Carbon-doped Anatase TiO_2 Powders as a Visible-light Sensitive Photocatalyst

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Carbon-doped TiO_2 powders in an anatase phase colored yellow were fabricated by oxidative annealing of TiC. Carbons were located at oxygen sites. The carbon substitution caused the absorbance edge of TiO_2 to be shifted to the higher wavelength region. Carbon-doped TiO_2 showed photocatalytic activities for the decomposition of IPA to CO_2 via acetone under visible light (400–530 nm) irradiation.

A main topic in the photocatalysts is the development of materials that provide sufficient photosensitivity in the visible (vis) light region. Titanium dioxide (TiO_2) is well known as an efficient photocatalyst;[1–3] however, it is activated only under UV light irradiation. The modification of TiO_2 sensitive to vis light is one of the current topics in this field. One approach is to substitute Cr, Fe, or Ni etc. for Ti[4–6] and another to form Ti^{3+} site by introducing oxygen vacancy in TiO_2.[7]

In 2001, nitrogen-doped TiO_2 in an anatase form was reported as a vis light sensitive photocatalyst[8–10] and attracted much attention. Actually in 1986, similar photocatalysts were reported by Noda et al.[11] and Sato,[12] though it was unnoticed. Except for nitrogen, Umebayashi et al.[13] reported sulfur-doped TiO_2 powders in the anatase form and the bandgap energy of it was calculated to be 1.4 eV and that of TiO_2 be 2.3 eV. Recently, Umebayashi et al.[14] and Ohno et al.[15] have reported the methylene blue degradation under vis light irradiation. The present authors also fabricated sulfur-doped TiO_2 powders and confirmed that the photocatalyst could decompose 2-propanol to acetone and CO_2 under both UV and vis light irradiations.[16] However, the photocatalytic activity was degraded as irradiating UV and vis lights, probably because of the catalytic poison caused by oxidation of SO_2 to SO_4^{2-}. As for carbon-doped TiO_2, "a chemically modified n-TiO_2" was reported[17] as a water oxidation material under vis light irradiation. However, its composition was mainly metal Ti and rutile phase of carbon-doped TiO_2 and it contained very small amount of anatase phase. As for carbon-modified TiO_2, Lettmann et al. reported the "carbon-containing TiO_2,"[18] which was highly condensed coke-like species covered TiO_2 and was not the carbon-doped one. The carbon-containing TiO_2 was fabricated by heating the Ti-alkoxide derived precursors at 250 °C in air and showed the vis light induced photodegradation of 4-chlorophenol. They concluded that the coke-like species was the photosensitiser. There has been no report on the fabrication of carbon-doped pure anatase TiO_2 and the evaluation of its photocatalytic activities under vis light irradiation. In this paper, carbon-doped anatase TiO_2 powders are reported as a photocatalyst for the decomposition of organic compound under vis light irradiation.

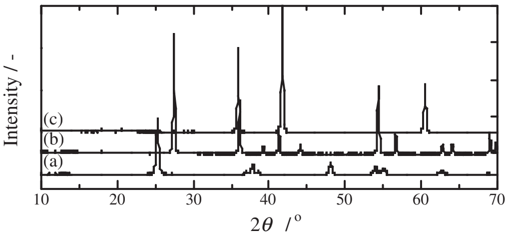

Figure 1. XRD profiles, (a) Anatase C-doped TiO_2, fabricated oxidizing TiC at 350 °C for 36 h in air atmosphere and then under O_2 flow at 600 °C for 5 h, (b) Rutile C-doped TiO_2, fabricated oxidizing TiC under O_2 flow at 600 °C, and (c) TiC raw material.

Carbon-doped anatase TiO_2 powders were obtained by oxidizing commercial TiC powders. TiC powders were packed into a double alumina crucible, oxidized mildly at 350 °C for 36 h in air atmosphere, and then annealed under O_2 flow at 600 °C for 5 h. The resulting sample was yellowish and identified to have a homogenous anatase phase, using an X-ray diffractometer (XRD), as shown in Figure 1 (profile (a)). When TiC powders were directly oxidized under O_2 flow at 600 °C, the TiC powders were converted to the rutile phase of carbon-doped TiO_2 as shown in Figure 1 (profile (b)), because the self-combustion was proceeded and the temperature became uncontrollably higher than that of the anatase to rutile phase transition. To investigate the carbon states in the photocatalyst, C 1s core levels were measured by X-ray photoemission spectroscopy (XPS), as shown in Figures 2a and b. Since the peak nearby at 281.8 eV, which have previously been found to result from Ti–C bonds,[19,20] was observed for the carbon-doped TiO_2 powders and the XRD did not indicate the TiC phase, it was determined that the oxygen sites were occupied by carbon atoms, not only at the surface of the powders but in the powders, as XPS measurements were performed after the surfaces were etched several nanometers in depth. The substituted carbon concentration at several nanometers from the powder surface was estimated to be 0.32% by comparing the product of the 281.8 eV peak area multiplied by the carbon sensitive factor to the product of the 531 eV peak area (O1s, Ti–O bonds) multiplied by the oxy-

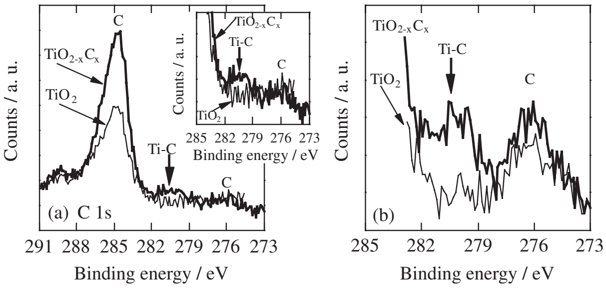

Figure 2. (a) C 1s XPS spectra of C-doped TiO_2 and TiO_2 powders, the inset is an enlargement of (a). (b) was remeasured precisely. The peak counts in the (a) and (b) of C-doped TiO_2 and TiO_2 were adjusted to be the same at 291 eV and 273 eV, respectively.

gen sensitive factor. The peaks at around 285 and 276 eV, which corresponded to carbon,[19] were observed for both TiO_2 and C-doped TiO_2. Figure 3 shows the optical absorbance spectra of C-doped TiO_2 and TiO_2 obtained by the diffuse reflection method. Noticeable shifts of the absorbance edge and shoulder to the vis light region were observed only for the C-doped TiO_2.

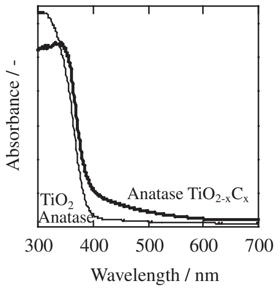

Figure 3. Optical absorbance spectra of C-doped TiO_2 and TiO_2 powders.

Photocatalytic oxidation activity was evaluated by the decomposition of gaseous 2-propanol (IPA) under vis (400–530 nm) light irradiation. The vis light intensity of about 1.2 mW/cm^2 was obtained by a Xe lamp with glass filters. 300 mg of C-doped TiO_2 powders was spread uniformly on an irradiation area of 15.9 cm^2, in the quartz-made vessel with a volume of 500 mL. About 300 ppm of reactant gas was injected. When the gas concentration became constant, the irradiation was started. Figure 4 shows IPA concentration and evolved CO_2 and acetone concentrations as a result of photodecomposition of IPA, as a function of time. Under vis light irradiation of C-doped TiO_2, IPA was decomposed producing acetone and CO_2. The C-doped TiO_2 powders were confirmed to have photocatalytic oxidation power under vis light irradiation.[21] As the peaks at around 285 and 276 eV were observed for both TiO_2 and C-doped TiO_2 in Figures 2a and 2b, and TiO_2 is not a vis light sensitive photocatalyst, it is considered that the peaks at around 285 and 276 eV were unrelated to the vis light responsibility and that the peak at around 281.8 eV was related to it. Therefore, the carbon atoms located at oxygen sites should be responsible for the vis light responsibility.

The quantum efficiency of this IPA decomposition to CO_2 under vis light irradiation was estimated to be 0.2%, which was lower in using $TiO_{2-x}N_x$ as a vis light sensitive photocatalyst (2-25%, which depended on x values in the $TiO_{2-x}N_x$).[22] It is considered that the bandgap narrowing was occurred in the C-doped TiO_2 as shown in Figure 3 and the upper level of the valence band shifted upward (toward the negative potential), which led to the decrease in the oxidation power, whereas bandgap narrowing was not occurred in the $TiO_{2-x}N_x$.[22] The other consideration is that the value of carbon substitution (0.32%) in the C-doped TiO_2 was not suitable for the high photocatalytic performance.

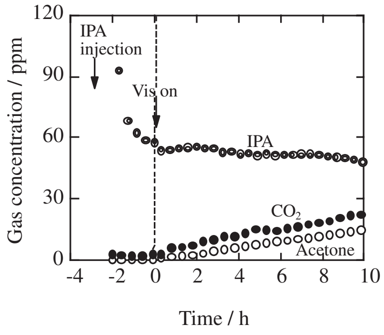

Figure 4. Changes of IPA, acetone and CO_2 concentrations as a function of time in the presence of C-doped TiO_2 powders under vis light irradiation.

In summary, C-doped TiO_2 anatase powders (0.32% substitution) were fabricated by oxidizing TiC powders. C-doped TiO_2 powders could decompose IPA to acetone and CO_2 under vis light irradiation. C-doped TiO_2 is therefore a promising Vis light induced photocatalyst. Further improvement of C-doped TiO_2, such as pursuing the most suitable carbon content, is desired and currently being investigated.

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References and Notes

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20 As shown in Figure 2, the Ti–C peak was observed at 280.5 eV, which was slightly deviated from the 281.8 eV, because the peak of Ti–C bonds at 281.8 eV was observed in the TiC structure. The peak of Ti–C bonds in the C-doped TiO_2 structure, that is, in the anatase TiO_2 structure, should be deviated from the one in the TiC structure.
21 The vis light induced photocatalytic decomposition of IPA in the presence of the rutile carbon-doped TiO_2 ((b) in Figure 1) under the same experimental condition as that in the presence of the anatase carbon-doped TiO_2 ((a) in Figure 1) was very small. After ten hours vis light irradiation, evolved acetone and CO_2 were nearly 0 ppm and 4.5 ppm, respectively.
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