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Improved Dispersion Stability of Surface-fluorinated TiO_2 Particles

Jae-Ho Kim,*[1] Hiroaki Sato,[1] Toshimasa Kubo,[1] Susumu Yonezawa,[2] and Masayuki Takashima[2]
[1]*Department of Materials Science and Engineering, Faculty of Engineering, University of Fukui,*
3-9-1 Bunkyo, Fukui 910-8507
[2]*Cooperative Research Center, University of Fukui, 3-9-1 Bunkyo, Fukui 910-8507*

(Received November 29, 2010; CL-101006; E-mail: kim@matse.u-fukui.ac.jp)

Fluorinated TiO_2 (F-TiO_2) particles with good dispersion stability were synthesized at a temperature lower than 100 °C using fluorine gas. The average particle sizes and ζ potentials of F-TiO_2 particles were around seven times smaller and 1.4 times larger, respectively, than those (2200 nm and −19.35 mV) of untreated TiO_2 particles in water. However, the existence of $TiOF_2$ prepared at a temperature higher than 100 °C might negatively affect the dispersion stability of TiO_2. To prepare the fluorinated TiO_2 without $TiOF_2$, it is essential for optimizing the beneficial effects of surface fluorination against the dispersion stability of TiO_2.

Among various oxide photocatalysts, titania (TiO_2) has proven to be the most suitable for various environmental applications because of its biological and chemical inertness, strong oxidizing power, and cost effectiveness.[1] TiO_2 can be used to catalyze many reactions such as those involving alcohol dehydration, oxidation of aromatic compounds, and degradation of paint pigments.[2,3] The photocatalytic activity of TiO_2 is best when it is well-dispersed. However, TiO_2 has found limited practical applications because of a number of problems, one being the spontaneous agglomeration of TiO_2 nanoparticles upon dispersion in aqueous media; it results in a rapid decrease in specific surface area and, in turn, the photocatalytic activity. Many studies[4] have focused on the agglomeration behavior of TiO_2 particles in water. Surface modification of TiO_2 nanoparticles has generally been found to be an effective strategy to minimize the agglomeration of TiO_2 particles.[5,6] Silane alkoxides with organic functional groups have been widely used for this purpose. However, it is important to consider the high cost of the surfactants and the residues generated. Many researchers[7] have reported that the photocatalytic activity of TiO_2 can be improved using various fluorinating agents other than F_2 gas. We actually found that the UV–visible absorption maximum spectrum was shifted from 375 (raw TiO_2) to 410 nm (fluorinated TiO_2) using surface fluorination.

However, there has been no report regarding the dispersion stability of TiO_2 particles using surface fluorination. The idea is to stabilize the TiO_2 particles by enabling their surfaces to carry electric charge to create electrostatic repulsive forces to repel each other.

In this paper, we report the effects of surface fluorination on the dispersion stability of TiO_2 particles using F_2 gas.

TiO_2 particles (ST-21, anatase) with 98% purity were obtained from Ishihara Sangyou Kaisha, Ltd. Fluorine gas (99.5% pure) was supplied by Daikin Industies Ltd. Details of the fluorination apparatus have been mentioned in our previous work.[8] Fluorinated TiO_2 (F-TiO_2) particles were synthesized using direct fluorination under various reaction conditions. Reaction temperature, fluorine pressure, and reaction time were set at 25–200 °C, 12.3–101 kPa, and for 1 h, respectively. The structural and electronic properties of samples were investigated using XRD and XPS analyses. Particle size distribution and ζ potential profiles were measured using a ζ-potential/paricle-size measurement (Otsuka electronics Co., Ltd, ELSZ-2). A solid sample was suspended in distillated water, and the pH of suspension was adjusted using a 1 M NaOH or HCl solution. The dispersion stability of samples in water was determined using a sedimentation experiment. A typical procedure was used to prepare the suspension; 15 mg of TiO_2 and 15 mL of distillated water were mixed and sonicated for 1 h.

Sample names and fluorine contents (x) in $TiO_{2-x}F_x$ are summarized in Table 1. The fluorine contents (x) in $TiO_{2-x}F_x$ were evaluated from XPS results indicated in Figure 2. Higher reaction temperature and F_2 pressure in the reaction led to larger fluorine contents (x) in $TiO_{2-x}F_x$. At temperatures higher than 200 °C, the fluorine contents (x) reached 2.00 indicating the formation of $TiOF_2$.

The effects of reaction temperature and F_2 pressure on the TiO_2 crystal structure are shown in Figure 1. From (a) to (e) samples, the anatase phase was only detected as a single phase in TiO_2. It can be seen that even though reaction temperature and F_2 pressure increased to 100 °C and 12.3 kPa, only surface reaction between fluorine and TiO_2 occurred. However, the $TiOF_2$ peak (●) started to appear in the XRD pattern of $TiO_{2-x}F_x$ samples [(f) and (g)] with an x value greater than 1, as indicated in Table 1.

Figure 2 shows XPS spectra of Ti and F electrons for untreated and fluorinated TiO_2 particles. All bonding energies were calibrated to the C 1s peak at 284.8 eV of carbon. In here, Ti and F electrons with peaks located at binding energies (BEs) of 465.0 (Ti $2p_{3/2}$), 458.6 (Ti $2p_{1/2}$), and 684.7 eV (F 1s) were observed in all samples except for F6-TiO_2.[9] The F and Ti peaks

Table 1. Reaction conditions of TiO_2 treated with F_2 gas and fluorine contents (x) in $TiO_{2-x}F_x$

Sample name	Temperature /°C	F_2 pressure /kPa	Time /h	x in $TiO_{2-x}F_x$[a]
TiO_2	—	—	—	0.00
F1-TiO_2	25	12.3	1	0.37
F2-TiO_2	25	50.5	1	0.39
F3-TiO_2	25	101.0	1	0.44
F4-TiO_2	100	12.3	1	0.58
F5-TiO_2	100	50.5	1	1.10
F6-TiO_2	200	50.5	1	2.00

[a]Fluorine contents (x) in $TiO_{2-x}F_x$ were evaluated from XPS results indicated in Figure 2.

of F6-TiO_2 shifted to higher binding energy because of the formation of $TiOF_2$. An asymmetric F 1s peak was observed, especially for the samples (F5-TiO_2 and F6-TiO_2) prepared at temperature higher than 100 °C, in which an obvious tailing peak could be found. This means that two chemical forms of F atoms might exist in the samples. Therefore, the F 1s peak of F5-TiO_2 and F6-TiO_2 was deconvoluted into two separate peaks with Gaussian distributions, as shown in Figure 2. The peak located at 687.5 eV was attributed to the F atom in $TiOF_2$. This is easy to understand for the F5-TiO_2 and F6-TiO_2 samples because an obvious $TiOF_2$ phase appeared in their XRD patterns as shown in Figure 1.

Figure 3A shows the suspension appearance of samples dispersed in water for (i) 2 and (ii) 24 h. In the untreated TiO_2 suspension, TiO_2 particles reformed back into large agglomerates within 2 h. The dispersion stability of fluorinated TiO_2 suspensions, meanwhile, was kept even for 24 h. The stability of colloidal suspensions is mostly governed by interparticle (or surface) forces, especially by the repulsive electrostatic interaction of these charges.

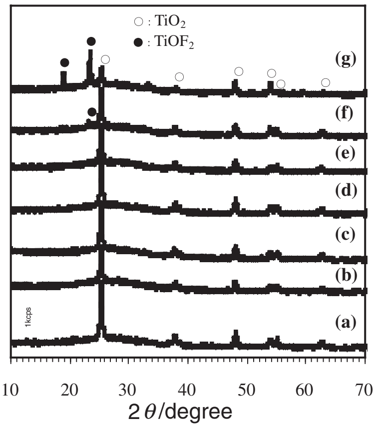

Figure 1. XRD patterns of the untreated TiO_2 [(a) TiO_2] and fluorinated TiO_2 [(b) F1-TiO_2, (c) F2-TiO_2, (d) F3-TiO_2, (e) F4-TiO_2, (f) F5-TiO_2, and (g) F6-TiO_2] particles.

Clearly, surface fluorination can alter the particle–particle interactions and consequently, the dispersion stability. However, the formation of $TiOF_2$ [(f) and (g)] in the TiO_2 particles could

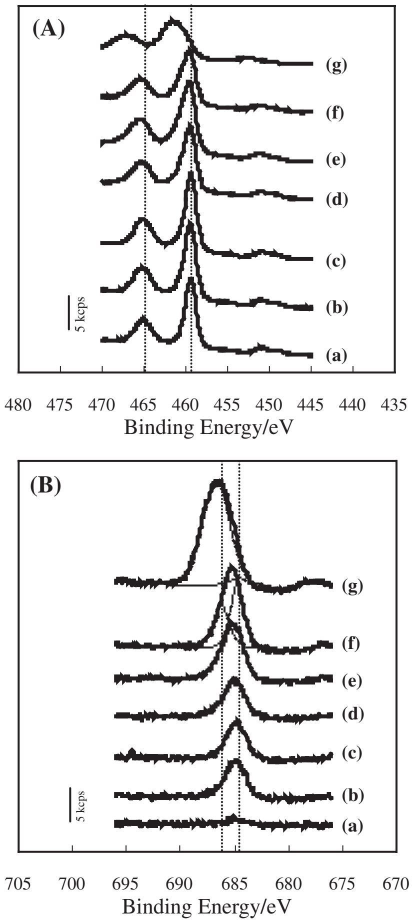

Figure 2. XPS spectra of the untreated and fluorinated samples: (A) Ti and (B) F electrons; (a) TiO_2, (b) F1-TiO_2, (c) F2-TiO_2, (d) F3-TiO_2, (e) F4-TiO_2, (f) F5-TiO_2, and (g) F6-TiO_2.

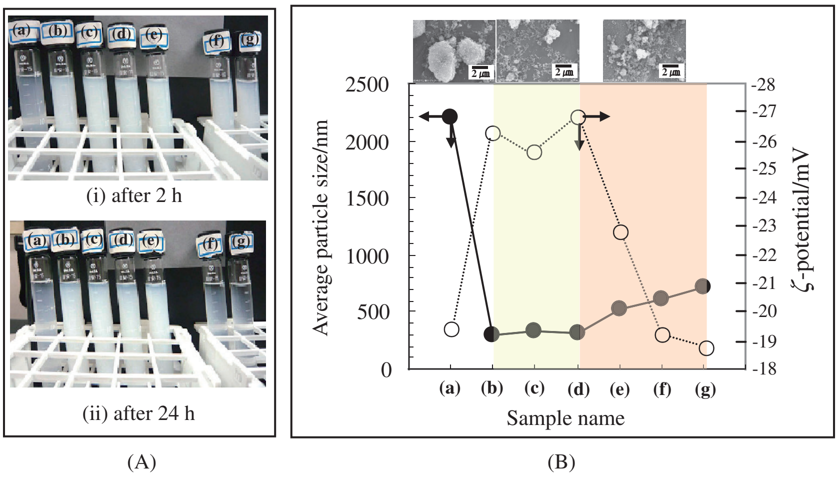

Figure 3. (A) The images of the dispersed samples in water: (i) after 2 h and (ii) after 24 h and (B) average particle size (●), ζ potential (○) and SEM images of the untreated TiO_2 and fluorinated TiO_2 particles in water (at pH 6.5) [(a) TiO_2, (b) F1-TiO_2, (c) F2-TiO_2, (d) F3-TiO_2, (e) F4-TiO_2, (f) F5-TiO_2, and (g) F6-TiO_2].

badly affect the dispersion stability. Figure 3B depicts the effects of surface fluorination on the particle size (●) and ζ potential (○) of TiO_2 particles in water at constant pH 6.5. The average particle sizes and ζ potentials of TiO_2 particles [(b), (c), and (d)] fluorinated at 25 °C were around seven times smaller and 1.4 times larger, respectively, than those (2200 nm and −19.35 mV) of untreated TiO_2 particles. SEM images of TiO_2 particles dried after the measurements also indicated that the fluorinated TiO_2 particles seemed to be dispersed without induced agglomeration, whereas the untreated TiO_2 particles formed large aggregation. It can be said that the fluorinated particles can be stabilized by the electrostatic forces against agglomeration because the electric charges resulting from surface fluorination enable creation of the electrostatic repulsive between particles.[10] However, the dispersion stability of TiO_2 particles [(e), (f), and (g)] fluorinated at above 100 °C degenerated, and it was due to the formation of $TiOF_2$ film on the particle surface. In here, the pH values (6.2–6.5) of all fluorinated TiO_2 suspensions were similar to the pH value (6.5) of untreated TiO_2 suspension. It means that the fluoride ion adsorbed on F-TiO_2 surface may be very stable without any release.

We have reported the effects of surface fluorination on the dispersion stability of TiO_2 particles. The fluorinated TiO_2 was synthesized by direct F_2 gas fluorination. The fluorine contents (x) in $TiO_{2-x}F_x$ mainly depended on the reaction temperature and existed in two chemical forms. At temperatures lower than 100 °C, the fluorine contents (x) remained at 0.4, and the fluorine existed in substitutional fluorine atoms on the TiO_2 crystal lattice. At greater than 100 °C, the fluorine contents (x) increased to 2.07 and the fluorine existed as $TiOF_2$. The former samples might take a positive role in the dispersion stability. Namely, to prepare the fluorinated TiO_2 without any $TiOF_2$ formation, it will be essential for optimizing the beneficial effects of surface fluorination against the dispersion stability of TiO_2.

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