Preparation of Hollow Anatase TiO₂ Nanospheres via Ostwald Ripening

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In this work, we report a simple "one pot" approach to prepare hollow anatase TiO₂ nanospheres via Ostwald ripening under hydrothermal conditions. Inner nanospace and highly organized crystallites in the shell structure and surface regions can be created with a wide range of controlling parameters. The formation mechanism has been investigated with TEM/ED/SEM/EDX/XRD/XPS methods. The approach shows a high versatility for structural engineering of various targeted morphological products, including inner material refills.

Introduction

In addition to the general core−shell nanostructures,[1−4] there has been an increasing interest in fabrication of hollow inorganic nanostructures owing to their important applications in optical, electronic, magnetic, catalytic, and sensing devices ranging from photonic crystals, to drug-delivery carriers, and nano-reactors.[5−8] The inner "nanospace" of these nanostructures, when coupled with chemical functionality of boundary materials, creates both aesthetic beauty and scientific attractions. Among the many investigations in this area, polymeric colloidal particles have been commonly utilized as templates to support the materials of interest via layer-by-layer technique.[5,6] Hollow interiors can be generated by removing the polymeric core supports. Recently, sacrificial metal templates have been introduced to prepare metal nanoshells that have higher standard reduction potentials.[7,8] During redox electrochemical reactions, these metal templates can be gradually evacuated through surface defects while the resultant metal shells preserve the shapes of original templates. In addition to the above two major methods, it would also be desirable to explore other wet-chemical means, aiming at a simple "one-pot" synthetic approach for important metal oxides. For example, hollow TiO₂ microspheres in the diameter range of 10 to 20 micrometers had been recently synthesized in ionic liquids.[9] In addition to this, smaller TiO₂ microspheres (ca. 3 μm in diameter) with mesoporous core−shell structures have also been prepared with a combination of wet (solvent used: EtOH/H₂O) and solid-state reactions very recently.[10] In this article, we will report an aqueous synthetic scheme for preparation of monodispersed hollow anatase TiO₂ nanospheres. With the hydrolysis of TiF₄, solid TiO₂ spheres can be formed; hollow interiors can be further created in 100% morphological yield via Ostwald ripening after a longer hydrothermal treatment. Owing to this new hollowing scheme, the crystallites formed in the nanosphere shell are well aligned; unique textural structures as well as inter-crystallite channels to the central interiors have been attained for the first time for the anatase hollow spheres. It is believed that the method will allow further preparations of other composite metal oxide nanospheres via a "refilling" process.

Experimental Section

The preparation of the tarting solution of TiF₄ has been detailed in our previous report.[11] In a typical experiment, 30 mL of the TiF₄ solution (1.33−2.67 mM) was added to a Teflon-lined autoclave, and the hydrothermal synthesis was conducted at 140−220 °C for 1.5−100 h in an electric oven. A total of 37 experiments were carried out to examine various synthetic parameters. In certain experiments, additives such as thiourea, urea, and HF were further mixed, respectively, with the starting TiF₄ solution. After the reactions, white TiO₂ products were harvested by centrifuging and washing with deionized water. The products were then characterized with a range of analytical techniques, as had been detailed in our previous publications.[11,12] In particular, scanning electron microscopy, energy-dispersive X-ray spectroscopy (SEM/EDX, JSM-5600LV), transmission electron microscopy, selected area electron diffraction (TEM/SAED, JEM-2010F), X-ray photoelectron spectroscopy (XPS; AXIS−Hsi, Kratos), and powder X-ray diffraction (XRD, Shimadzu XRD-6000, Cu Kα radiation) were employed in the present investigation.

Results and Discussion

Figure 1A illustrates the formation process of hollow TiO₂ nanospheres. As indicated, the solid TiO₂ spheres are comprised of numerous smaller crystallites. Compared to those in the outer surfaces, the crystallites located in the inner cores have high surface energies, because they can also be visualized as a smaller sphere having a higher curvature (i.e., higher surface energies and thus easy to be dissolved). When the reaction time is short, the TiO₂ spheres have a solid core (entirely dark; Figure 1B). A hollowing effect is observed for those with a longer reaction time. Reported in Figure 1C and 1D, the inner nanospace (the lighter part) of the spheres is further increased in comparison to the shell (darker spherical circle) when the reaction time is longer (20 h vs 100 h). Furthermore, a higher starting concentration of TiF₄ will give a thicker shell due to a higher growth rate. It should be mentioned that there was no such hollowing effect observed in our previous work,[11] because those TiO₂ nanospheres were single-crystalline (they were epitaxially grown on the (010) surface of α-MoO₃). There are two basic types of hollowed spheres, type (i) and type (ii), as indicated in Figure 1A. The nanospheres reported in Figure 1D can be classified as the type (i) that has a relatively dense and smooth surface.

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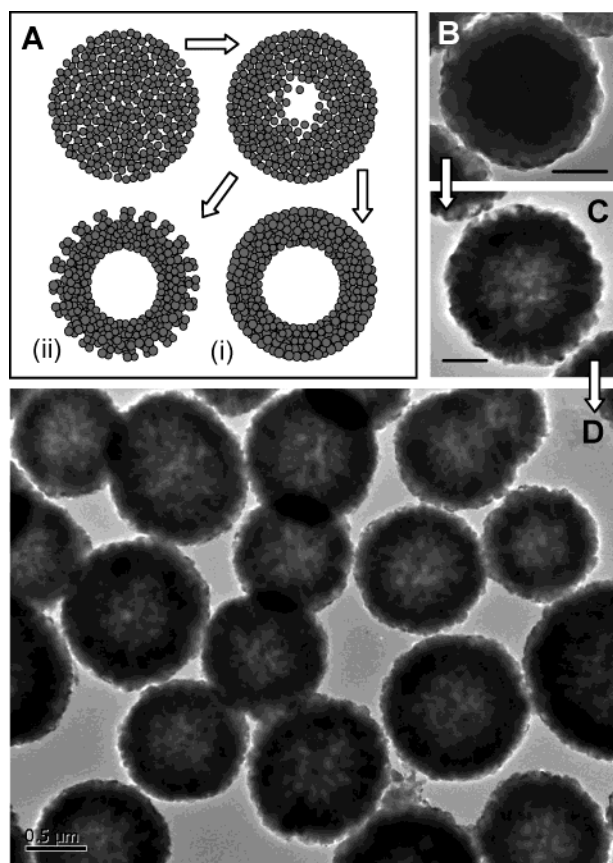
Figure 1. (A) Schematic illustration (cross-sectional views) of the ripening process and two types (i & ii) of hollow structures. Evolution (TEM images) of TiO$_2$ nanospheres synthesized with 30 mL of TiF$_4$ (1.33 mM) at 180 °C with different reaction times: (B) 2 h (scale bar = 200 nm), (C) 20 h (scale bar = 200 nm), and (D) 50 h (scale bar = 500 nm).
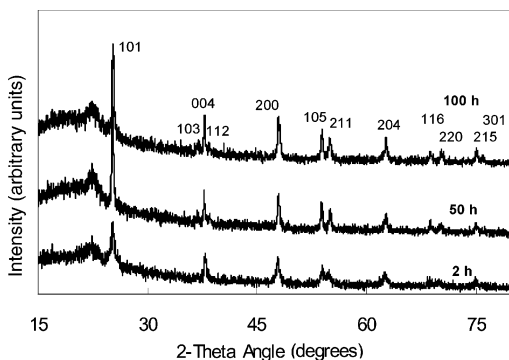

Figure 2. Representative XRD patterns of anatase TiO$_2$ nanospheres. The samples were synthesized with 30 mL of TiF$_4$ (1.33 mM) at 180 °C with reaction times of 2, 50, and 100 h, respectively. The intensity humps at $2\theta = 15-25°$ are due to the signal generated by a silica sample holder used.

The type (ii) spheres have a less compact surface where the extruding crystallites can be observed (will be shown soon). The XRD investigation shown in Figure 2 indicates that the crystallographic phase of all studied TiO$_2$ nanospheres prepared in this work belongs to the anatase-type (SG: *I*4$_1$/*amd*; JCPDS no. 21-1272), and the measured lattice constants of a_o and c_o of this tetragonal phase are 3.79 and 9.51 Å respectively. In particular, the crystallinity of the products is indeed increased gradually with the reaction time (e.g., from 2 to 100 h; Figure 2), which indicates that Ostwald ripening (crystallites grow at the expense of the smaller ones)[13] is an underlying mechanism
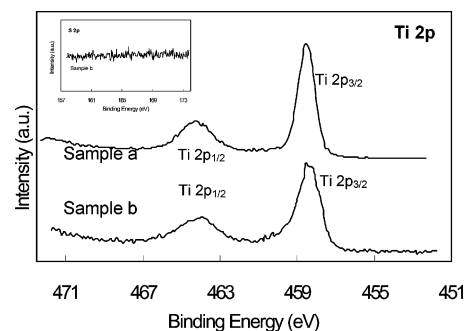
Figure 3. Representative XPS spectra [Ti 2p and S 2p (inset)] of TiO$_2$ hollow structures. Synthetic conditions: (a) 30 mL of TiF$_4$ solution (1.33 mM) at 180 °C for 10 h; and (b) 30 mL of TiF$_4$ solution (2.67 mM) + 100 mg of thiourea at 170 °C for 17 h.
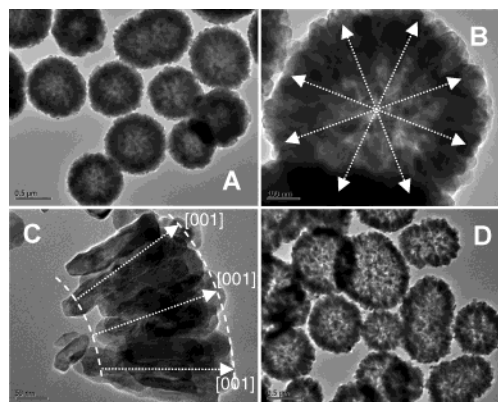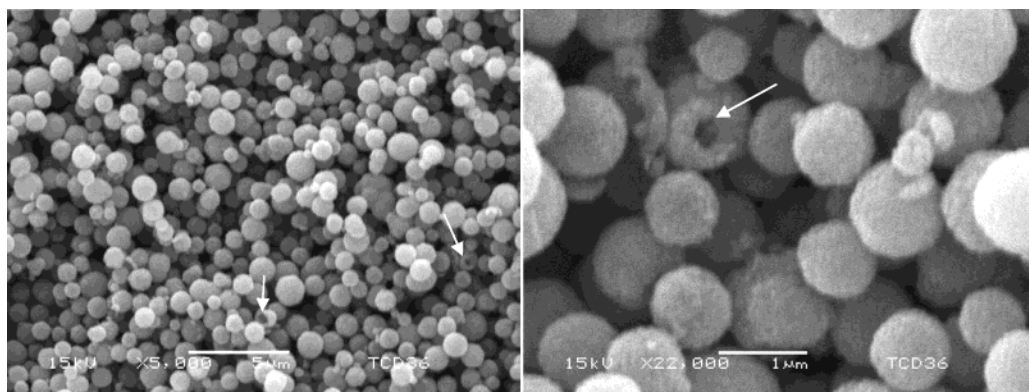

Figure 4. TEM images of TiO$_2$ nanospheres synthesized with 30 mL of TiF$_4$ (1.33 mM) + 25 mg of thiourea for 20 h (180 °C): (A) overall appearance, (B) center-projecting crystallites, (C) the texture of a shell fragment, and (D) TEM image of TiO$_2$ nanospheres synthesized with 30 mL of TiF$_4$ (2.67 mM) for 11 h + 0.4 mL (HF 10%) for another 9 h; both steps at 180 °C. Scale bars in (A) to (D) are equal to 500, 100, 50, and 500 nm, respectively. Arrows indicate the projecting direction along [001] while the dashed lines define the shell thickness.
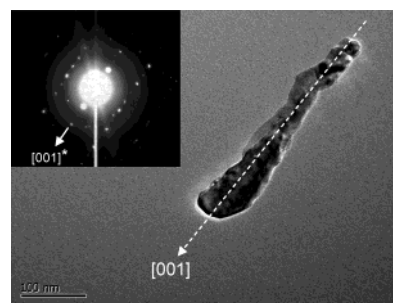

Figure 5. A representative TEM image and its related electron diffraction pattern of anatase TiO$_2$. Synthetic conditions: 30 mL of TiF$_4$ solution (1.33 mM) at 180 °C for 50 h.

operative in this hollowing process. The stoichiometric composition of the anatase nano-products was further confirmed with our EDX analysis (atomic ratio of Ti/O, 1:2, see Supporting Information). As reported in Figure 3, XPS investigation on the titanium chemical state shows that the binding energy of Ti 2p$_{3/2}$ is equal to 458.5 eV and the binding energy of Ti 2p$_{1/2}$ is equal to 464.1 eV, which are identical to that reported in the literature for the same anatase phase.[14] The chemical state of Ti^{IV} is thus confirmed.

On the basis of above TEM/XRD/EDX/XPS investigations, it is suggestive that Ostwald ripening is also associated with the chemical nature of ionic species present in the solution during the synthesis. This point is further addressed in the

Figure 6. SEM images of anatase TiO$_2$ nanospheres. Hollow interiors of some fractured spheres are indicated with arrows. Synthetic conditions: the same as those in Figure 4A.
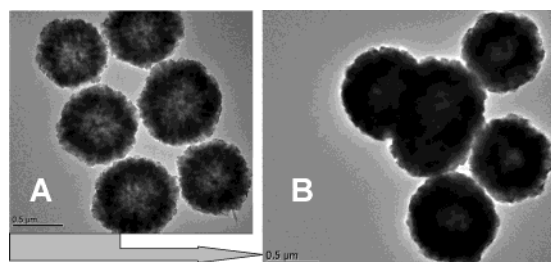

Figure 7. Refilling process of TiO$_2$ nanospheres (TEM images): (A) synthesized with 30 mL of TiF$_4$ (2.67 mM) + 10 mg of thiourea at 180 °C for 10 h, and (B) synthesized with the same conditions of (A) for 11 h, then added with 2 mL of TiF$_4$ (40 mM) for another 9 h (total 20 h) at 180 °C; both scale bars = 500 nm.

following three different synthetic experiments. When the solid TiO$_2$ nanospheres (2 h; Figure 1B) were separated from the mother liquor and heat-treated again in deionized water for another 18 h, no hollowing was observed. This is understandable, because there is no chemical species to generate necessary ionic transport in solution during the ripening process. When thiourea was added, as reported in Figure 4A−4C, the hollowing process could be accelerated, but no obvious effect was observed when using urea as an additive. The observed difference can be attributed to different chelating abilities of :S=C and :O=C to the titanium cations and different chemical natures of their hydrolysis products. Both EDX result (see Supporting Information) and XPS analysis on S 2p core electrons indicate that there is no sulfur contaminant on the samples synthesized with thiourea (see inset, Figure 3). It is interesting to note that the cellular crystallites of the TiO$_2$ spherical shells are highly organized with respect to a common center (Figure 4B & 4C).

The diameter and length of these crystallites are in the ranges of 30−50 nm and 150−250 nm, respectively. Confirmed with SAED in Figure 5, the individual elongated TiO$_2$ crystallites are largely single-crystalline with their axes pointing along [001] of the crystal. It is also noted that the hydrolysis of TiF$_4$ will generate HF, a corrosive chemical that may also be responsible for this ripening process. To investigate this effect, a two-step reaction was carried out with a deliberate addition of HF in the second step (Figure 4D). Indeed, the evacuation of the TiO$_2$ solid core has been significantly speeded up with the additional HF, giving away thinner shells comprising of well-faceted TiO$_2$ nanocrystallites (30−70 nm in size, Figure 4D). Note that some of the spheres are "fused" together forming a peanut-shell-like structure.

In addition to the above TEM observations, where the observation of hollow interiors is largely based on the image contrast, the hollow interiors of the TiO$_2$ nanospheres is also directly reconfirmed with our SEM investigation of Figure 6 for the as-prepared nanospheres; the same hollow interiors are also observed more clearly for our crashed samples (not shown). Although size of these nanospheres may be relatively large (up to 1 μm in diameter), it has been recently shown that the TiO$_2$ microspheres with hollow interiors are also highly demanded in the application of chemical reactors, etc.[9,10]

Regarding the formation of hollow interiors, it is recognized that the ripening process must involve the mass transfer between the solid core and outside chemical solution through inter-crystallite interstitials of the nanospheres. This is demonstrated in an evacuation-then-refilling process reported in Figure 7. With a high concentration of TiF$_4$, type (ii) hollow spheres were readily formed after 10 h of reactions (Figure 7A). When more
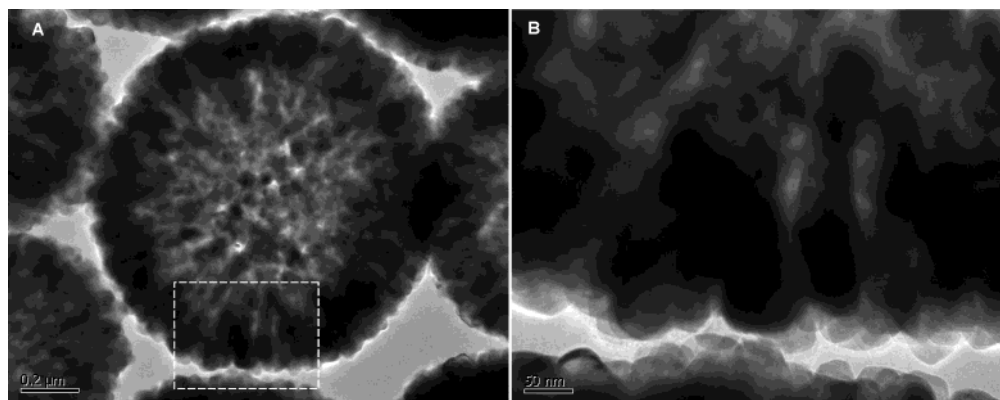
Figure 8. TEM images of the anatase TiO$_2$ spheres. Note that there are inter-crystallite spaces formed perpendicularly to the surface of spheres (whiter areas in the central area of Image A and in the edge area of Image B (the framed area of A). Synthetic conditions: 30 mL of TiF$_4$ solution (1.33 mM) at 180 °C for 50 h.

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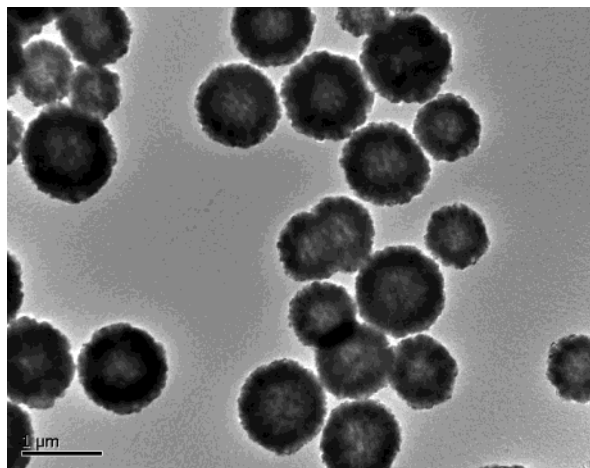
Figure 9. A TEM image of the anatase TiO_2 nanospheres synthesized at a higher temperature. Note that a much shorter reaction time is needed at higher temperatures. Synthetic conditions: 30 mL of TiF_4 solution (2.67 mM) + 10 mg of thiourea at 220 °C for 5 h.

TiF₄ nutrient was supplied in a second stage of synthesis, the nanospheres synthesized from the stage one could be "refilled" with the TiO_2 solid through the shell surfaces (Figure 7B), noting that this process did not cause obvious size change. In view of the well-aligned shell texture attained in Figure 4C, furthermore, it can be deduced that there must exist inter-crystallite interstitials formed perpendicularly to the sphere surface. Indeed, this postulation is further confirmed with our TEM examination reported in Figure 8, where the electron beam of TEM was focused perpendicularly to the sphere center. Brighter contrasts (with a diameter of about 10−25 nm) in the central part of the sphere image reveal these "channels" for chemical entities traveling in and out of the sphere during either hollowing or refilling process. It should be mentioned that the oriented nanostructures fabricated and thus oriented nanochannels provide encapsulated materials with an easy access to the central cavities of the spheres. In addition to the general encapsulation application, this type of hollow nanospheres may also be utilized for synthesis of other composite nanospheres (or other core/shell nanostructures) with the refilling process investigated in Figure 7. Indeed, our recent preliminary investigations have shown that the same refilling process is applicable to other metal oxide inclusions.[15]

By varying the reaction temperature, it has been found that an appreciable hollowing process commences at ≥160 °C, although the TiO_2 nanospheres with a solid core can be formed at much lower temperatures.[11] Furthermore, core evacuation time can be significantly shortened by choosing a higher reaction temperature (220 °C, 5 h), as exampled in Figure 9.

The present method also shows a high versatility for structural and morphological engineering. In addition to the hollow structures, the solid core and surface region of a sphere can be further differentiated with a higher dose of thiourea in the
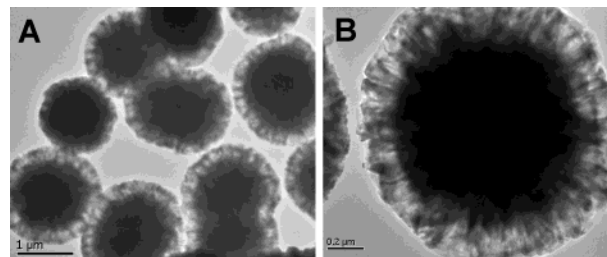
Figure 10. Sunflowerlike TEM images of TiO_2 spheres with a less compact surface and a solid core: (A) overall appearance (scale bar = 1000 nm), and (B) a detailed view on the surface region (scale bar = 200 nm). Synthetic conditions: 30 mL of TiF_4 (1.33 mM) + 300 mg of thiourea at 180 °C for 3 h.

synthesis. As shown in Figure 10, an abrupt core−surface interface within the TiO_2 spheres has been further attained. This structure can also be viewed as a variation of the type (ii) spheres with a solid core.

Conclusion

In summary, we have developed a simple "one-pot" method to prepare hollow anatase TiO_2 nanospheres via Ostwald ripening in aqueous mediums. Inner nanospace and highly organized crystallites in the shell and surface regions can be created with a wide range of controlling parameters. This approach shows a high versatility for structural engineering of various targeted morphological products. In addition to the general encapsulation, this type of hollow nanospheres could be utilized for synthesis of other composite core−shell nanostructures with a refilling process.

Supporting Information Available: Information on our EDX analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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