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Chemical Etching Route to Prepare Nanometer-size Spherical Titania–Octadecylamine Hybrid Particles

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Spherical titania–octadecylamine hybrids (tens of nm to hundreds of nm) were obtained by the dissolution of presynthesized well-defined spherical particles with different size (70, 120, and 240 nm). The dissolution proceeds homogenously to give well-defined and size-controlled products when the reaction is conducted at room temperature in methanol.

Nanometer-size oxide particles have advantages for a wide range of uses including bio, environmental, and optoelectronic applications.[1] Monodispersed particles without aggregation are ideal materials for understanding structure–property relationships as well as to achieve well-controlled materials performance, while nanometer-size particles tend to assemble, forming aggregates which are difficult to redisperse due to the high surface energy of nanoparticles. In order to satisfy the requirements and interests, efforts have been made to prepare monodisperse nanoparticles as well as to disperse the particles homogeneously. When source materials are reactive, the nucleation and growth are likely to occur simultaneously, resulting in the formation of polydisperse and/or aggregated particles. Monodisperse nanoparticles can be obtained under limited conditions, and thus careful experimental investigations are required.

We have reported the preparation of monodisperse spherical titania–octadecylamine (titania–ODA) particles, which was achieved using a flow reactor.[2] The method is quite useful because one can easily change various synthetic conditions (flow rate, tube length, tube diameter, and reaction sequence) to adapt to the requirements of the products (size, homogeneity, quantity, etc.). In addition, the preparation is reproducible, resulting in the precisely controlled size and size distribution of spherical titania–ODA in the size range of 70 to 900 nm.[3] In this communication, we report a way to decrease the size of monodispersed spherical titania–ODA hybrid particles by chemical etching, a break-down approach. Break down approach is another way to achieve small particles and, among possible methods to make particles smaller, chemical etching including photoirradiation induced etching[4] and etching by chemicals[5] is a method applicable to nanoparticles. The size of various semiconductor particles has been reduced by dispersing particles into solvent, and size was controlled depending on synthetic parameters, while it is worth exploring the possibility to conduct the etching under mild conditions and with common solvents. Here, the titania–ODA particles[2] were dispersed into methanol (MeOH) and aged at room temperature to obtain smaller size particles.

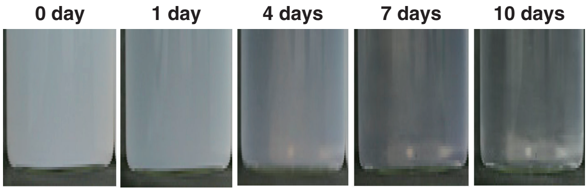

Figure 1. Photographs of titania–ODA (240 nm) dispersed in MeOH and aged for a certain period.

The starting materials (spherical titania–ODA hybrid particles) were prepared by the procedure reported previously,[2,3] and those with the size of 70, 120, and 240 nm, which are abbreviated as titania–ODA (70 nm), titania–ODA (120 nm), and titania–ODA (240 nm), respectively, were used in the present study. The titania–ODA particles were dispersed into MeOH (2.5 mg of titania–ODA particles were dispersed into 30 mL of MeOH), and the dispersion was aged at room temperature.

Photographs of a dispersion containing titania–ODA (240 nm) are shown in Figure 1. Starting from milky suspension, the dispersion gradually became translucent and almost transparent after 2 weeks, indicating particles in the dispersion dissolved to become smaller particles. The particle size was determined by TEM and was plotted against aging time in Figure 2. The particle size of titania–ODA (240 nm) gradually decreased and reached 105 nm after aging for 74 days while maintaining narrow particle size distribution (Figure 2). The surface of titania–ODA particles after the dissolution became rough. In addition, some particles aggregated and seemed to be fused together possibly because dissolved species may reprecipitate during the sample preparation for TEM observations. The as-synthesized titania–ODA particles contained ODA of ca. 37 wt %, as determined based on TG-DTA analysis,[2] while titania–ODA particles after the dissolution for 4 days contained ODA of ca. 20 wt %. The size change was also seen when smaller size particles (titania–ODA (120 nm)) were used as the starting material. The particle size of titania–ODA (120 nm) became 64 nm after aging at room temperature for 75 days. The amount of titania–ODA dissolved into MeOH was estimated based on the volume calculated from the decrease of particle size. The value is nearly the same (ca. 0.065 mg mL^{-1}) irrespective of the particle size, indicating that the particle size was determined by solubility. When a larger amount of titania–ODA (240 nm; 5, 12.5, and 25 mg) was dispersed into MeOH and aged at room temperature for ca. 2 weeks, the decrease of particle size was suppressed. The dissolution was suppressed as larger amount of titania–ODA was added, supporting the

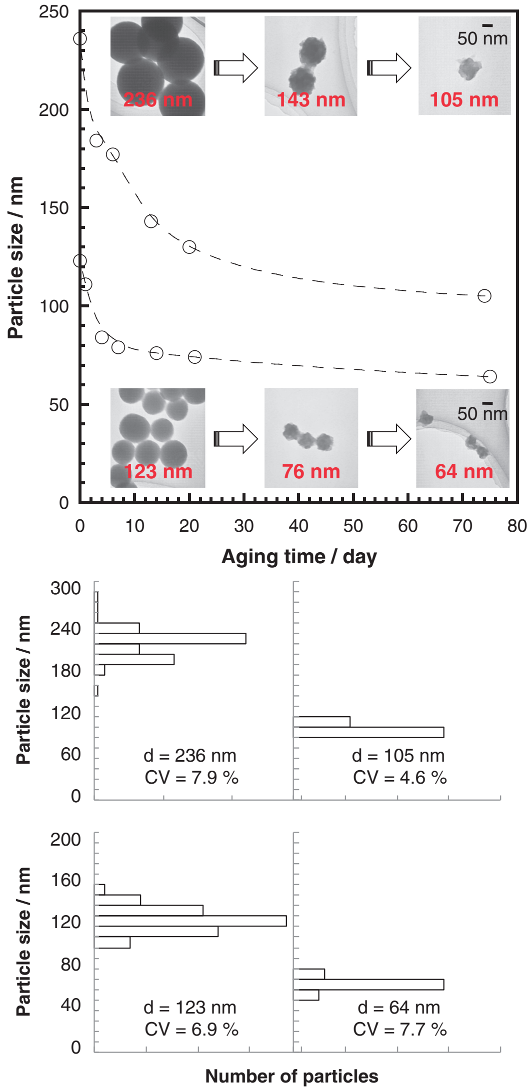

Figure 2. Particle size change of titania–ODA (120 and 240 nm). The inset shows TEM images of the titania–ODA particles after aging for a certain period. Particle size distributions of titania–ODA (120 and 240 nm) before and after the chemical etching are shown below.

proposed hypothesis of the mechanism of the etching. Judging from these results, it expected that smaller size particles may form by decreasing the concentration of titania–ODA particles.

When the dissolution of titania–ODA (120 nm) was examined at −15 °C, the decrease of particle size was dramatically suppressed (Figures 3a and S1),[6] while the dissolution was accelerated by the aging at 70 °C. In the aging at 70 °C, particle size reached ca. 55 nm only after 4 days (Figures 3a and S2).[6] This size is smaller than that obtained by the aging at room temperature for 75 days (64 nm). These results also support the hypothesis that the size is determined by solubility of titania–ODA into MeOH. We have obtained titania–ODA particles with 40 nm in size from the MeOH dispersion containing titania–ODA (70 nm) at 70 °C after aging for 27 days (Figures 4 and S3).[6]

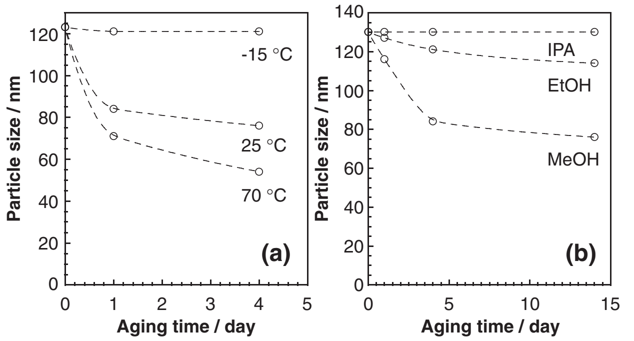

Figure 3. Particle size change of titania–ODA (120 nm), (a) dispersed in MeOH at different temperature (−15, 25, and 70 °C) and (b) dispersed in different alcohols (MeOH, EtOH, and IPA) at 25 °C.

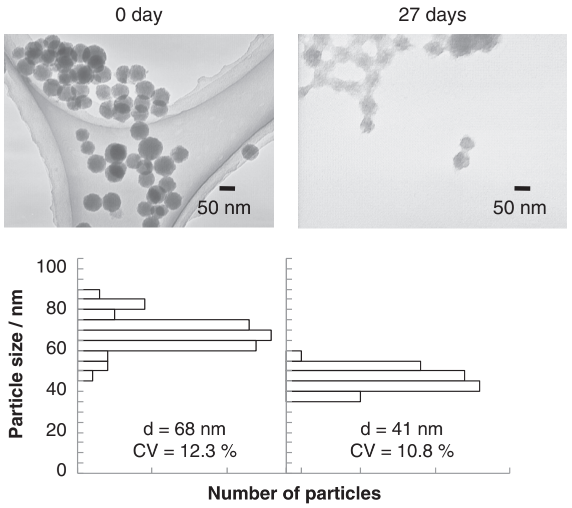

Figure 4. TEM images of titania–ODA (70 nm) dispersed in MeOH at 70 °C and aged for 27 days. Particle size distributions of titania–ODA (70 nm) before and after the chemical etching are shown below.

We also used ethanol (EtOH) and isopropanol (IPA) instead of MeOH, and the size change of titania–ODA (120 nm), which was determined by TEM, is shown in Figures 3b and S4.[6] The decrease of particle size was suppressed when EtOH was used, and the size did not change when IPA was used (Figure S5).[6]

The UV–vis spectra of titania–ODA (240 nm) showed a broad absorption band in the visible wavelength region and showed a peak at around 310 nm (Figure 5), suggesting the presence of band structure of amorphous titania in the wavelength range up to 350 nm.[7] The peak shifted to a wavelength of around 230 nm after 3 days. The dispersion was turbid at first and gradually became translucent, thus all the spectra except for that of titania–ODA (240 nm) after aging for 74 days were influenced by scattering in the visible range. The longer the aging time was, the larger the absorption at around 230 nm was while the smaller the effect of light scattering was, due to the decrease of particle size. Taking these reports into account, titania particles in the range of several nm to tens of nm and isolated titanium species may be present in the MeOH dispersion.

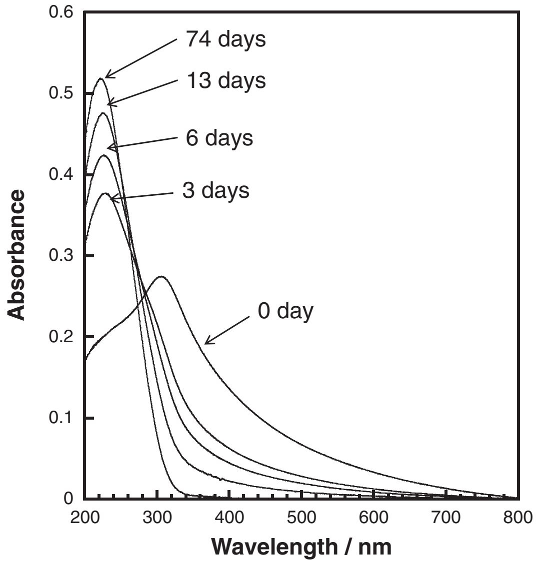

Figure 5. UV–vis spectra of titania–ODA (240 nm) dispersed in MeOH and aged for a certain period.

The dispersion with high transparency and long-term stability has various advantages for the use as a precursor solution for titania film, monolith, core–shell particles, etc. We can convert the titania–ODA particles to porous titania particles.[2] Further investigation on the optical, rheological, and other physical/chemical properties of the nanoparticles is worth conducting for a variety of practical applications as well as for the fundamental understanding of various phenomena.

In summary, spherical titania–ODA hybrid particles with the size of 70, 120, and 240 nm were dispersed into alcohol (methanol, ethanol, and isopropanol), and the dispersion was aged at various temperatures to obtain smaller particles. The size of titania–ODA particles decreased at room temperature depending on the aging time. The decrease of particle size accelerated at higher temperature (70 °C), and the smallest particles with the size of 40 nm were obtained from the methanol dispersion containing titania–ODA particles with 70 nm in size.

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