Hierarchical hollow TiO₂ spheres: facile synthesis and improved visible-light photocatalytic activity†Cite this: *Dalton Trans.*, 2013, **42**, 8541

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We demonstrate here a simple one-pot approach to directly fabricate hierarchical hollow anatase TiO₂ spheres with a mesoporous shell architecture, which show improved visible light photocatalytic activity owing to their unique structure.

It is widely recognized that the performance and properties of nanomaterials depend considerably on their morphology, shape, size and dimensionality.¹ As a consequence, metal oxides of hierarchical structures organized from 1D or 2D nanobuilding units have drawn significant attention and shown great potential applications in adsorption, separation, photocatalysis, biology, electronics, sensor, dye-sensitized solar cell, and lithium ion storage.² Among them, hollow spheres with a unique micro-/nanostructure have been an intense focus for the specific features (*e.g.*, low density, high surface-to-volume ratio, and the effect of void space).³ A range of methods are now available for preparing hollow spheres, of which removable or sacrificial templates, including hard (*e.g.*, monodisperse polymer latex, carbon, silica spheres and reducing metal nanoparticles) or soft templates (*e.g.*, micelles, microemulsions, macromolecules, oil droplets, and gas bubbles), are usually used to direct the formation of inorganic nanoparticles on their surface through adsorption or chemical reaction.^{3c,4} Recently, template-free methods involving Ostwald ripening,⁵ Kirkendall effect,⁶ and chemically induced self-transformation have been developed for one-pot synthesis of hollow inorganic micro- and nanostructures.⁷ Aforementioned methods devoted by research groups worldwide make it

possible to delicately and controllably prepare a variety of hollow spheres. However, developing simple fabrication approaches to hollow spheres with better performance still remains a challenge.

Titanium dioxide, one of the most promising semiconductor material, has been extensively studied owing to its wide band gap, environmental friendliness, low cost and the subsequent vast range of applications.^{2a,8} Recently, research interest has tended to construct TiO₂ of hierarchical structure, of which hollow TiO₂ spheres (HTS) built by nanoscale subunits have been deemed attractive candidate for sensors, solar cells, and photocatalysts, *etc.*^{3b,7b,9} Thus far, hollow TiO₂ spheres, like other inorganic hollow structures, have been usually fabricated by complicated template methods, and the primary product needs a further annealing process to realize crystallization.

Herein, we develop a simple one step strategy for fabrication of anatase HTS with photocatalytic activity under visible light irradiation. Briefly, 0.5 g titanium acetate was added into 50 mL absolute ethanol and magnetically stirred until the solution turned transparent. Then, the solution was transferred into a 100 mL Teflon-lined stainless steel autoclave, sealed and heated at 200 °C for 8 hours. The precipitated product was then cooled to room temperature, centrifuged, washed with ethanol and deionized water several times, vacuum dried, and then anatase HTS were directly obtained with no need of any further annealing process.

As shown in Fig. S1 (ESI†), the as-synthesized TiO₂ is of well-defined spherical morphology with a dimension of micrometer scale, of which the surface is not condensed smooth but hierarchically constructed by small TiO₂ particles of nanoscale (Fig. S2, ESI†). From the broken sphere (inset of Fig. 1a), the inner hollow space is clearly observed. This hollow spherical structure was further proved by transmission electron microscopy (TEM) image (Fig. 1b). What is also evident from Fig. 1b is the interconnected nanoporosity in the shell, deriving from the assembly of the TiO₂ nanoparticles. Fig. 1c is the high resolution transmission electron microscopy (HRTEM) image of the HTS, which not only shows the

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Fig. 1 (a) SEM image of the prepared HTS. (b) TEM image of the prepared HTS. (c) HRTEM image of the prepared HTS. The inset shows the SAED pattern. (d) XRD pattern of the prepared HTS.

polycrystalline characteristic of the HTS, but also reveals that the diameter of the assembly units (nanoparticles) is about 7 nm. The lattice fringe with a spacing of 0.35 nm is attributed to the spacing of the (101) planes of anatase TiO_2 . The selected area electron diffraction (SAED) image (inset of Fig. 1c) indicates that the nanocrystallites are random in orientation, which further confirms the polycrystalline nature of HTS. The X-ray diffraction (XRD) pattern of the HTS (Fig. 1d) can be indexed to tetragonal anatase TiO_2 (JCPDS No. 75-2546), showing high purity nature of the product. Crystallite size of the sub-unit nanoparticles calculated from the full-width at half-maximum (FWHM) of XRD peaks using the Scherrer formula was 6.9 nm which is in good accordance with the TEM result.

X-ray photoelectron spectroscopy (XPS) was used to verify the surface binding state of the HTS (Fig. S3, ESI†). The full survey spectra of HTS show that the prepared HTS are of high purity. The high resolution XPS spectrum of Ti 2p shows two peaks, representing Ti 2p_{3/2} and Ti 2p_{1/2}, at 458.5 eV and 464.2 eV respectively. The separation of the two peaks is 5.7 eV, which indicates that it is in the oxidation state of Ti^{4+} , a typical pure TiO_2 style.¹⁰ Elemental analysis (EDX, Fig. S4, ESI†) also reveals that there is no other element present in the prepared HTS, except Ti and O. In addition, it was confirmed by thermogravimetry-differential scanning calorimetry (TG-DSC, Fig. S5, ESI†) that there is no other obvious exothermic or endothermic peak but a weight loss of 8.9% coming from the loss of absorbed water, which further confirms the purity of the HTS.

In order to study the porous structural characteristic of the prepared HTS, a N_2 adsorption-desorption experiment was performed. Fig. 2-top shows the typical isotherm of nitrogen adsorption onto the prepared HTS, which displays the typical IV curve with an obvious hysteresis loop, indicating that the products are of mesoporous structure. Fig. 2-bottom, the

Fig. 2 (Top) N_2 adsorption-desorption isotherm of HTS. (Bottom) BJH pore size distribution plot of HTS.

corresponding Barrett-Joyner-Halenda (BJH) pore diameter distribution curve of the HTS obtained from the adsorption branch, shows that the majority of the pores are mainly around 10 nm. The BET surface area and the pore volume of HTS were measured to be $51.87 \text{ m}^2 \text{ g}^{-1}$ and $0.134 \text{ cm}^3 \text{ g}^{-1}$, respectively. Such mesoporous structure endows the HTS with two advantages in organic pollutants removal: (1) large surface area makes it adsorb as much chemicals as possible; (2) communicable channels for chemicals travelling from the outer space into the inner void of the hollow spheres.

To cast light on the formation process of the HTS, we carried out experiments with different reaction time. A four-stage reaction mechanism was proposed, as illustrated in Fig. 3: (i) the first stage is the initial nucleation and growth of primary nanoparticles, during which nanoparticles nucleated after solvothermal reaction of the precursor solution. It took about 1 hour to fulfill this process forming primary nanoparticles with diameters smaller than 3 nm (Fig. 3a). With the reaction proceeding, it went to the stage (ii): rapid aggregation, during which a core of randomly oriented primary nanosphere formed. A large number of nanoparticles formed in the first stage induce high collision frequency leading to the formation of much larger spherical particles with open porosity due to the random fashion of the collision by simple contact. This was supported by the TEM image of the product obtained after 2 hours of reaction, the particles have a texture of incompact density (Fig. 3b). Furthermore, the porous structure was proved by the large surface area ($15.13 \text{ m}^2 \text{ g}^{-1}$) and pore volume ($0.039 \text{ cm}^3 \text{ g}^{-1}$). By further prolonging the reaction, stage (iii) took place at the complete expense of the small nanoparticles. With the crystallization processing in a more ordered fashion, the spherical particles tend to compact and grow to eliminate the solution-solid interface and minimize

Fig. 3 Evolution scheme of the preparation process and TEM images of products prepared for (a) 1, (b) 2, (c) 4 and (d) 8 h.

the system free energy. In addition, the poor-crystallized nanoparticles with high surface energy in the inner part of the sphere have a tendency to gradually dissolve, forming a core-shell hollow structure.¹¹ TEM image of the samples obtained after 4 hours reaction typically materialized the process of this stage (Fig. 3c). Then came stage (iv): a relevantly slow process of ripening and recrystallization. In this stage, the samples evolved steadily into fully-crystallized TiO₂ hollow spheres with mesoporous architecture (Fig. 3d).

Although TiO₂ is considered as a potentially convenient and inexpensive catalyst for decomposing environmental organic pollutants, it is usually available under UV light irradiation. How to make it effective under sunlight or visible light has been the major challenge for its practical application. Herein, we performed the degradation of azo-dye Rhodamine B under visible light irradiation ($\lambda > 400$ nm) to evaluate the visible-light photocatalytic activity of the prepared HTS. For comparison, DeGussa P25, a typical commercially available TiO₂ photocatalyst, was used as reference. As proved in Fig. 4,

Fig. 4 Changes of relative concentration of RhB under visible light irradiation ($\lambda > 400$ nm) catalyzed by prepared HTS and P25.

the decrease of the concentration of RhB in the dark reveals that HTS has stronger adsorbability than P25 due to its hierarchical porous structure and large surface area.¹² Under visible light irradiation, RhB was almost completely decomposed (98%) in 240 min. Whereas, under the same experimental condition, only 50% of RhB was removed by P25. The result shows that the HTS exhibits higher Vis-photocatalytic activity than that of P25. The UV-Vis diffuse reflectance spectra (UV-Vis DRS) of HTS and P25 (Fig. S6, ESI†) clearly display that the absorption spectrum of HTS has a slight red-shift and exhibits stronger absorption in the visible light range of >400 nm. It is evident that the hierarchical architecture of the hollow TiO₂ sphere allows more light scattering and reflecting inside the porous structure and the inner void (Fig. S7, ESI†), which renders light utilization more effective.¹³ The other reason lies in the large surface area and pore volume of the HTS. When they are irradiated by light, the generated photoreactive species (e.g., OH[•] and O₂^{•-}) can be enriched in caves of the HTS (Fig. S7, ESI†) and therefore significantly accelerate the photocatalytic reaction.¹⁴ Furthermore, the hierarchical porous structure was also beneficial to enhancing the flow and transfer rate of reactant and products molecules.¹⁵

In summary, we have developed a simple approach to synthesize hollow TiO₂ sphere. As synthesized HTS were built with micro-/nano-scale structures, and thus possess a hierarchically porous shell and hollow inner space to concurrently improve the Vis-photocatalytic activity. This novel structure would further promote the extensive applications of TiO₂ in photocatalysis and other potential fields.

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