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Effects of size and shell thickness of TiO_2 hierarchical hollow spheres on photocatalytic behavior: An experimental and theoretical study

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ABSTRACT

Through a self-sacrificing template method, highly uniform hollow-spheres of TiO_2 anatase are synthesized with controllable diameter from 365 nm to 930 nm. Compared to large hollow spheres, a large enhancement in the photocatalytic activity is reported for the small hollow spheres (with a thickness of 50 nm). By extending Mie's scattering theory from solid- to hollow-spheres, for a spherical scatter with a diameter of 300–900 nm, theoretical calculation reveal that each singular hollow sphere has absorption power equivalent to a solid sphere as the shell thickness parameter reaches a critical value of 0.3–0.6. This critical thickness parameter is independent to the size of a single hollow sphere, demonstrating that hollow spheres have quantitative advantages over solid spheres of the same weight. Moreover, calculation supported that small hollow spheres have stronger absorption power than large hollow spheres due to higher thickness. This greatly enhance the performance of small hollow spheres under a photocatalytic test. Our theoretical results showed good agreement to the experimental measurements, and provided a framework for the design of hollow-sphere nano-particles for optimized absorption power.

1. Introduction

In the last few decades, nano-sized TiO_2 had attracted much interest due to its wide range of applications, which include lithium ion batteries [1,2], electrochromism [3,4], bio-technology [5,6] and photocatalysts [7–9]. Photocatalyst, which converts solar light into chemical energy, has attracted lots of attention, in particularly for its green energy applications. Instead of electrolyzing water, TiO_2 can be used as a major photocatalyst to decompose water into its constituents of hydrogen and oxygen, also functioning as a clean and recyclable energy access to hydrogen fuel [10,11]. To improve the photocatalytic activity, several methods are demonstrated, such as reducing the recombination of separated electron–hole pairs by blending various TiO_2 phases, or differing the size of TiO_2[12–14], depositing metal materials on a TiO_2 surface to form a heterojunction at the interface, introducing electron–hole scavengers or trapping sites to inhibit the recombination [15–19], and doping specific metal or non-metal elements to extend the absorption regime to visible wavelengths [20–23]. Additionally, enhancing light-harvest by utilizing hierarchical structured TiO_2 triggers great interests in recent years. As the size of the particle approaches the wavelength of incident light, resonance effect in light-scattering emerges, which is known as the Mie's scattering effect [24]. These special hierarchical structured materials keep both micron- and nano- scale inherent properties that could harvest more light by the scattering effect in micron structure whilst maintain high surface area as primary nano-sized particles. Inspired by materials in nature like seashells and plant seeds, the intricate structure and morphology have exhibited fascinating properties [25]. Instead of solid-spheres, hollow spheres have been widely used as adsorbents, delivery carriers, catalysts and biomedical detectors [26,27]. By considering hollow spheres, it is expected that synthesized material with a controlled structure should be better performing than that with an ordinary composition. It has been shown that hollow structures could enhance reaction efficiency remarkably for several applications such as in photocatalytic degradation of pollutants, dye-sensitized solar cells and H_2 generation, by increasing light utilization caused by resonance in the structure [28–34]. To meet the resonance condition, peaks in the scattering (extinction) spectrum only exist for some specific sizes. However, there remain a lack of published reports exploring the relationship between size effect and efficiency due to difficulty in synthesizing differently-sized uniform hollow spheres. In this study, highly uniform size-controllable TiO_2 hollow particles

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are synthesized by using a self-sacrificing template method, in which amorphous TiO_2 spheres act as both the precursor and the template in *NaF* solution. The scattering properties and photocatalytic activity of these highly uniform size-controllable TiO_2 are reported for a range of different particle diameters from 365 nm to 930 nm. Compared to solid nano-particles (without a hollow -sphere structure), by crushing solid particle samples into powder form, a greatly enhanced photocatalytic activity is demonstrated for the hollow nano-particles, even though there is no large difference between the measured total surface areas in the crushed powders and hollow sphere nano-particles. By extending Mie's scattering theory, a quantitative analysis is developed for the extinction and absorption spectra of the hollow particles, in which reveal a crucial thickness for the hollow particles to enhance absorption. Our theoretical results not only give good agreement to experimental data, but also explain the mechanism for a counter-intuitive scattering property for these hollow-sphere nanoparticles. Based on the experimental and theoretical observations presented here, it provides a basis for the design of more complicated particle structures.

2. Experimental

2.1. Synthesis method

The method to prepare amorphous precursor spheres can be found in earlier work [5,35]. In brief, various sizes of nano-particles are synthesized using titanium isopropoxide (TTIP, 97%, Aldrich), valeric (99%), and butyric (99.5%) acids in anhydride alcohol (99.5%), which are all directly purchased from the Aldrich Company without pretreatment. First, valeric acid is injected into 20 mL ethanol. After that, 0.3 mL (1 mmol) TTIP is added. The solution is then heated to 85 °C for six hours under reflux in air. Solution with a variable amount of deionized water and 10 mL ethanol is added to induce hydrolysis and condensation, causing the particles to precipitate in a few minutes and making the solution turbid. The precipitate is recovered by centrifuging (1000 and 4000 rpm for micron- and submicron-sized spheres, respectively) and decanting the liquid. Through several washes in ethanol, with the centrifuging and decanting processes performed after each wash, the residual ethanol is pumped out by a vacuum oven at 50 °C for 30 min. Through a typical hydrothermal process, particles of a hollow shape are prepared as follows: 0.2 g of precursor sphere is dispersed in 25 mL *NaF* solution with different concentrations ranging from 0.00625 M to 0.2 M. The mixture is sealed in a 45 mL Teflon-lined stainless autoclave, followed by heat treatment at 190 °C for 18 h. The hydrothermal treatment transforms the amorphous precursor spheres into crystalline hierarchical hollow anatase spheres. The hollow-spheres are washed twice in ethanol and dried in a oven at 100 °C overnight.

2.2. Preparation for photocatalytic test

After mixing 0.01 g of the TiO_2 nano-particles with 50 mL of 25 ppm *Methylene Blue* solution, the solution is illuminated on top with a *Xe* bulb, from Osram Inc., operated at an output power of 180 W and maintained at a temperature of 20 °C. Samples of 0.5 mL are taken out every 5 min, filtered with a 0.2 mm filter, and diluted with 2 mL of deionized water. The filtrate is analyzed to determine the dye concentration, by a Hitachi UV-vis 3010 spectrophotometer.

3. Results and discussion

3.1. Hierarchical structured hollow spheres

Highly uniform TiO_2 anatase hollow-spheres are synthesized by using amorphous TiO_2 spheres as both the precursor and template. Fig. 1(a) shows the typical Scanning Electron Microscopy (SEM) image of our precursor spheres with a mean diameter of 514 nm.

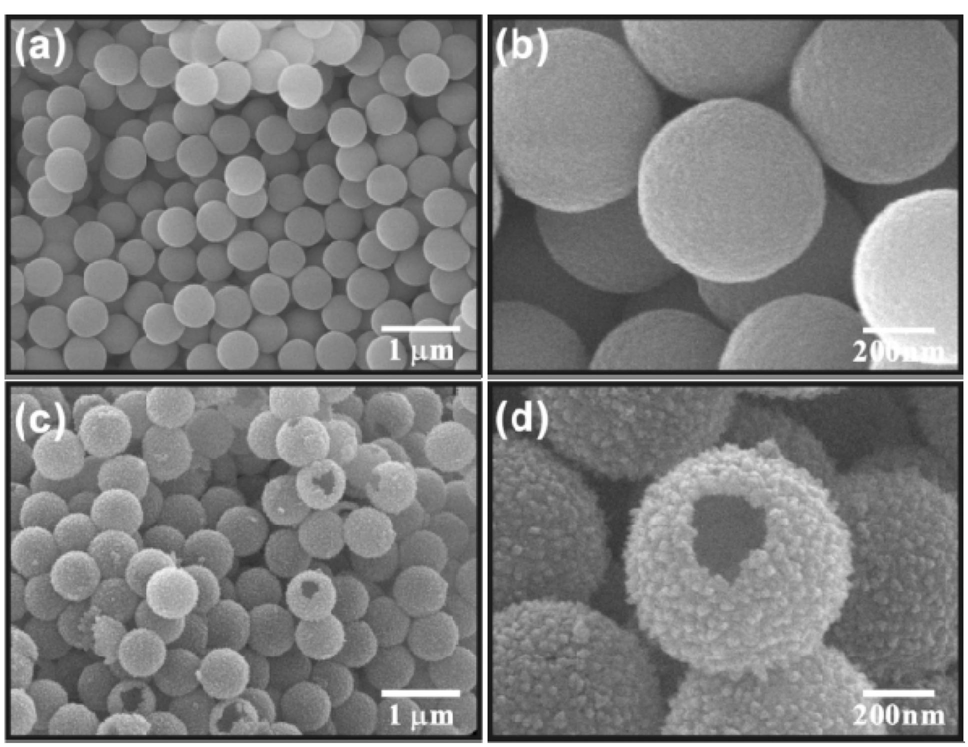

Fig. 1. SEM images at various magnifications of amorphous TiO_2 nano-particles in shape of (a and b) solid-spheres with an average diameter of 514 nm and (c and d) hollow spheres synthesized in 0.025 M NaF solution for 18 h with an average diameter of 590 nm.