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Titanium Dioxide Hollow Microspheres with an Extremely Thin Shell

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Sol−gel processing is a powerful technique to shape-control materials into fine particles, thin films, fibers, and so on. Preparations of sols are generally involved by hydrolyzing the appropriate salts, most typical ones being metal alkoxides. Most of the colloidal particles thus synthesized have a spherical shape the size of which ranges from nano- to micrometer scale, depending on the degree of hydrolysis or polymerization.

A number of layered materials have been exfoliated into their elementary sheets by the action of some particular chemical species.[1−7] The resulting suspensions may be regarded as a new class of sol, in which colloidal nanosheets or exfoliated single layers are dispersed. They are characterized by their unusual two-dimensional nature, well-defined composition, and high crystallinity with an ordered array of active sites or charge. Therefore, these nanosheets may be useful as precursors for synthesis of new materials and also for novel shape-control, which cannot be achieved by using the conventional sols.

From a standpoint of shape-control, Alberti et al. have prepared thin films or pellicles of α-zirconium phosphate by flocculating the dispersion of the exfoliated compound with acid solutions and subsequent filtration.[2a] They reported that the pellicles possess some mechanical strength since the two-dimensional crystallites are assembled having their face parallel to the surface of the film.

Recently we have demonstrated that self-standing thin flakes of titanium dioxide can be derived from a colloidal suspension of an exfoliated layered titanate.[8] Freeze-drying was applied as a gelation method of the suspension. A limited number of the titanate nanosheets are restacked upon freeze-drying to give a very thin lamella which can be converted into titanium dioxide by heating. The thin flakes, tens of nanometers thick and tens of micrometers in lateral size, arrange themselves in an irregular way to produce into slit-shaped mesopores.[8]

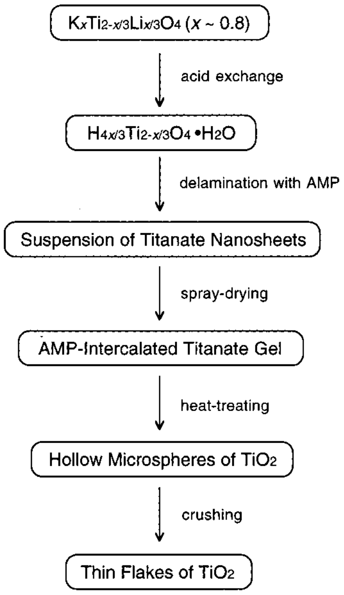

Figure 1. Synthetic process of the titanium dioxide hollow microspheres.

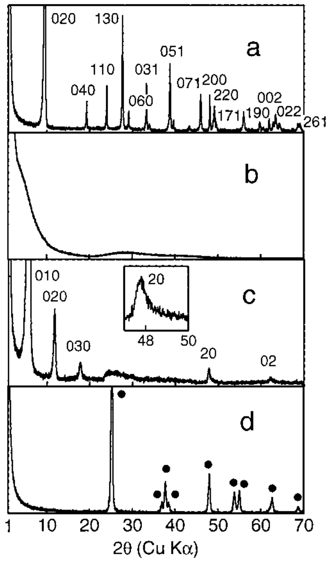

Figure 2. XRD profiles at various stages of the synthetic process: (a) starting material, $H_{4x/3}Ti_{2-x/3}O_4 \cdot H_2O$ ($x \sim 0.8$), (b) colloidal suspension of the exfoliated titanate, (c) spray-dried product of the suspension, (d) titanium dioxide hollow microspheres prepared by heat-treating the gel at 650 °C for 1 h. Peaks indicated by circles in part d are for anatase.

Spray-drying has widely been employed to solidify sols into fine powders.[9] Although a number of ceramic

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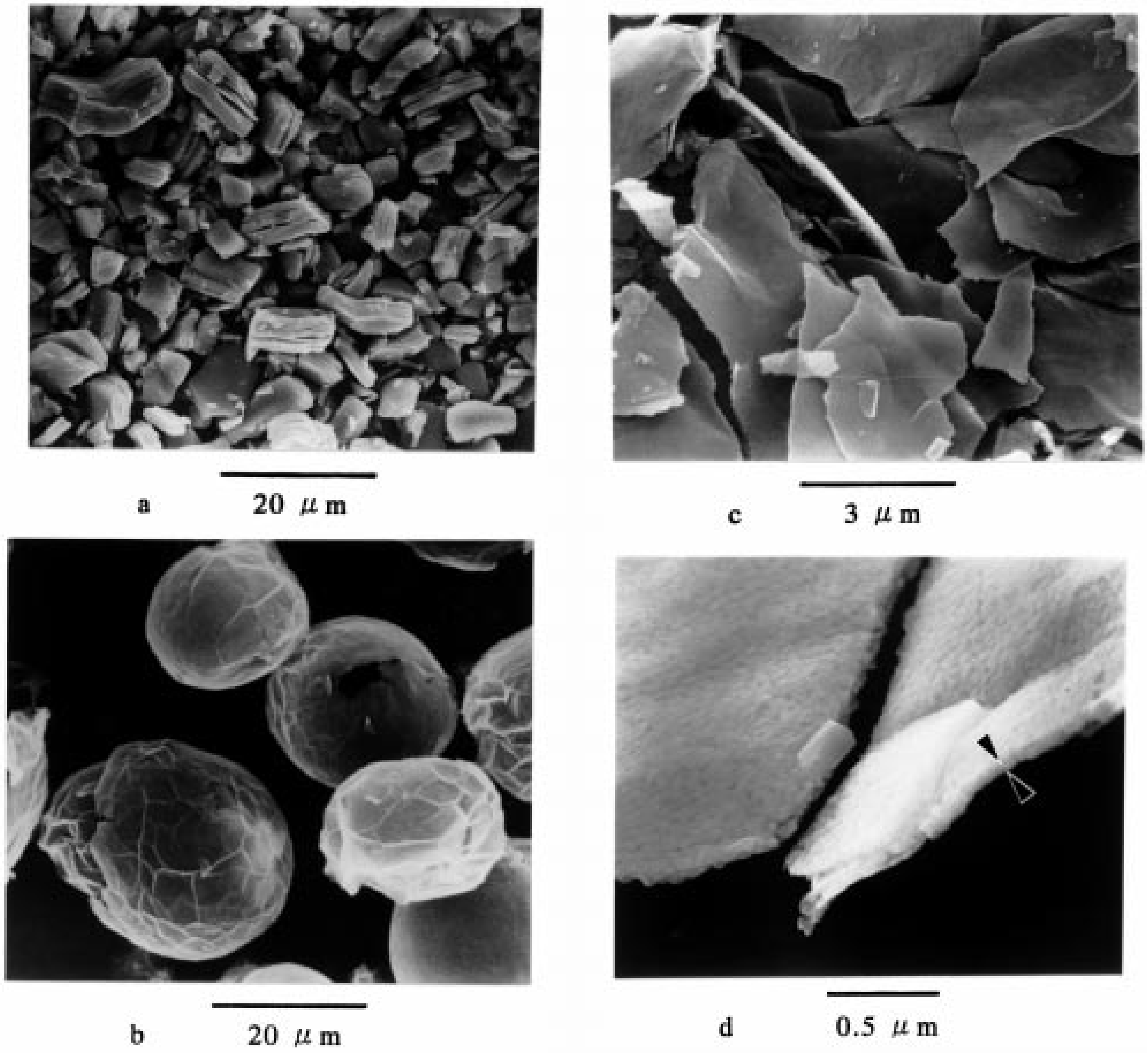

Figure 3. Scanning electron micrographs: (a) platy microcrystals of $H_{4x/3}Ti_{2-x/3}O_4 \cdot H_2O$, (b) hollow microspheres of titanium dioxide heat-treated at 650 °C, (c) thin flaky particulates formed by crushing the microspheres, and (d) edge view of a thin flaky particulate.

powders of fine spherical particles have been synthesized through this processing, this technique has never been applied to suspensions of exfoliated compounds.

We report here formation of novel hollow microspheres of titanium dioxide with an extremely thin shell by spray-drying of the colloidal suspension of the exfoliated titanate sheets. Figure 1 illustrates the synthetic route. X-ray diffraction (XRD) and SEM data at various stages of the process are shown in Figures 2 and 3.

The protonic layered titanate used as a starting material, $H_{4x/3}Ti_{2-x/3}O_4 \cdot H_2O$ ($x \sim 0.8$), was prepared from $K_xTi_{2-x/3}Li_{x/3}O_4$ by acid exchange.[10] $K_xTi_{2-x/3}Li_{x/3}O_4$ is isomorphous to $Cs_xTi_{2-x/4}\square_{x/4}O_4$ ($x \sim 0.7$; □, vacancy) with the lepidocrocite-type layered structure,[11] which we used in the fabrication of the thin flakes of TiO_2 described above.[8] Acid exchange was carried out by leaching 100 g of $K_xTi_{2-x/3}Li_{x/3}O_4$ in 0.67 dm^3 of a 3 mol dm^{-3} H_2SO_4 aqueous solution. To achieve complete extraction, the solid was transferred into a Buchner funnel and then washed with 4.7 dm^3 of a 0.5 mol dm^{-3} H_2SO_4 solution through aspirating. X-ray fluorescence spectrometry on the product confirmed that alkali metal ions were almost completely removed (residue < 1.8% of initial content). Formation of the layered protonic titanate was confirmed by XRD data (Figure 2a) and its characteristic platy morphology was seen in Figure 3a.

The protonic titanate $H_{4x/3}Ti_{2-x/3}O_4 \cdot H_2O$ was delaminated by being treated with an aqueous solution containing 2-amino-2-methyl-1-propanol (hereafter AMP), $(CH_3)_2C(NH_2)CH_2OH$. The solid-to-solution ratio was

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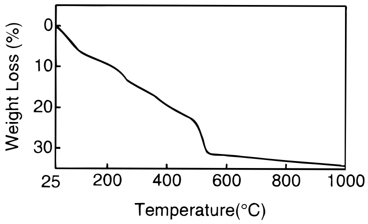

Figure 4. Thermogravimetric curve of the spray-dried gel.

0.06 g cm^{-3} and the concentration of AMP was adjusted to a chemical equivalent of the exchangeable protons in the titanate. High-speed stirring (Tokushu Kika Kogyo T.K. Homo Disper, 3000 rpm; diameter of impeller, 50 mm) of the mixture gave an opalescent suspension. Figure 2b shows the XRD pattern of the dispersion itself, which was recorded with a powder diffractometer equipped with a horizontal sample stage (Rigaku Rint 2000S). The broad profile without sharp reflections from the layered structure was similar to the diffraction pattern observed for exfoliation of the isomorphous titanate $H_xTi_{2-x/4}\square_{x/4}O_4 \cdot H_2O$,[7b] which suggests substantially complete exfoliation into single nanosheets.

The suspension of the titanate nanosheets was spray-dried with Niro mobileminor spray-drier with a rotary atomizer operating at 31 000 rpm (i.d. 50 mm). The dispersion was fed at a speed of 0.1 dm^3 min^{-1} into a drying chamber at 240 °C. The dried titanate gel was very light and voluminous (apparent density, ~ 0.02 g cm^{-3}). Its XRD pattern (Figure 2c) revealed a 0*k*0 diffraction series, which is indicative of a lamellar structure with a basal spacing of 1.51 nm. The turbostratic nature of the structure is suggested from absence of *hkl* reflections as well as asymmetric line profiles for *hl* diffraction bands. The data indicate that the titanate sheets were restacked upon spray-drying, producing an AMP-intercalated compound. The composition of the gel was determined to be $[(CH_3)_2C(NH_2)CH_2OH]_{0.51\pm0.02}H_{1.07}Ti_{1.73}O_4 \cdot 0.9H_2O$ by elemental analysis (organic components by Perkin-Elmer 2400-type CHNS/O analyzer, Ti content by gravimetry).

In the next step, the spray-dried gel was calcined at 650 °C for 1 h, which did not bring about a significant change in its voluminous appearance but destroyed the lamellar structure and induced crystallization of a single-phase of anatase (see Figure 2d). The gel underwent a total weight loss of ~34%, as depicted in Figure 4, which is due to liberation of interlayer AMP and H_2O molecules.

The final product was the hollow microspheres, as visualized in Figure 3b. The particle size ranged from 10 to 50 μm, while its shell thickness was well below 0.1 μm. This diameter/thickness ratio is one of the highest values among those of hollow ceramic microspheres reported so far. Several methods for the formation of microspheres have been reported, including spray pyrolysis of solutions or sols,[12] fusion of precursor powders in a dc plasma,[13] and water extraction of colloidal droplets in emulsions.[14] However, these hollow particles have a much thicker shell, being >10% of the diameter.

Surprisingly, 99% of its volume is estimated to be void by taking the average particle size of 30 μm and crust thickness of 50 nm. If we assume that the particles are closely packed, the apparent density of the powder is calculated to be 0.029 g cm^{-3}. This is comparable with the observed value of 0.02 g cm^{-3}. In addition to this microstructural feature, the particles were separated from one another without coagulation, which makes the powder light enough to move as if it were a fluid.

It is of interest to discuss how these unusual hollow microspheres were formed. Let us consider the formation of the particles with the average dimensions of a 30 μm diameter and a 50 nm crust thickness. A density of the anatase shell is assumed to be 50% of the theoretical value for anatase crystal of 3.90 g cm^{-3}.[15] The initial size of sprayed droplets can be estimated to be 22 μm by taking into consideration all these data and the solid content of the suspension (0.06 g cm^{-3}). This calculation indicates that the sprayed droplets expanded by 2.5 times in volume during the drying process. Vaporization of water inside the droplet should be responsible for this swelling. The dispersed nanosheets are expelled to the outer aqueous crust by a bubble inside of the droplet and are restacked to produce the thin solid shell upon complete drying. The two-dimensional crystallites may be favorable for formation of the hollow spheres, preventing their fracture.

These microspheres can be converted into thin flaky particulates by gentle milling, as exemplified by Figure 3c. Their particle size, controllable by milling strength, ranged from 1 to 10 μm while its thickness was below 0.1 μm, corresponding to the thickness of the hollow sphere shell. The high aspect ratio as well as their thinness is comparable to those for TiO_2 flakes prepared by freeze-drying, for which excellent slipping or extensible properties may be expected.

In conclusion, hollow microspheres of titanium dioxide were synthesized through spray-drying of the colloidal suspension of the exfoliated titanate nanosheets and subsequent heating. Their thickness of ~50 nm was only 1−2% of the diameter, providing a large open space inside. The processing reported here may be applied to a variety of materials to allow their shape-control into hollow microspheres.

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[15] This low density of 50% is generally the case for loosely sintered bodies like the present material (see Figure 3d) and is also reasonable because AMP and water were eliminated from the precursor lamellar lattice upon crystallization, which most likely makes the voids in the material.