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Fabrication and characterization of C-doped anatase TiO_2 photocatalysts

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Titanium dioxide (TiO_2) has attracted great attention as a photocatalyst due to its excellent photochemical properties, non-toxicity and low cost. TiO_2 appears in three crystalline polymorphic phases: rutile, anatase and brookite. Among them, anatase TiO_2 exhibits the highest photocatalytic activity. The anatase, therefore, is the most effective and widely used photocatalyst. However, its shortcomings include a large band gap ($\sim$3.2 eV), which causes most of the solar spectrum to go unutilized. In order to extend the optical absorption of TiO_2 to the visible spectral region, various impurities have been added into the oxide [1–3]. For example, Anpo *et al.* showed that doping transition metal ions (Cr or V) into TiO_2 catalysts by a high energy metal ion-implantation method allowed the efficient absorption of visible light, thus enabling the photocatalysts to operate under visible light irradiation. Recently, other researchers have reported that doping with non-metal atoms such as N or S shifted the optical absorption edge of TiO_2 to lower energies, thereby increasing the photocatalytic activities in the visible region [4, 5].

TiO_2 photocatalysts have been fabricated by high-temperature oxidation of TiC powders, as previously reported [6]. The photocatalysts were prepared by the heating of TiC at 623 K for 50 h in air, and they showed higher activity than pure anatase TiO_2 under ultraviolet light irradiation. We thought that carbon (C) doping into TiO_2 might cause an improvement in the photocatalytic activity. Several researchers have also reported studies on C-doped TiO_2. These C-doped samples prepared by an acid-catalyzed sol-gel process or a controlled combustion of Ti metal showed photocatalytic activity under visible light irradiation [7, 8]. However, the C-doping effects on the optical and photocatalytic properties in the visible region as well as the chemical states of the C atoms in TiO_2 were not clear. The purpose of this letter, therefore, is to clarify the roles of the C atoms in the photocatalytic activity in the visible irradiation.

TiO_2 photocatalysts were prepared by oxidative annealing of TiC powders. The crystallographic structure and optical properties of the samples were investigated by X-ray diffraction (XRD) analysis and diffuse reflectance spectroscopy (DRS), respectively. The chemical states of C in TiO_2 were analyzed by X-ray photoelectron spectroscopy (XPS). The binding energy scale calibration was verified using the binding energy position of Au $4f_7$ state at 85 eV. The photocatalytic activities of samples were evaluated by measuring the decomposition rates of methylene blue (MB) adsorbed on the surface under visible light irradiation. Then, the light of a halogen lamp was reduced by two color filters to produce a visible light source of 420–500 nm [9]. Because MB cannot absorb light in this region, the electron transfer from MB to the conduction band of the TiO_2 does not occur. This means that the effect of self-photodegradation of MB [10] can be ignored.

Fig. 1 shows XRD patterns of the pure TiC and annealed samples at 623 K. When the TiC powders were annealed for 10 h, peaks due to TiC and anatase TiO_2 were observed as shown in Fig. 1b. The peaks of the former decreased with increasing annealing time (Fig. 1c), and they disappeared completely after annealing over 50 h (Fig. 1d and e). As a result of the annealing under this condition, TiC transformed into anatase. In contrast, the samples annealed at 673–873 K were composed of anatase and rutile TiO_2. By annealing at 1023 K, single phase rutile TiO_2 was formed (not shown in Fig. 1).

Fig. 2 shows XPS spectra for the C 1s core level of the sample annealed at 623 K for 100 h before and after Ar^+ etching. Before Ar^+ etching, the C 1s spectrum was composed of peaks I ($\sim$282 eV) and II ($\sim$285 eV). The peaks of I and II were assigned to the C 1s signals due to the Ti-C (281.9 eV) and C–C (285.3 eV) bonds, respectively [11, 12]. After Ar^+ etching for 300 s, peak II disappeared, whereas peak I became clear. Therefore, C atoms should be bonded to Ti atoms in the TiO_2. On

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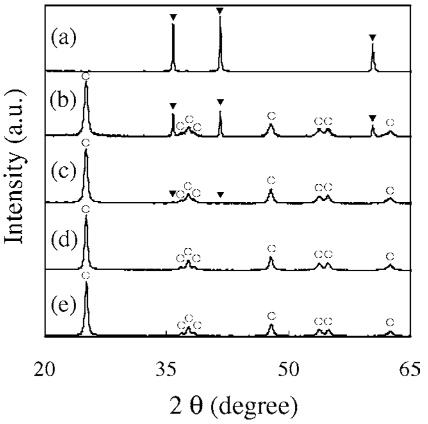

Figure 1 XRD patterns of TiC powders annealed in air for (b) 5, (c) 10, (d) 50, and (e) 100 h at 623 K. The pattern of pure TiC powder (a) is also presented for comparison. ▼: TiC, ○: anatase.

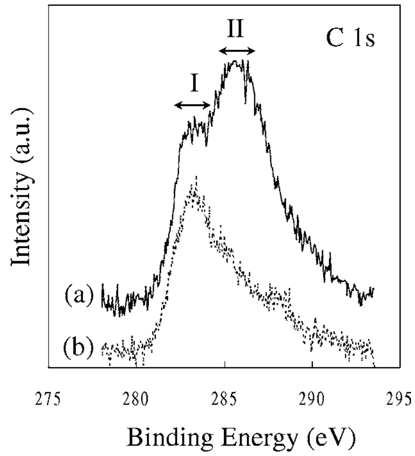

Figure 2 XPS spectra for the C 1s states (a) before and (b) after Ar^+ etching of the sample annealed at 623 K for 100 h in air.

the other hand, the XPS signals of Ti 2p were observed at binding energies at around 459 eV (Ti $2p_{3/2}$) and 465 eV (Ti $2p_{1/2}$). The Ti 2p peaks were in good agreement with those of pure TiO_2 [13, 14]. Based on the XRD and XPS results, it was proved that the C-doped anatase TiO_2, where O is replaced with C, was synthesized by the oxidation of the TiC powder at 623 K over 50 h.

Fig. 3 shows diffuse reflectance spectra of (a) pure anatase TiO_2 and (b) C-doped anatase TiO_2. The optical absorption edge of the doped sample shifted to the lower-energy region compared with the undoped sample. It is expected that C atoms doped onto O sites contribute to the red-shift. Asahi *et al.* [4] have calculated densities of states of the substitutional doping of C for O in the anatase TiO_2 crystal, by the full-potential linearized augmented plane wave formalism in the framework of the local density approximation. They showed that the C-doping into the TiO_2 lattice contributed to the formation of impurity states in the band gap. This leads to the red-shift of the optical absorption spectrum for the C-doped TiO_2. Consequently, C-doped TiO_2 may act as a photocatalyst under visible light irradiation.

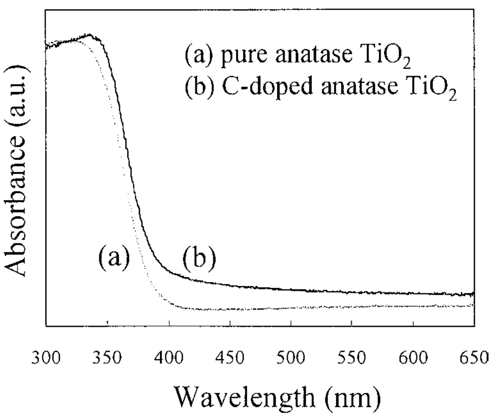

Figure 3 Diffuse reflectance spectra of (a) pure anatase TiO_2 and (b) C-doped anatase TiO_2 prepared by the annealing of TiC at 623 K for 100 h.

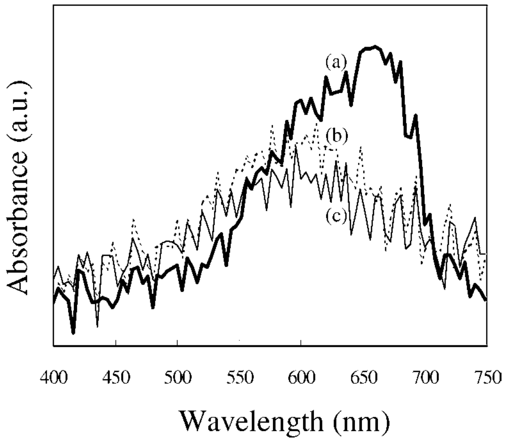

Figure 4 Absorption spectra of methylene blue adsorbed on the C-doped anatase TiO_2 during the visible light irradiation (420–500 nm) for (a) 0 min, (b) 10 min, and 20 min.

The photocatalytic activity in the visible region of the C-doped anatase TiO_2 and pure anatase TiO_2 were examined in terms of the degradation of MB adsorbed on the surface. Fig. 4 presents the absorption spectra of MB adsorbed on C-doped TiO_2 during visible light irradiation. Before the light-irradiation (Fig. 4a), the optical absorption due to MB adsorbed on the sample was observed around 660 nm. Because undoped TiO_2 cannot absorb the visible light, the dye on the undoped sample was not decomposed. On the other hand, the C-doped sample showed a large color decrease under visible light irradiation (Fig. 4b and c). This color degradation is probably caused by the photocatalytic reactions in C-doped TiO_2.

In conclusion, C-doped anatase TiO_2 photocatalysts have been prepared by the oxidative annealing of TiC powders at 623 K for 50–100 h. From XRD and XPS analysis, we can conclude that C is incorporated onto O sites of the TiO_2 lattice. DRS showed that the optical absorption edge of the C-doped anatase TiO_2 shifted to a lower energy compared with pure anatase TiO_2. The decomposition of MB adsorbed on the C-doped sample was observed under a visible light range of 420–500 nm. We conclude that substitution of C for O in the TiO_2 leads to a photocatalytic decomposition of MB under visible light irradiation.

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