14,18</sup> was not observed for the carbonate species-doped TiO<sub>2</sub> powders. A XPS peak assigned to the carbonate species was also observed after Ar<sup>+</sup> 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub>. Furthermore, the XRD measurements of the powders observed the only anatase phase of TiO<sub>2</sub>. No peaks assigned to TiC were found by XRD measurements.

The diffuse reflectance spectra of carbonate species-doped TiO<sub>2</sub> 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<sub>2</sub> is very large. The photoabsorption in the visible region is much stronger than that of N-, C-, or S-doped TiO<sub>2</sub> powder reported previously.<sup>9,10,12-14</sup> The absorption in the visible region of the TiO<sub>2</sub> powder calcined at 400 °C is stronger than that of the TiO<sub>2</sub> powder calcined at 500 °C.



**Figure 2.** Optical absorbance spectra of carbonate species-doped TiO<sub>2</sub> calcined at 400 and 500 °C and a pure TiO<sub>2</sub> (ST-01; anatase).

Photocatalytic activity of the carbonate species-doped TiO<sub>2</sub> powder was evaluated by measuring the decomposition rate of methylene blue (50 mmol dm<sup>-3</sup>) in an aqueous solution (5 mL) containing 100 mg of the TiO<sub>2</sub> photocatalyst. As the photocatalyst, a carbonate species-doped TiO<sub>2</sub> or a fine TiO<sub>2</sub> 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<sub>2</sub> was about four-times higher than that of pure TiO<sub>2</sub> 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<sub>2</sub> powder showed activity. Figure 3 shows the activities of carbonate species-doped TiO<sub>2</sub> (calcined at 400 and 500 °C for 5 h) and pure TiO<sub>2</sub> (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<sub>2</sub> powder or without irradiation.



**Figure 3.** Decomposition of methylene blue using carbonate species-doped TiO<sub>2</sub> calcined at 400 and 500 °C and a pure TiO<sub>2</sub> (ST-01; anatase).

It is of importance that we obtained a new class of TiO<sub>2</sub> powders. The activity of a carbonate species-doped TiO<sub>2</sub> photocatalyst for decomposition of methylene blue is much stronger than that of a fine anatase TiO<sub>2</sub> photocatalyst (ST-01) under a wide range of light including the visible region. Further development in carbonate species-doped TiO<sub>2</sub>, such as pursuing the most suitable carbonate species content, is desired and currently being investigated.

This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas (417) from the Ministry of Education, Culture, Science and Technology (MEXT), Japan.

#### References

- 1 D. A. Tryk, A. Fujishima, and K. Honda, *Electrochim. Acta*, **45**, 2363 (2000).
- 2 T. Ohno, F. Tanigawa, K. Fujihara, S. Izumi, and M. Matsumura, *J. Photochem. Photobiol., A*, **127**, 107 (1999).
- 3 M. Anpo, *Catal. Surv. Jpn.*, **1**, 169 (1997).
- 4 E. Borgarello, J. Kiwi, M. Grätzel, E. Pelizzetti, and M. Visca, *J. Am. Chem. Soc.*, **104**, 2996 (1982).
- 5 W. Choi, A. Termin, and M. R. Hoffmann, *J. Phys. Chem.*, **98**, 13669 (1997).
- 6 R. G. Breckenridge and W. R. Hosler, *Phys. Rev.*, **91**, 793 (1953).
- 7 D. C. Cronmeyer, *Phys. Rev.*, **113**, 1222 (1957).
- 8 I. Nakamura, N. Negishi, S. Kutsuna, T. Ihara, S. Sugihara, and K. Takeuchi, *J. Mol. Catal. A: Chem.*, **161**, 205 (2000).
- 9 R. Asahi, T. Morikawa, T. Ohwaki, A. Aoki, and Y. Taga, *Science*, **293**, 269 (2001).
- 10 Y. Sakatani, K. Okusato, H. Koike, and H. Ando, *Photocatalysis*, **4**, 51 (2001).
- 11 T. Ihara, M. Ando, and S. Sugihara, *Photocatalysis*, **5**, 19 (2001).
- 12 T. Umebayashi, T. Yamaki, H. Ito, and K. Asai, *Appl. Phys. Lett.*, **81**, 454 (2002).
- 13 S. U. M. Khan, M. Al-Shahry, and W. B. Ingler, Jr., *Science*, **297**, 2243 (2002).
- 14 H. Irie, Y. Watanabe, and K. Hashimoto, *Chem. Lett.*, **32**, 772 (2003).
- 15 S. Sakthivel and H. Kisch, *Angew. Chem., Int. Ed.*, **42**, 4908 (2003).
- 16 T. Ohno, T. Mitsui, and M. Matsumura, *Chem. Lett.*, **32**, 364 (2003).
- 17 T. Ohno, M. Akiyoshi, T. Umebayashi, K. Asai, T. Mitsui, and M. Matsumura, *Appl. Catal., A*, accepted.
- 18 L. Zang and R. V. Koka, *Mater. Chem. Phys.*, **57**, 23 (1998).
- 19 E. Papirer, R. Lacroix, J.-B. Donnet, G. Nansé, and P. Fioux, *Carbon*, **33**, 63 (1995).