Materials Science

Creation of Intestine-like Interior Space for Metal-Oxide Nanostructures with a Quasi-Reverse Emulsion**

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Hollow inorganic micro- and nanostructures have attracted great attention in recent years because of their promising properties for scale-dependent applications such as photonic devices, drug delivery, active-material encapsulation, ionic intercalation, surface functionalization, robust catalysts/carriers, and size-selective reactions.[1–5] Until now there have been two basic templating methods, with either hard or soft templates, for synthesizing these hollow structures. For example, colloid particles, fibers, organogelators, anodic alumina membranes, or sacrificial cores are commonly utilized in the hard-templating method, and the inorganic layers are coated onto the inner or outer surfaces by layer-by-layer, sol-gel casting, redox replacement, or nanoparticle adsorption methods;[1–9] the desired hollow interiors are generated upon removal of the templates by calcination or dissolution. In the soft-templating method ionic organic surfactants, such as sodium dodecyl sulfate (SDS, in nonaqueous emulsions),[10] or nonionic polymeric surfactants, such as alkyl poly(ethylene oxide),[11,12] have been widely used; even gas bubbles generated in situ can be used to form microscale hollow spheres.[13] To overcome the complexity associated with templating methods a number of template-free methods for hollow inorganic microspheres have been developed very recently, in which large quantities of an inorganic additive such as $(NH_4)_2SO_4$, NH_4OH, KCl, or an ionic liquid, are involved,[14–17] including the Ostwald ripening and Kirkendall effect for solid-hollowing in solution.[18,19] Nonetheless, the reported syntheses are not perfect either, because it is hard to avoid inclusion of additive impurities and is difficult to achieve size control in the sub-micrometer regime or other morphological tuning.[14,17]

In searching for other synthetic methods it seemed possible that existing solution inhomogeneity (that is, microheterogeneity) in common cosolvent systems could be utilized. For example, it has recently been confirmed by Raman spectroscopy, small-angle X-ray scattering, and molecular dynamics simulations that alcohols such as *n*-propanol and 2-propanol tend to self-assemble in dilute aqueous solution and result in solution microheterogeneities (that is, local compositions which differ from the average ones).[20–22] It is now known that, despite the fact that these alcohols and water are infinitely miscible, the solution is far from homogeneous.[22] We report here a novel "quasi-reverse-emulsion" solvothermal method to generate hollow nanostructures for metal oxides with monodisperse morphologies in a mixture of water and 2-propanol. In particular, intestine-like or spherical hollow interiors have been created for phase-pure anatase TiO_2 nanostructures with 100% morphological yield. The success of this method can be attributed to the presence of microheterogeneities in the solvent mixture.

Figure 1 shows the results of our transmission electron microscopy and selected-area electron diffraction (TEM/SAED) investigations. The wall thickness of intestine-like TiO_2 can be controlled precisely in the present template-free synthesis by varying the reactant concentrations. As an illustration, a uniform wall thickness of about 125–150 nm (Figure 1A) can be prepared with a higher concentration of TiF_4 in the starting solution, while the wall thickness can be reduced to as little as 20–30 nm by reducing the amount of TiF_4 present (Figure 1B and C). A similar concentration dependency is also observed for the outer diameters (500–550 nm in Figure 1A can be reduced to 400–450 nm in Figure 1B). A further reduction in diameter to about 250–300 nm can be achieved with an even lower concentration of TiF_4 (see Supporting Information). The inner cavities of the nanostructures were clearly identified by TEM contrast images as well as the corresponding scanning electron microscopy (SEM) and field-emission SEM (FESEM) images. Interestingly, either a hollow interior or a partially filled interior (with a solid core) can be selected (compare Figure 1A with 1B and see the Supporting Information). SAED patterns from the as-prepared TiO_2 intestines show diffraction rings typical of the anatase phase (Figure 1),[23,24] which is consistent with the X-ray diffraction (XRD) finding of the same polymorph (see the Supporting Information; phase-pure anatase TiO_2, space group: $I4_1/amd$; JCPDS file

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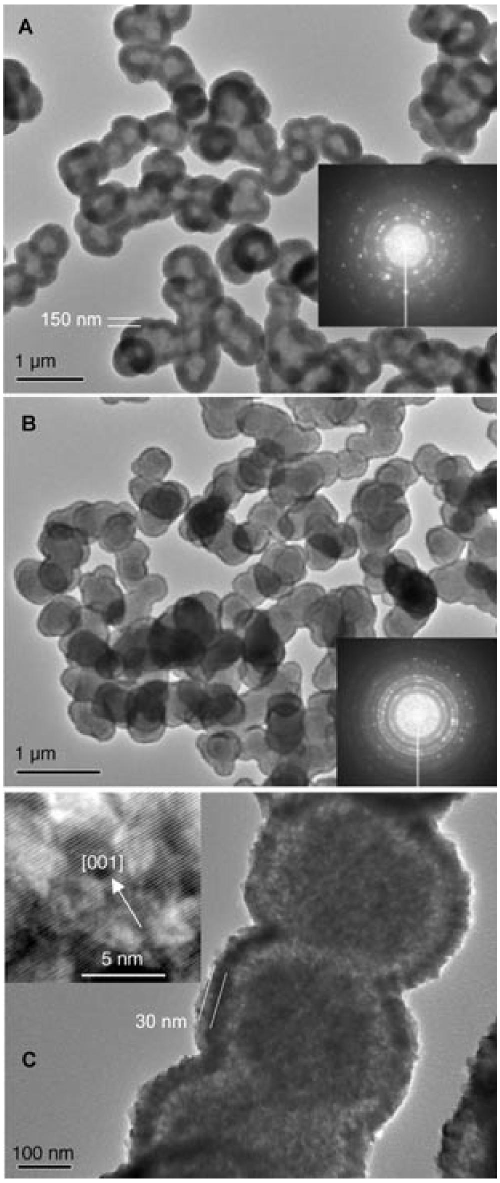

Figure 1. TEM images and SAED patterns (inset) of intestine-like TiO_2 hollow structures synthesized at 180 °C (water/alcohol = 20:80 w/w): A) 5.0 mL of 0.040 M TiF_4 + 20.0 g of 2-propanol, 20 h; B) 2.0 mL of 0.040 M TiF_4 + 3.0 mL of H_2O + 20.0 g of 2-propanol, 22 h; C) high magnification image of (B), together with an HRTEM image of the shell (inset).

No. 21-1272) and energy-dispersive X-ray (EDX) analysis of the solid composition (atomic ratio Ti/O = 1/2; see the Supporting Information). The crystallite size is about 10–20 nm (high-resolution TEM (HRTEM); see Figure 1 C and the Supporting Information); within a set of growth parameters, the crystallinity increases with aging time (see the Supporting Information). In particular, the lattice fringes of d_{004} (2.3 ± 0.2 Å) can be easily identified and indicate a preferred $\langle 001 \rangle$ alignment of the TiO_2 nanocrystallites along the shells of the intestines. The specific surface areas of these samples are in the range 50–60 $m^2 g^{-1}$, and depend on the synthetic conditions employed (see Experimental Section).

As shown in Figure 2, smaller and less interconnected TiO_2 intestines with diameters ranging from 300 to 450 nm can also be tailored with a shorter reaction time (for example, 5 h versus the 22 h of Figure 1 B). More interestingly, these short TiO_2 hollow structures can self-aggregate into microscale hollow spheres, or “colloidosomes” (Figure 2 B–D). Compared to the colloidosomes fabricated recently with polymeric beads in water/oil emulsions,[5] the present mesostructures possess more-complex hierarchical pores, with an interior space within the short TiO_2 intestines, an inter-intestine space created by the intestines, and a large central cavity within the colloidosomes. In addition to the above thick-shelled colloidosomes, thinner spherical organizations or curved platelets assembled from the primary TiO_2 intestines can also be prepared by microemulsion methods (see the Supporting Information).

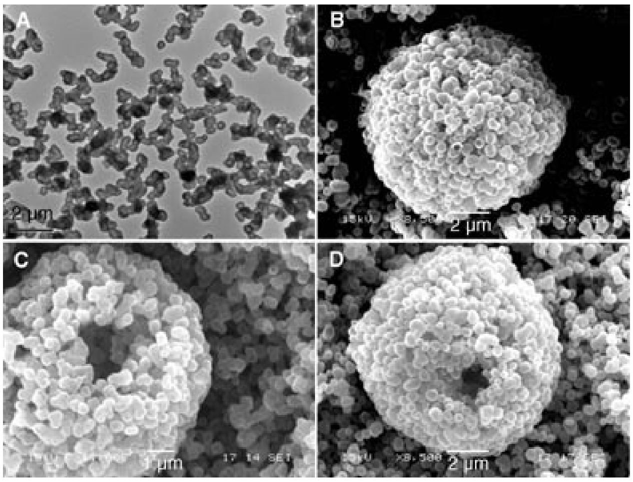

Figure 2. Primary short intestine-like TiO_2 hollow nanostructures (A: TEM image) and their microscale-assembled colloidosomes (B–D: SEM images). Synthetic conditions: 2.0 mL of 0.040 M TiF_4 + 3.0 mL of H_2O + 20.0 g of 2-propanol, at 180 °C for 5 h (water/alcohol = 20:80 w/w).

The formation of the intestine morphology is sensitive to the composition of the solvent mixture: isolated discrete TiO_2 hollow nanospheres can be fabricated with a diameter of 250–450 nm and a wall thickness of about 40 nm if the water content is reduced (Figure 3). Both the sphere diameter and crystallite size in the shells can be tuned by varying the aging time (Figure 3 B) and starting TiF_4 concentration. For example, freestanding TiO_2 hollow spheres with a diameter ranging from 100 to 450 nm can be synthesized when the reaction time is as short as 1.5 or 3 h (see the Supporting Information; the size of the nanocrystallites is around 20–30 nm). In addition to the SAED result shown in Figure 3 A, an XRD investigation (see the Supporting Information) further confirmed the same anatase phase for the hollow spheres.

On the basis of the above results, a growth mechanism is proposed (Figure 4). It is noted that alcohols such as 2-propanol possess self-hydrophobic interactions even though they are miscible with water.[20–22] The water molecules in the aqueous phase interact preferentially amongst themselves

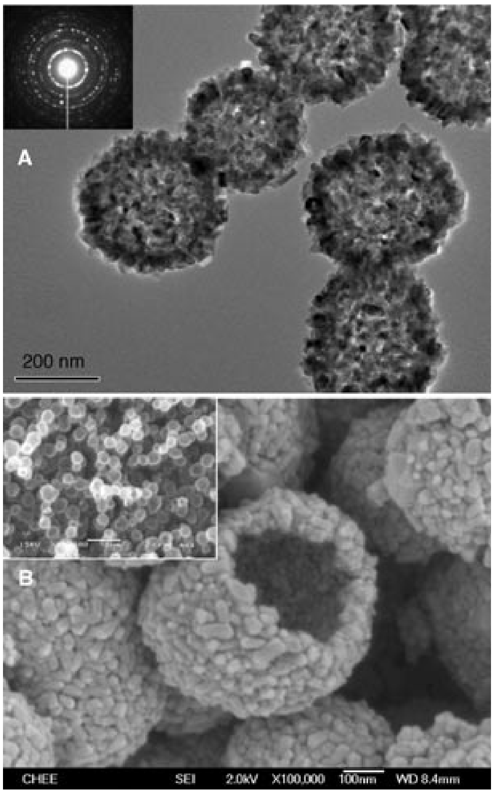

Figure 3. Isolated, discrete TiO_2 hollow nanospheres: A) TEM image and SAED pattern, and B) FESEM image of the wall crystallites and inner cavity; the insert (SEM image) shows an overview of the nanospheres. Synthetic conditions: 1.0 mL of 0.040 M TiF_4 + 3.0 mL of H_2O + 21.0 g of 2-propanol, at 180 °C for 42 h (water/alcohol = 16:84 w/w).

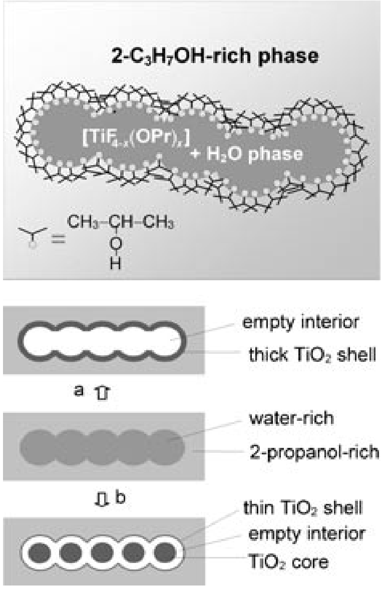

Figure 4. Proposed formation mechanism of intestine-like TiO_2 in a "quasi-reverse-emulsion" (water is the minor phase): a) formation of thick-walled TiO_2 nanostructures, and b) formation of smaller thin-walled TiO_2 nanostructures with some internal cores.

through strong hydrogen-bonding interactions, which result in microheterogeneities, since 2-propanol has only a small disrupting effect on the hydrogen bond between water molecules.[20–22] Considering the electronegativity sequence $F > O \gg C$ and the hydrophobic interactions between the 2-propanol molecules, it is expected that TiF_4 and its other forms of complexes[25], [26] will exist primarily in the water-rich regions (that is, emulsified spherical droplets, Figure 4) because of various hydrogen-bonding interactions (for example, H–O···H and O–H···F). In other words, TiF_4 can also help water to stabilize aqueous droplets, and this means that the dimensions of the resultant TiO_2 intestines are indeed proportional to the starting concentration of TiF_4 (see Figure 1 and the Supporting Information). The water-rich region, in which a series of aqueous droplets are linked together, is then surrounded by a self-assembled 2-propanol-rich phase and vice versa. In good agreement with this model, the aqueous droplets become more isolated when the water to alcohol ratio is decreased, thus resulting in the formation of isolated nanospheres (see Figure 3 and the Supporting Information). Figure 5 displays three UV/Vis spectra measured for different starting solutions. It is apparent that in acidic aqueous phase TiF_4 is first stabilized as complex fluoro ions, predominantly in the form of stable TiF_6^{2-} ions (which is colorless).[25] After the addition of 2-propanol an alkoxylation reaction takes place to give alkoxy-substituted Ti^{IV} complexes such as $[TiF_{4-x}(OPr)_x]$ (for example, $x = 2$).[26] The peak at 366 nm is assigned to the absorption of this type of complex; the absorbance increases linearly with the initial concentration of TiF_4. Addition of a small amount of HF caused the yellowish solution to become colorless again, thus indicating that the TiF_6^{2-} ion had been regenerated. Under these conditions, TiO_2 would nucleate and grow at the interface (shell) as well as in the bulk aqueous phase (core) by hydrolysis and adopt the shape of the aqueous phase (See Figure 4. To a certain extent, therefore, the water/2-propanol system used is analogous to a "quasi-reverse-emulsion", albeit with a weaker hydrophobic effect of 2-propanol than the oil hydrocarbons used in standard reverse-emulsion methods.[27] Indeed, a series of syntheses using ethanol, *n*-propanol, 2-propanol, and 2-methyl-2-propanol indicated that larger TiO_2 hollow structures can be generated when the

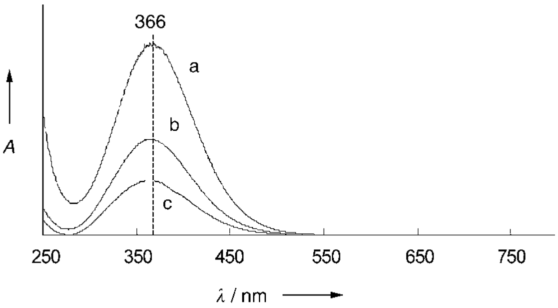

Figure 5. UV/Vis spectra of various solution phases at room temperature: a) 5.0 mL of 0.040 M TiF_4 + 20.0 g of 2-propanol, b) 2.0 mL of 0.040 M TiF_4 + 3.0 mL of H_2O + 20.0 g of 2-propanol, and c) 1.0 mL of 0.040 M TiF_4 + 3.0 mL of H_2O + 21.0 g of 2-propanol.

hydrophobicity of the aliphatic alcohols is increased; the structure of the shell wall is sensitive to the alcohol used, which confirms the tendency to form larger "micelles" with an increase in the hydrophobic interaction of the aliphatic alcohols (see the Supporting Information). These results confirm the generality of this synthetic approach using water–alcohol mixtures. As a final remark, the present solvent system has also been applied to our preliminary work on the fabrication of other metal-oxide hollow nanostructures; generally it works well.[28]

In summary, we have developed a solvothermal process for the controlled creation of interior space in metal-oxide nanostructures. In particular, anatase TiO_2 with either an intestine-like or spherical morphology can be selected by varying the starting chemical composition and reaction time. Apart from the size control, an entirely empty or partially filled interior can be further tailored with this one-step approach. The self-aggregation of micrometer-scale TiO_2 colloidosomes indicates the possibility of constructing even more complex hierarchical hollow structures. The method has also been shown to be general for other metal oxides; the formation of hollow structures can be ascribed to the existence of microheterogeneities in the mixed-solvent system.

Experimental Section

Hydrochloric acid (1.5 M) was used to adjust the pH of deionized water (1.0 L) to around 2. Titanium tetrafluoride (Aldrich Chemical) was then dissolved in this solution to a concentration of 0.040 M, during which the pH value changed to 1.8. The water/2-propanol mixture used was prepared by weight. In a typical synthesis, the aqueous TiF_4 solution (1–5 mL, 0.040 M) and H_2O (0–3 mL) were first added to a teflon-lined autoclave, then 20–21 g of 2-propanol added; the mixture was kept at 180 °C for 1.5–42 h in an electric oven. When mixed with TiF_4, the colorless 2-propanol became clear yellowish. After completion of the reaction the solution became colorless again (since Ti^{4+} complexes were consumed) and a white precipitate (TiO_2 product) formed on the bottom of the teflon reactor. Organization of the as-prepared TiO_2 intestines into spherical or curved assemblies was conducted in oil–water emulsions. In addition to 2-propanol, similar syntheses using ethanol, *n*-propanol, and 2-methyl-2-propanol were also carried out to verify some of the conclusions drawn from this work. The solid products obtained were washed three times with deionized water (10 mL each time) and then dried in vacuum for further characterization.

The crystallographic phase of the hollow TiO_2 structures was determined by powder X-ray diffraction (XRD, Shimadzu XRD-6000, CuK_α radiation) and selected-area electron diffraction (SAED).[23,24] The particle size, crystal morphology, and chemical composition of the TiO_2 products were determined by scanning electron microscopy (SEM/EDX, JSM-5600 LV; FESEM/EDX, JSM-6700F), transmission electron microscopy, and energy dispersive X-ray diffractometry (TEM/SAED, JEM 2010, 200 kV; HRTEM/EDX, JEM 3010, 300 kV).[29] The specific surface areas of the TiO_2 samples were also measured by the BET method (NOVA-3000). A UV/Vis scanning spectrophotometer (UV-3101PC, Shimadzu)[30] was also used to investigate the formation of Ti^{4+} complexes in water/2-propanol mixtures at room temperature.

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