



Short communication

Self-development of hollow TiO₂ nanoparticles by chemical conversion coupled with Ostwald ripening



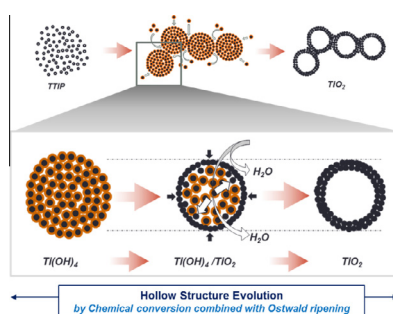
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HIGHLIGHTS

- The porous/hollow TiO₂ nanostructures were self-developed without template.
- A plausible mechanism was proposed based on the systematic experiments and analysis.
- The chemical conversion and Ostwald ripening induced the evolution of nanostructures.

GRAPHICAL ABSTRACT



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ABSTRACT

In this communication, the TiO₂ materials with porous and hollow nanostructures were successfully synthesized through one-pot solvothermal process without any surfactant and template. Our study demonstrated that, the chemical conversion could induce the self-development of hollow TiO₂ nanostructures coupled with the physical Ostwald ripening process. In particular, the chemical conversion took place progressively from the particle surface to the core of an assembly, generating the converted TiO₂ materials. The exterior TiO₂ grains were quickly transformed to be a solid and stable surface shell of spheres. Continuous chemical conversion process for inner grains of spheres would lead to the formation of loose package of grains and thus could facilitate would the outward migration and deposition of inner grains onto the stable exterior shell of spheres. The depletion of interior material resulted in generation and development of hollow core structure. This study can be basis for the fabrication of hollow structures of different solid materials by one-pot solvothermal process.

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1. Introduction

In recent years, there has been an extensive interest in fabrication of numerous materials with porous and hollow nanostructures for diverse application fields, including catalysis, nano- and microreactors, and drug delivery, owing to their unique structural and physical properties [1–4]. Regarding the fabrication of porous/hollow structure, a one-step and template-free method based on

an inside-out Ostwald ripening has been widely used to explain the development of interior space and shell porosity for a wide range of inorganic materials [5–7]. For this approach, it is suggested that the central materials of a colloidal solid aggregate with relatively small size and/or less crystallinity would have a strong tendency to dissolve into solution, and then be subsequently relocated to the surface by a recrystallization process thus generating nanostructures with hollow interior spaces [8,9]. The relocation and transformation of materials were also observed for the generation of core-shell nanostructures [10]. Regarding the fabrication of porous/hollow nanostructures for various applications in a very

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recent study, the TiO₂ hollow spheres which were first fabricated based on the Ostwald ripening process and then were modified with SnO₂ could promote the dye adsorption, light harvesting, and electron transport, leading to 28% improvement in the conversion efficiency compared to film-based SnO₂ [11]. In another study, Fei et al. [12] fabricated the hollow cobalt spheres via Ostwald ripening process and observed that the hollow spheres exhibited high discharge capacity and good cycling stability as anode materials for lithium-ion batteries. Cao et al. [13] prepared gas permeable, photoactive and crack-free titania–silica aerogels of high titanium content (i.e., up to Ti/Si = 1) with good mechanical strength, large surface area, mesoporous structure and good gas permeation. The porous aerogel network could trap and filter airborne particulates as well as exhibited excellent photocatalytic performances.

Considering the matter relocation, the Ostwald ripening has been widely suggested as underlying mechanism for the formation of hollow structure within a colloidal solid aggregate. The hollowing phenomena based on Ostwald ripening, therefore, is involved with solid-solution-solid transformation and transportation accompanying with recrystallization of primary crystallites or particles as building materials. Detailed analysis on this hollowing process should also consider the chemical conversions of building materials, because the chemical conversions can influence such transformation and transportation of the building materials both on solid–liquid interfaces and in surrounding media. However, investigation in this aspect of research has not been well established. More systematic studies are required to understand this intriguing physical/chemical process and also to establish more controllable procedures to prepare nanostructures by this process.

In this communication, we synthesized the porous/hollow TiO₂ nanostructures by one-pot and template-free solvothermal process and observed the chemical conversion of Ti-based materials within a solid sphere along with the hollowing process. Our experimental analyses supported that the chemical conversion should be involved in the structure evolution and this conversion coupled with physical Ostwald ripening process could induce the self-development of hollow TiO₂ nanostructures. This study can contribute to a better understanding of the hollowing mechanisms of different solid materials for various applications such as adsorbents, encapsulation and delivery carriers, catalysts and biomedical uses.

2. Experimental

In this communication, we synthesized porous/hollow TiO₂ nanostructures by one-pot and template-free solvothermal process and systematically characterized the structure evolution. In a typical experiment, 35 mL ethanol containing titanium tetraisopropoxide (TTIP) was added to a Teflon-lined autoclave reactor which was then placed in an electric oven. The solvothermal synthesis was conducted at 220 °C for different processing times in order to elucidate the structural evolution of the hollow TiO₂ nanoparticles. After the scheduled processing time, the product particles were obtained by centrifuging and were washed with absolute ethanol for several times and then were dried in a vacuum oven before characterization.

The SEM measurement was carried out with a Hitachi S-4800 ultra-high resolution SEM equipment. The TEM images of those particles were taken by a JEOL JEM-2011 transmission electron microscope. Powder XRD patterns were recorded with a Philips X'Pert PRO MPD X-ray diffractometer using Cu K α radiation ($\lambda = 1.54060$ Å, 40 kV, 30 mA). The FT-IR spectra were obtained with an EXCALIBER UMA-500 spectrophotometer. The simultaneous TGA/DTA was operated on SDT Q600 with balance sensitivity of 0.1 μ g and temperature sensitivity of 0.001 °C.

3. Results and discussion

The structural evolution of TiO₂ hollow nanostructures was observed by a series of time-dependent experiments. The morphologies and structures of typical product particles obtained for different processing times were investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) measurements. As indicated in Figs. 1a and 2a, the spheres with solid core structure were initially formed after 1 h of the solvothermal reaction. Some spheres were connected to each other, forming a chain structure. The corresponding X-ray diffraction (XRD) pattern exhibited that the product was very poor crystalline. No XRD peak was clearly identified as shown in Fig. 3a. The hollowing phenomena as well as crystallization occurred for those spheres with a longer reaction time. The porous/hollow structures were observed for particles obtained after 4 h as shown in Figs. 1d and 2d. Fig. 1e exhibits the morphology of particles obtained for 5 h of the solvothermal reaction by SEM measurement. Obviously, some broken spheres were clearly observed, confirming the formation of particles with solid shell. The hollow structure of the product particles was further confirmed by TEM measurement as shown in Fig. 2e. An intensive contrast between the black margin and the bright center of particles indicated the existence of hollow structure in the resulting spheres. Along with the hollowing process, the XRD peaks of anatase TiO₂ were observed for particles obtained after 2 h of processing time. Those XRD peaks became sharper with time. As indicated in Fig. 3e, the XRD pattern of product particles obtained after 5 h revealed that all the reflections could be indexed to anatase TiO₂ (Reference code: 03-065-7514), indicating the formation of pure anatase phase of the product particles. As shown in Figs. 1f, 2f and 3f, no significant further development of particle morphology and crystallinity was observed when the processing time was prolonged to 7 h. It was found that the TiO₂ hollow nanostructures were fully developed for 5 h of processing time. The ultra-high resolution SEM and TEM images of particles obtained after 5 h of processing time exhibited that the TiO₂ hollow particles were comprised of closely packed grains which assembled together to form robust shells with possibly porous structure (Fig. 4). Such porous structure provides efficient transport pathways to their interior voids, which is critical for catalyst, delivery, and other applications.

The compositional change associated with structural evolution of product particles was characterized using Fourier transform infrared spectroscopy (FT-IR). The FT-IR spectra of the nanostructures obtained after 1 h and 5 h (Fig. 5a and b, respectively) processing times showed a strong absorption of Ti–O band at 540 cm⁻¹ and 531 cm⁻¹, respectively. This slight shift of Ti–O band might be caused by whether the crystallization of product particles from amorphous to anatase phase of titania or the chemical transformation of Ti-based compounds from covalent bond Ti–O–H belonging to Ti(OH)₄ to covalent bond Ti–O of TiO₂ which would possibly absorb relatively higher energy [14]. The broad band around 3300–3400 cm⁻¹ was associated with the stretching vibration of the –OH group belonging to adsorbed H₂O molecules on the particle surface and/or the surface hydroxyl groups of the TiO₂ particles, while a band around at 1634 cm⁻¹ and 1633 cm⁻¹ of particles obtained after 1 h and 5 h, respectively, could be assigned to the bending vibrations of the –OH group. Other absorption peaks in the range of 1000–1700 cm⁻¹ could be attributed to the vibrations of C–H and C–O bonds due to the existence of organic molecules adsorbed on the spheres. These observations were consistent with previous literatures [15–17].

The chemical conversion of the product particles was determined by simultaneous thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of the particles obtained after 1 h

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