Facile Template-free Alcohothermal Route to Synthesize Hollow TiO_2 Microspheres with Nanocrystal Grain Structure

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A convenient template-free approach was founded for the synthesis of almost uncracked hollow titania (TiO_2) microspheres with nanocrystal grain structure, which size and shell thickness of microspheres can be altered in a controllable way.

In recent years, considerable research activity has been directed toward the synthesis of hollow microspheres owing to these special structures exhibited low densities, high surface area and interesting electronic, magnetic, and chemical properties in a wide range of applications.[1] Nanosized TiO_2, as one of the most important oxide semiconductor materials, has attracted increasing attention because of its unique physicochemical properties in the wide applications of solar energy conversion,[2] photocatalysis,[3] sensors,[4] fine ceramics,[5] etc. Especially, nanocrystalline TiO_2 has a great many of advantages on the wastewater treatment, such as high catalysis efficiency, energy-saving, nopollution, chemical inertness, etc. and can degrade all kinds of organic pollutants from water effectively.[6] Unfortunately, aggregation and being recovered difficulty often limit its application in practice. To resolve this problem, many supported photocatalysts of TiO_2 are prepared. However, the immobilization of the TiO_2 catalyst on certain supporting materials weakens its photocatalytic degradation efficiency.[7,8] On the contrary, the hollow TiO_2 microspheres with nanocrystal grain structure enjoy an attractive advantage for photocatalyst in water treatment.[8,9]

Until now, a variety of routes have been investigated to synthesize hollow TiO_2 microspheres, most among which base on sacrificial templates including polystyrene latex spheres,[10] macroporous polymer,[11] colloidal particles,[12] liquid droplets,[9] microemulsion droplets,[13] micelles,[14] and so on. An important procedure in these methods is the removal of the templates or the usage of two immiscible liquid phases, which results in the complication of the preparation, cracking of microsphere shell and limits of their application. Although several new techniques with chemical vapor deposition[15] and interfacial synthesis in ionic liquids[16] have been reported, it is still highly desirable to develop an efficient, template-free, and surfactant-free method to prepare hollow TiO_2 microspheres. In this letter, we report a simple template-free route for the synthesis of hollow TiO_2 microspheres via alcohothermal technique using tetra-*n*-butyl titanate [$Ti(OC_4H_9{}^n)_4$] as a precursor at the mild conditions.

Figure 1 shows a representative scanning electron micrograph (SEM, Hitachi S-570) of the TiO_2 microspheres. It can be seen that well-defined TiO_2 microspheres, 6–10 μm in diameter, were formed. A mechanically fractured particle demonstrates that the spheres possess hollow structures, and the shell thickness observed is ca. 1 μm.

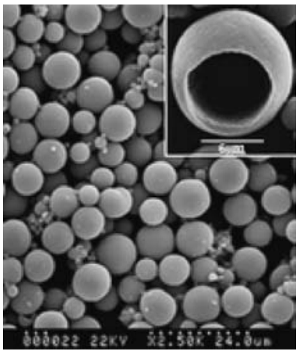


Figure 1. SEM images of as-prepared hollow TiO_2 microspheres. The inset shows a fractured sample.

Moreover, the experiments show that the molar ratios of water to alkoxide and sulfuric acid to alkoxide play a key role to give the specific hollow microspheres. Only when the $H_2O:Ti(OC_4H_9{}^n)_4$ molar ratio is ≤ 3, and $H_2SO_4:Ti(OC_4H_9{}^n)_4$ molar ratio ranges between 0.2 and 0.8, can hollow microspheres be produced. Otherwise, the titania precipitate is small nanoparticles. A larger scale SEM image of surface and XRD pattern of microspheres (Figure 2) reveal that shell structure appears to be composed of anatase titania nanocrystals, and the crystallite size estimated from the Debye–Scherrer's equation is approximately 10 nm.

In addition, size and shell thickness of microspheres can be controlled to certain extent, depending on the experimental conditions (see Supporting Information Figures S1 and S2).[20]

To our knowledge, hydrolysis of alkoxides is the most common method of producing TiO_2 nanoparticles, and there have been several research groups[17] that have reported the hydrolysis of titanium alkoxides in alcoholic solvent for synthesis of TiO_2 nanoparticles, but not hollow microspheres. Although

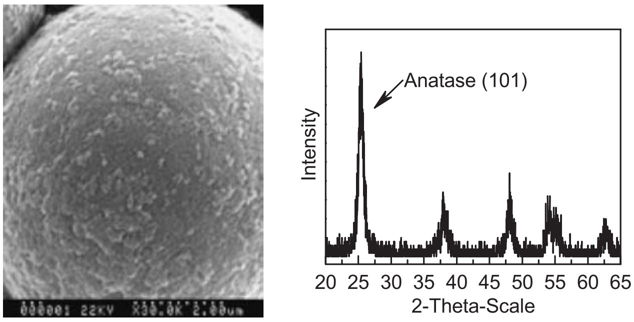
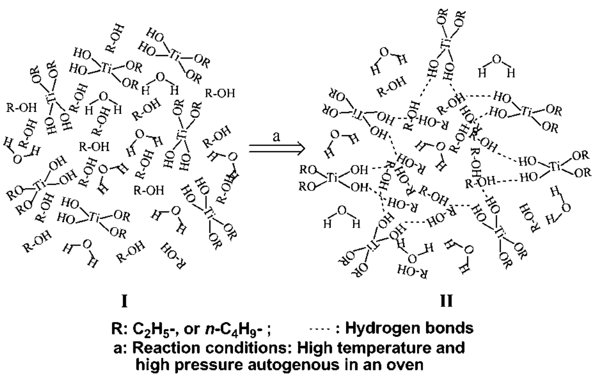


Figure 2. A larger scale SEM image of surface (left) and XRD (Bruker, D8 Advance) pattern (right) of TiO_2 hollow microspheres.



Scheme 1. Schematic illustration of the formation mechanism of hollow TiO_2 microspheres via an auto-orientation assembly.

the mechanism for the formation of the hollow TiO_2 microspheres in our study is not very clear, it is noteworthy that H_2O:$Ti(OC_4H_9{}^n)_4$ molar ratio in these prior works[17] is much higher than the threshold (≤ 3) presented during our research. Based on the mentioned results, an auto-orientation assembly mechanism is proposed in Scheme 1.

According to the reference,[18] an exchange reaction can partly occur between the ethanol solvent and the n-butyl-based reactant, which is almost simultaneous with the hydrolysis and polycondensation reactions of titanium alkoxides. If the H_2O:$Ti(OC_4H_9{}^n)_4$ molar ratio is extremely low, the hydrolysis reaction is limited. Consequently, a mixture of $Ti(OR)_x(OH)_{(4-x)}$, R–OH (R denotes C_2H_5– or n-C_4H_9–) and trace amounts of water comes into being in disorder (Scheme 1-**I**) before solvothermal treatment, in which no particles were observed with SEM or TEM. However, under the high-temperature and high-pressure autogenous in an oven, the molecular polarity of n-butanol molecules compelled them to auto-orientate for the aggregation, which led to the formation of initial skeleton of the hollow spheres through hydrogen bonds. (Scheme 1-**II**). Meanwhile, $Ti(OR)_x(OH)_{(4-x)}$ in the skeleton is attacked by water and alcohol molecules and forms into titanium oxides, which consequently strengthens the hollow structure.

As supposed above, the interior vapor pressure of microspheres is lower than that of the exterior, once the firm shell of microspheres constructed. The results that the fragments formed in the autoclave were almost enclosed in the corresponding shells provide an evidence for our hypothesis (see Supporting Information Figure S3).[20]

Furthermore, the consensus appears to be that, inorganic acid in this method can act as catalyst for the hydrolysis and polycondensation reactions of titanium alkoxides.[17b,19] Therefore, a high H_2SO_4:$Ti(OC_4H_9{}^n)_4$ molar ratio results in a higher rate of the hydrolysis and polycondensation reactions than that of auto-orientation to aggregate of titanium alkoxides, which determines that the final product is nanoparticle. However, the formation mechanism of hollow TiO_2 microspheres is still unclear. The detailed discussion will be the subject of a forthcoming full paper.

In summary, the present study provides a simple, efficient, template-free route to synthesize hollow TiO_2 microspheres. We have demonstrated for the first time the synthesis of the hollow TiO_2 microspheres via alcohothermal technique using tetra-n-butyl titanate as a precursor, if H_2O:$Ti(OC_4H_9{}^n)_4$ molar ratio is <3. And more importantly, the size and the shell thickness of the as-synthesized hollow TiO_2 microspheres can be readily controlled by altering the experimental conditions. In addition, since these TiO_2 microspheres have small crystal grains and almost uncracked structure, they might have good potential applications in catalyst supports, coatings, and catalysis in wastewater treatment etc.

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20 Supporting Information is available electronically on the CSJ-Journal web site, http://www.csj.jp/journals/chem-lett/index.html.