Characteristics of Amorphous TiO_2 Particles Prepared in Various Reaction Systems

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Amorphous TiO_2 particles were prepared by the various reverse systems such as reverse micelle, reverse microemulsion, reverse emulsion, and by the sol–gel method, and investigated on their photocatalytic properties. After calcinating for 3 h at 200 °C, we found that they indicated two kinds of band-gap energies and gave the photocatalytic activity with irradiation of either UV or visible light, while anatase state did not work with visible light. However, any amorphous states were gradually converted into crystalline anatase with continuous irradiation, even without heating.

A significant amount of research is currently being devoted to titanium dioxide (TiO_2) photocatalysts.[1–4] This is because electrons and holes generated by irradiation with light energy greater than the band-gap energy ($E_g = 3.2\,eV$) can initiate redox processes, whereas TiO_2 itself is chemically and biologically inactive, cheap, and nontoxic.[5–12] Various kinds of modified TiO_2 photocatalysts have been interesting in as effective photofunctional materials for self-cleaning, antifogging, or stain-proof materials.

We reported that Pt, Ag, and SiO_2 particles formed by reverse micelle method indicated the peculiar phenomena.[13] Therefore, the present study will make clear the differences in photocatalytic activities of TiO_2 particles prepared by reverse micelle, reverse microemulsion, reverse emulsion, and sol–gel methods and then try to discuss the properties of amorphous TiO_2 prepared in these systems.

We have prepared TiO_2 particles by $C_{12}(EO)_5$/cyclohexane reverse micelle (RM), reverse microemulsion (RμE), reverse emulsion (RE), and sol–gel methods. The TiO_2 particles prepared in such a way that tetraethyl-*o*-titanate for precursor of TiO_2 had been hydrolyzed on the water-pool surface. The TiO_2 particles were dried and annealed at temperatures between 200 and 400 °C in an oven for 3 h. The photocatalytic activities were examined in aqueous solution of Methyl orange (MO) with irradiation of either UV and/or visible light ($\lambda \geqq 470$ nm). We made an estimation of photocatalytic activity by means of UV–vis and FT-IR.

Figure 1 shows the XRD patterns (RU-200B: RIGAKU) for TiO_2 particles prepared by reverse micelle method at different calcination. These particles were indicative of amorphous state in the temperature range from ambient temperature to 350 °C by XRD. However, nonstained TiO_2 samples of (c) in Figure 1 were not absolutely in the amorphous state, but gave a partial crystal as shown in Figure 1f taken by HRTEM (JEM-2000EX/FX II: JEOL). Such partial crystal states present locally in amorphous could be observed similarly to TiO_2 obtained by other reaction systems.

When calcined for 3 h at 400 °C, these particles absolutely changed from amorphous into anatase (JCPDS NO. 21-1272) as shown in Figure 2. Notice that the sharpness and intensity of XRD patterns in Figure 2 seem to increase with the order of size of water pool (reverse emulsion > reverse microemulsion > reverse micelle) in reverse systems. This means probably that since less hindered structure may be formed in large water pool, such TiO_2 particles allows us to prepare the different degrees of crystallization at transition from amorphous to anatase states when calcined.

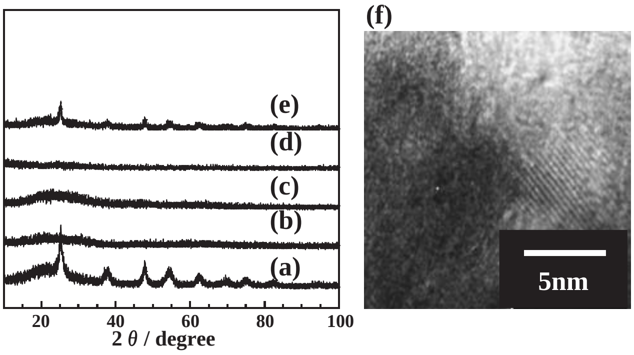

Figure 1. XRD patterns of: (a) commercial; (b)–(e) TiO_2 prepared in reverse micelle method. (b) dry, (c) 200 °C, (d) 300 °C, (e) 400 °C. (f) TEM image for TiO_2 particles prepared in reverse micelle method.

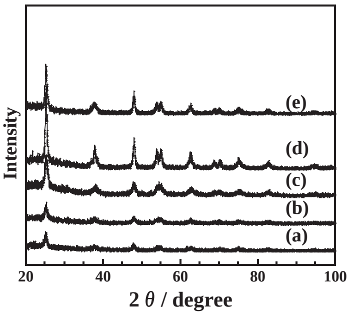

Figure 2. XRD patterns of: (a) reverse micelle, (b) reverse microemulsion, (c) reverse emulsion, (d) sol–gel method, and (e) commercial. (a)–(d) TiO_2 particles was heated for 3 h at 400 °C.

The interesting feature of the amorphous state leads us to investigate whether or not the amorphous state of TiO_2 possesses the properties of photocatalytic activity for aqueous solution of MO with irradiation of light including the UV and visible light ($470 > \lambda > 800\,nm$, $30\,mW/cm^2$). The rate of photolysis in the MO solution was estimated by the variation in UV absorption intensity for MO molecules. Figure 3 shows the decomposition rate of MO as a function of irradiated time by amorphous TiO_2 heated for 3 h at 200 °C. We found that the decomposed rate of MO by the amorphous states was much faster than that of commercial substance of a typical anatase (TAYKA, AMT-100). This phenomenon let us examine various TiO_2 particles heated

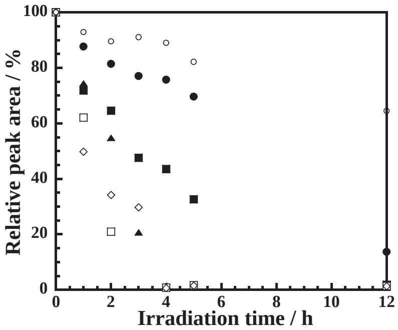

Figure 3. Relative peak area vs. irradiation time for commercial (●), reverse micelle (■), reverse microemulsion (▲), reverse emulsion (◇), sol–gel method (□) heated at 200 °C and sol–gel method (○) heated at 400 °C. Catalysts; 10 mg, decomposed solution; 10 mL of a 0.03 mM Methyl Orange solution, light source; 30 mW/cm^2 with UV-light.

at 400 °C as shown in Figure 3. On the other hand, it has been reported[14–16] that photocatalyst of typical TiO_2 responds the illumination of ultraviolet light. However, we found in the present work that TiO_2 in the amorphous state is more effective than crystalline anatase on photocatalytic activity in our experimental conditions. Moreover, we would like to emphasize that photocatalytic activity in amorphous TiO_2 particles may be enhanced with size of water pool in various reverse systems.

If photocatalytic activity of TiO_2 is different by preparation method, we have to expect the different band-gap energies in those amorphous states. Actually, their band-gap energies were measured on these amorphous TiO_2 particles with UV–vis absorption spectra. These TiO_2 particles calcined at 200 °C shows brown, though these materials was shown white same as typical TiO_2(anatase) after preparation. Then, in the case of amorphous TiO_2 heating at 200 °C, we found two band-gap energies from the absorption spectra for each TiO_2 material. These band-gap energies were estimated to be as follows: (a) 1.231 and 3.283 eV for the RM, (b) 1.283 and 3.366 eV for the RμE, (c) 1.626 and 3.252 eV for the RE, though amorphous state of TiO_2 without calcining took only the value of 3.0 eV. TiO_2 heated at 400 °C gave 3.0 eV corresponding to that for crystalline anatase independent of the preparation methods. The significant difference in band-gap energy for each sample may be due to the differences in the presence of many small scattered crystals confirmed by the TEM observations as shown in Figure 1f. We think that amorphous carbon particles, which came out after heating at 200 °C, probably generate the low band-gap energy, though the low band-gap energy for the amorphous TiO_2 particles without heating could not be observed. But we have no information that these materials have enough potential to oxidize MO into CO_2 or H_2O.

Since the irradiation light used in experiments of Figure 3 has included the light of UV region, the further confirmation is very important to know the properties of amorphous TiO_2 particles in that whether or not the photocatalysis of MO molecules takes place only with the irradiation of visible-light ($\lambda \geqq 470$ nm). Figure 4 shows the results of photocatalytic decomposition with various kinds of amorphous TiO_2 for MO molecules in solution. We found that all of the amorphous states prepared in various reaction systems decomposed the MO molecules at the recognizable rate, though the rate of decomposition was apparently smaller than that shown in Figure 3, and that the amorphous TiO_2 prepared by the RE method gave the highest photocatalytic activity. However, such a photocatalytic activity could not be sustainable, because these amorphous states were easily transited into anatase type with the continuous irradiation of light. As a matter of course, the reference commercial particles did not decompose the MO molecules.

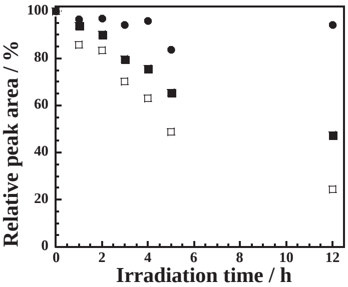

Figure 4. Relative peak area vs. irradiation time for commercial (●), reverse micelle (■), and reverse emulsion (□). Catalyst heated at 200 °C; 10 mg, decomposed solution; 10 mL of a 0.03 mM Methyl Orange solution, light source; 30 mW/cm^2 with cut-off filter ($\lambda \geqq 470$ nm).

In present work, we found that (1) TiO_2 particles prepared by the restrictive reaction systems of RM, RμE, and RE methods were able to be in the amorphous state, after heating for 3 h at 200 °C, (2) the amorphous TiO_2 particles had the two kinds of band-gap energies and gave the high photocatalytic activity when irradiated with visible light larger than 470 nm in wavelength, but (3) the amorphous states were easily transited into anatase with the continuous irradiation of light.

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