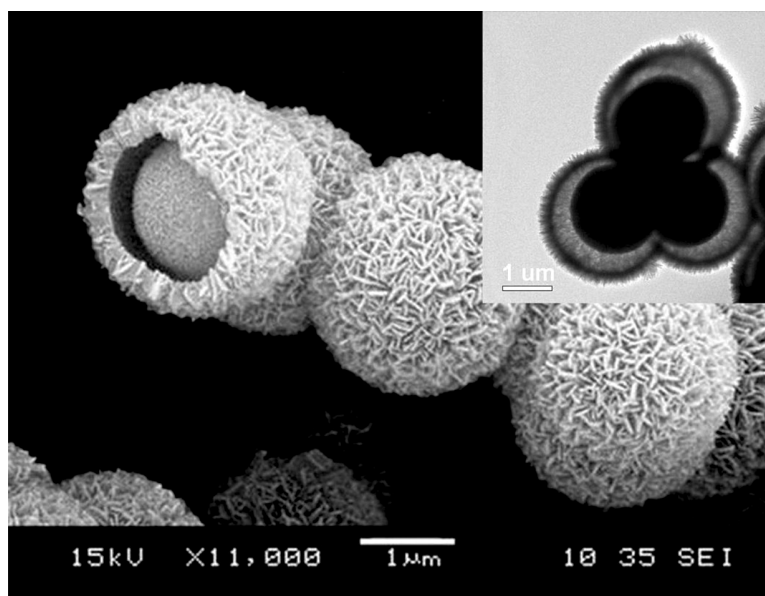


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Mesoporous Titania Spheres with Tunable Chamber Structure and Enhanced Photocatalytic Activity

Hexing Li,^{*,†} Zhenfeng Bian,[†] Jian Zhu,[†] Dieqing Zhang,[†] Guisheng Li,[†] Yuning Huo,[†] Hui Li,[†] and Yunfeng Lu^{*,‡}

Department of Chemistry, Shanghai Normal University, Shanghai 200234, China, and Chemical and Biomolecular Engineering Department, University of California, Los Angeles, California 90095

Received March 28, 2007; E-mail: hexing-li@shnu.edu.cn; luucla@ucla.edu

Many natural materials, like seashell and lotus leaf, are composed only with ordinary composition but exhibit fascinating property owing to their unique structure.¹ Such intricate natural designs have inspired extensive research in synthesizing materials with controlled structure and morphology, with expectations of achieving novel or enhanced properties.^{2,3} This work, for the first time, reports the synthesis of hollow titania spheres with tunable interior structure and urchinlike morphology and examines their photocatalytic activity enhanced by such unique structure.

Hollow spheres, generally, are of great interest for a large spectrum of applications, such as adsorbents, delivery carriers, catalysts, and biomedical uses.^{4–6} Their synthesis often relies on templating approaches, in which hard (e.g., inorganic, metal, and polymer particles) or soft sacrificial templates (e.g., supramolecular assemblies of surfactant and polymer) were used to create a hollow structure.^{7–12} The template approach can be easily implemented; however, the capability of constructing complicated structure is limited by the availability of a template. As an alternative, template-free approaches based on different mechanisms were also developed to synthesize hollow spheres with more complicated structure.^{13–16} To synthesize the hollow titania spheres with such complicated structure and morphology, we adapted a template-free approach, in which a titania precursor, TiOSO_4 , was solvothermally reacted in glycerol, alcohol, and ethyl ether. Judicious choice of the alcohol molecules (e.g., methanol, ethanol, and propanol) and reaction time affords the synthesis of spheres with adjustable morphology, size, and interior structure that is tunable from solid, sphere-in-sphere, to hollow (see Supporting Information).

Figure 1 shows electron micrographs depicting the structural evolution with reaction time. Uniform, smooth, solid spherical particles (a) were obtained after 1-hour reaction. Small surface platelets (b) were formed after 12 h and further grow with time, forming an urchinlike prickly surface (c–f). It was also found that the platelets formed shells on the solid cores, creating a core–shell structure (c) after 1-day reaction. Interestingly, these cores shrink with time, forming a unique sphere-in-sphere structure with continuously reducing innersphere size (d–f). The innerspheres finally diminished after 14-days of reaction and created a hollow spiny structure (f). Accompanying this interesting structural evolution is the growth of the outside-sphere diameter from 1.6 to 3.1 μm (Table S1). The outside-sphere diameter can also be tuned by choosing the alcohol molecules. For example, the spheres synthesized with methanol, ethanol, and propanol under similar conditions for 2 days display a similar sphere-in-sphere structure and urchinlike morphology, while their outside-sphere diameter systematically increases from 2.0 and 2.4 to 5.2 μm (Figure S1). Although the as-synthesized spheres are amorphous, they turn to be highly crystalline (anatase) after calcination at 550 $^\circ\text{C}$ for 3 h while

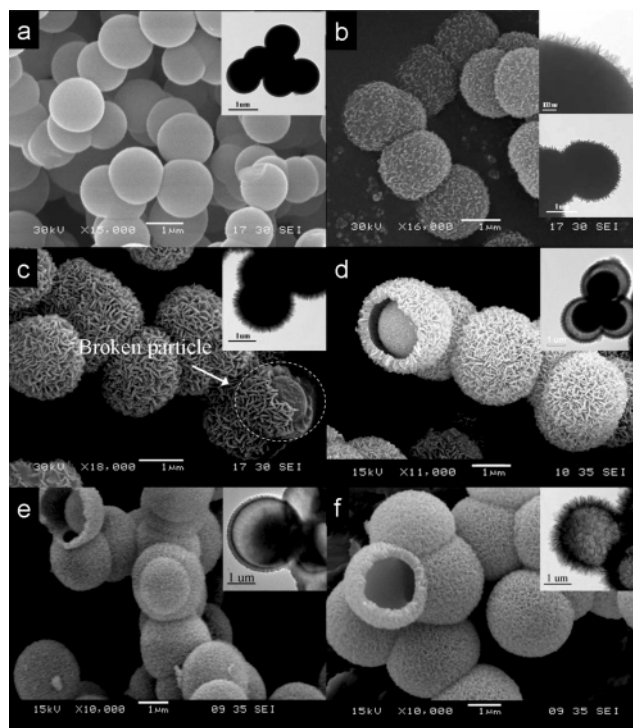


Figure 1. SEM and TEM (insets) images of the titania spheres synthesized for (a) 1/24, (b) 0.5, (c) 1, (d) 2, (e) 7, and (f) 14 days, showing transitioning interior structure from dense, to sphere-in-sphere, to hollow and surface morphology from smooth to prickly.

maintaining their sphere-in-sphere structure, as confirmed by X-ray diffraction (XRD), high-resolution TEM, and selected area electron diffraction studies (Figures S2–3).

Such a spiny structure possesses mesoporous networks evidenced by the nitrogen sorption experiment (Figure S4). Surface area and pore volume of the uncalcined spheres increase from 46 to 167 m^2/g and 0.11 to 0.32 cm^3/g , respectively, when reaction time was increased from 0.5 to 2 days, and remain similar or slightly decrease for a longer reaction time (Table S1). Such porous structure provides efficient transport pathways to their interior voids, which is critical for catalyst, delivery, and other applications. More importantly, the unique sphere-in-sphere structure allows multireflections of electromagnetic waves, such as ultraviolet and visible light, within their interior cavities, endowing these spheres with greatly enhanced properties.

To demonstrate this intricate structure–function correlation, we examined photocatalytic activity of the calcined spheres using phenol degradation as a probe reaction (Figure 2). The solid spheres (12 h, also see Figure 1a) show the lowest activity of 55% while other spheres show significantly higher activities. In particular, the spheres with sphere-in-sphere structure (2 day, denote as P2, also

[†] Shanghai Normal University.

[‡] University of California.

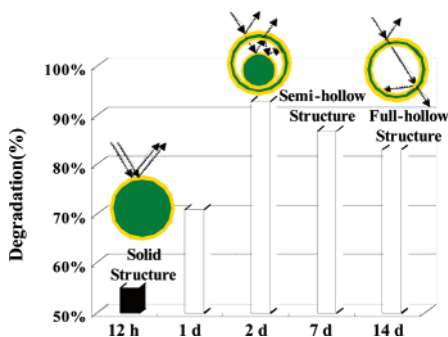


Figure 2. Comparison of photocatalytic activities of the titania spheres with solid, sphere-in-sphere, and hollow structure. Inset shows a schematic illustration of multiple reflections within the sphere-in-sphere structure.

see Figure 1d) show an activity as high as 93%. Since all these spheres possess similar crystalline structure (Figure S2) and surface area (e.g., 32 m²/g for the solid spheres and 62 m²/g for P2, see Table S1), such dramatic activity enhancement is raised from the unique sphere-in-sphere structure. In fact, destroying the sphere-in-sphere structure by grinding the spheres slightly increases the surface area from 62 to 68 m²/g; however, the crushed sample showed a dramatically decreased activity of 57%, similar to that of the solid spheres. As schematically illustrated in the inset, we believe that a sphere-in-sphere structure with an appropriate innersphere diameter allows multiple reflections of UV light within the interior cavity, allowing more efficient use of the light source and therefore offering an improved catalytic activity (Figure S7). The spheres synthesized with 7-day reaction (Figure 1e) display a lower activity (87%) than P2, possibly because of their smaller innerspheres that reduce reflection within their interior cavity. Consistently, the hollow spheres (14 day, also see Figure 1f) show even lower activity (83%) because of the even less reflections. The above results unambiguously suggest that such unique structure provides titania with greatly enhanced photocatalytic activity. More importantly, this multiple-reflection concept may be generalized to the design and fabrication of novel materials with enhanced properties for microelectronics, optoelectronics, and other applications.

The formation of such spheres may involve aggregation of titania building clusters into spheres and their subsequent reaction, dissolution, and re-deposition process. During the solvothermal condition, etherifying reactions between alcohol and glycerol produce water continuously. Titania building clusters may be generated through alcoholysis reaction or hydrolysis–condensation reactions of TiOSO₄. As-formed clusters aggregate and react forming solid spheres that contain a large number of hydrolyzable ligands (e.g., -SO₄, glyceroxy, and ethoxy groups) possibly due to slow reaction kinetics. With increasing reaction time, water is produced continuously through the etherifying reactions and reacts with the spheres, leading to the dissolution and rearrangement of the surface building clusters. As a result from this process, surface plates (Figure 1b) were initially formed and grown into a thin shell layer (Figure 1c). Continuation of this process gradually dissolves the core spheres, sequentially creating the observed sphere-in-sphere and hollow structure.

The occurrence of etherifying reactions was clearly proved by GC-MAS and NMR studies, evidenced from the formation of ethyl ether and the ethers from ethanol and glycerol (Figure S5). It is worth pointing out that reacting TiOSO₄ with glycerol in the absence of ethanol could not lead to any precipitant, possibly because of a steric effect that hinders the etherifying or alcoholysis reactions. Similarly, the presence of hydrolyzable ligands within the spheres was also confirmed by TGA–DTA analysis. As shown in Figure S6, the spheres after 1-hour reaction show multiple exothermic

peaks and a weight loss of 60%; while the spheres after 2-day reaction only show a single exothermic peak and a lower weight loss of 49%. Consistent with the TGA analysis, energy dispersive X-ray spectroscopy (EDXS) analysis suggests an increasing Ti and decreasing carbon composition with increasing reaction time (Table S2). The presence of these hydrolyzable moieties allows redissolution and re-deposition of the building clusters upon further reactions. Therefore, the formation of larger spheres is expected from building clusters containing more and larger removal ligands. Indeed, as shown in Figure S1, increasing the carbon-chain length of the alcohol slows the alcoholysis and etherifying reactions and produces building clusters with more removal ligands, which leads to the formation of larger spheres.

It is also worth mentioning that replacing TiOSO₄ with other titanium sources, such as tetrachloride, tetrabutyl titanate, and tetraisopropyl titanate, only resulted in solid particles. This is possibly attributed to the sulfuric acid produced from the alcoholysis reaction or the sulfuric group itself that catalyzes the etherifying reactions. Meanwhile, we discovered that use of ethyl ether as a cosolvent is essential to ensure the formation of such a unique structure. The optimum molar ratio of ethyl ether/TiOSO₄ was around 11, and only dense particles were obtained for an ethyl ether/TiOSO₄ ratio higher than 20 or less than 5. More detailed investigation is under way.

In summary, we have demonstrated the synthesis of photocatalytic hollow titania spheres with unique urchinlike morphology and tunable interior structure. As-created sphere-in-sphere structure endows the spheres with greatly enhanced photocatalytic activity possibly attributed to multiple reflections of UV light within the sphere interior voids. This work provides a novel pathway to the synthesis of hollow spheres with complicated structure, offering a new material platform for catalyst, microelectronic, and other applications.

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Supporting Information Available: Detailed information on the sphere synthesis, activity characterization, XRD, sorption, GC-MAS, NMR, TEM, TGA, and EDS studies. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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