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An external template-free route to uniform semiconducting hollow mesospheres and their use in photocatalysis†

Di Yang,^{*a,b} Mengye Wang,^{b,c} Bin Zou,^a Gu Ling Zhang^a and Zhiquan Lin^{*b}

Solid amorphous TiO₂ mesospheres were synthesized by controlled hydrolysis of Ti-containing precursors. Subsequently, solid TiO₂ mesospheres were exploited as scaffolds and subjected to a one-step external template-free hydrothermal treatment, yielding intriguing hollow anatase TiO₂ mesospheres. The synthetic protocol was optimized by investigating the effect of buffer reagents and fluoride ions on the formation of hollow TiO₂ spheres. The diameter of hollow mesospheres, ranging from 308 to 760 nm, can be readily tailored by varying the precursor concentration. The average thickness of a shell composed of TiO₂ nanocrystals was approximately 40 nm with a mean crystal size of 12.4–20.0 nm. Such hollow TiO₂ mesospheres possessed a large surface area and were employed in photocatalytic degradation of methylene blue under UV irradiation. Interestingly, the synthetic conditions were found to exert a significant influence on the photocatalytic ability of hollow TiO₂ mesospheres. The correlation between the degradation ability of hollow TiO₂ mesospheres and the precursor concentration as well as the hydrothermal time was scrutinized. The optimal photocatalytic performance of hollow TiO₂ mesospheres was identified.

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1. Introduction

Semiconducting TiO₂ nanoparticles have been widely used in lithium-ion batteries, dye-sensitized solar cells, photocatalysis, gas sensors, and biomedical implants.^{1–5} The physicochemical properties of TiO₂ depend heavily on its crystalline phase, crystal size, specific surface area, and architecture. The ability to construct three-dimensional TiO₂ suprastructures is of great interest for many practical applications noted above with potentially improved performance. In this context, TiO₂ hollow spheres constituted by nanoparticles have received much attention due to their higher specific surface area, better permeation, lower density, and higher light-harvesting capacity.^{6,7} It is worth noting that TiO₂ hollow spheres are typically produced by template-assisted techniques. A variety of templates such as polymer spheres, silica, carbon, and CaCO₃ spheres have been employed to form hollow spheres, which

have proven to be effective.^{8–11} However, these methods generally require multi-step processes as the template needs to be removed by calcination or dissolution. In this regard, the external template-free approach for controlled synthesis of hollow structures overcomes these disadvantages. To date, several template-free means of preparing hollow spheres have been developed, including chemically induced self-transformation,^{12–14} Ostwald ripening,^{15,16} and formation involving the Kirkendall effect.¹⁷

The morphology of hollow spheres relies largely on the precursors used. The hollow anatase TiO₂ microspheres were prepared using titanium tetrafluoride as a precursor *via* the Ostwald ripening process.¹⁸ The hollow TiO₂ spheres with a unique urchin-like morphology were solvothermally synthesized with TiOSO₄ as a precursor.¹⁹ Recently, solid TiO₂ microspheres were converted into hollow microspheres *via* the microwave-assisted technique.²⁰ Nevertheless, there are few reports on creating hollow TiO₂ spheres utilizing solid TiO₂ mesospheres as the starting material. As the preparative techniques for colloidal solid spheres are mature and their controllable growth in size and performance are well established, it is expected that hollow spheres with uniform dimension and improved performance can be obtained by employing solid colloidal spheres as a template.

Herein, we report on the crafting of hollow anatase TiO₂ mesospheres with uniform size and large porosity by

^aCollege of Science, Minzu University of China, Beijing 100081, China.

E-mail: diyang@muc.edu.cn

^bSchool of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332, USA. E-mail: zhiquan.lin@mse.gatech.edu^cState Key Laboratory of Physical Chemistry of Solid Surfaces, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China

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capitalizing on solid TiO_2 mesospheres as scaffolds. First, solid TiO_2 mesospheres were synthesized by the hydrolysis of Ti-containing precursor $\text{Ti}(\text{OBu})_4$ in ethylene glycol. Subsequently, the resulting solid mesospheres were subjected to a one-step external template-free hydrothermal treatment in the presence of NH_4F , yielding intriguing hollow anatase TiO_2 mesospheres. The area of the hollow interior can be adjusted by controlling the concentration of fluoride ions. More importantly, the diameter of hollow mesospheres can also be readily altered by adjusting the precursor concentration in ethylene glycol. Such hollow TiO_2 mesospheres possessed a large surface area and were thus exploited in the photocatalytic degradation of methylene blue (MB) under UV irradiation. The influence of reaction conditions including the precursor concentration and hydrothermal reaction time on the photocatalytic activity of hollow anatase TiO_2 mesospheres was scrutinized.

2. Experimental section

2.1 Preparation

In this work, $\text{Ti}(\text{OBu})_4$, ethylene glycol, sodium chloride, acetone, ammonium fluoride, and urea are of analytical grade and used as received.

Synthesis of solid TiO_2 mesospheres. A certain amount of $\text{Ti}(\text{OBu})_4$ was added to 20 ml ethylene glycol and sodium chloride acetone solution (0.4 mL, 0.1 M). The solution was magnetically stirred for 8 h at room temperature, and then immediately poured into 243 ml acetone under vigorous stirring for 10 min. The transparent solution became turbid. The molar concentration of $\text{Ti}(\text{OBu})_4$ in acetone was systematically varied from 0.68, 1.03, 1.21, 2.30, to 3.50 mM in the experiment. After aging for 12 h, the white precipitate was collected by centrifugation, followed by washing with deionized water and ethanol three times. The product was dried in a vacuum oven at 45 °C for 12 h, and solid spheres were obtained.

Synthesis of hollow anatase TiO_2 mesospheres. The as-prepared sample noted above, ammonium fluoride, and urea at various molar ratios (R), *i.e.*, $R = 1:0:2$, $1:0.5:2$, and $1:1:2$, were dissolved in 35 ml deionized water. After 30 min of stirring, the mixture was transferred into a 50 ml Teflon autoclave and maintained at 180 °C for different hydrothermal reaction times, namely, 12, 15 and 18 h, respectively. Finally, hollow mesospheres were obtained by centrifugation and washing with deionized water and ethanol three times.

2.2 Characterization

The morphology of hollow TiO_2 mesospheres was examined by field emission scanning electron microscopy (SEM, Hitachi S4800) at a high voltage of 8 kV, and high resolution transmission electron microscopy (HRTEM, JEM-2100) at an accelerating voltage of 300 kV. X-Ray diffraction (XRD) patterns were obtained using an X-ray diffractometer (PG Instruments Limited XD-3) with $\text{Cu K}\alpha$ radiation at a scan rate of $0.02^\circ \text{ s}^{-1}$. The average crystallite size of anatase TiO_2 was determined according to the Scherrer equation. The nitrogen (N_2) adsorp-

tion-desorption isotherms were measured at the temperature of liquid nitrogen (77 K), using a Micromeritics ASAP 2010 system. The sample was degassed for 5 h at 150 °C prior to measurement. Raman spectra were recorded using a LabRAM HR800 Raman spectrometer excited with a He-Ne laser, emitting at 632.8 nm.

The photocatalytic activity of hollow anatase TiO_2 mesospheres was evaluated by photodegrading methylene blue (MB) under UV light irradiation at room temperature. The samples were dried in a vacuum oven at 45 °C for 8 h prior to the photocatalytic reaction. A 20 mg sample was then used to decompose 20 mL MB at an initial concentration of 10 mg L^{-1} . A 100 W 365 nm UV lamp (Upland, CA, USA) was used as the light source to trigger the photocatalytic reaction.

3. Results and discussion

3.1 Formation of solid amorphous and hollow crystalline mesospheres

The key to uniform solid mesospheres is to reduce the hydrolysis rate of the precursors. To this end, sodium chloride and ethylene glycol were used as buffer reagents, respectively. Fig. 1a and b compare the SEM images of as-prepared spheres by using sodium chloride (Fig. 1a) and ethylene glycol (Fig. 1b), respectively. Clearly, the size distribution of the former was nonuniform with meso- and micro-spheres coexisting in the product. In contrast, solid TiO_2 mesospheres synthesized by using ethylene glycol as the buffer reagent possessed a smooth surface and a uniform size distribution. $\text{Ti}(\text{OBu})_4$ and ethylene glycol completely reacted to produce glycolates or alkoxide/glycolate derivatives, which have a relatively low hydrolysis rate, and thus are advantageous to the formation of uniform solid TiO_2 mesospheres.

The as-prepared solid mesospheres with a uniform size distribution were employed for subsequent hydrothermal treatment. Interestingly, after the hydrothermal reaction, hollow mesospheres with rough surfaces were yielded as shown in Fig. 1c and d. They are randomly aggregated with a wall thickness of $\sim 40 \text{ nm}$. From a broken hollow sphere, the grain size of the inner layer was seen to be much smaller than that of the outer layer (Fig. 1d). The morphology and structure of hollow mesospheres were further examined by TEM (Fig. 1e) and HRTEM (the inset in Fig. 1e and Fig. 1f). The TEM images confirmed the formation of TiO_2 hollow mesospheres after the hydrothermal reaction. The inset in Fig. 1e suggested that the growth of polygonal shaped nanocrystals on the surface of TiO_2 hollow mesospheres. The lattice spacing of 0.351 nm corresponded to the (101) plane of the anatase form of TiO_2 .

In order to investigate the effect of fluoride ions on the formation of hollow TiO_2 mesospheres, we synthesized various TiO_2 mesospheres at different molar ratios of ammonium fluoride to $\text{Ti}(\text{OBu})_4$ (R ; see the Experimental section), and compared the as-prepared products as shown in the TEM images (Fig. 2a, d and e). It is worth noting that solid colloidal meso-

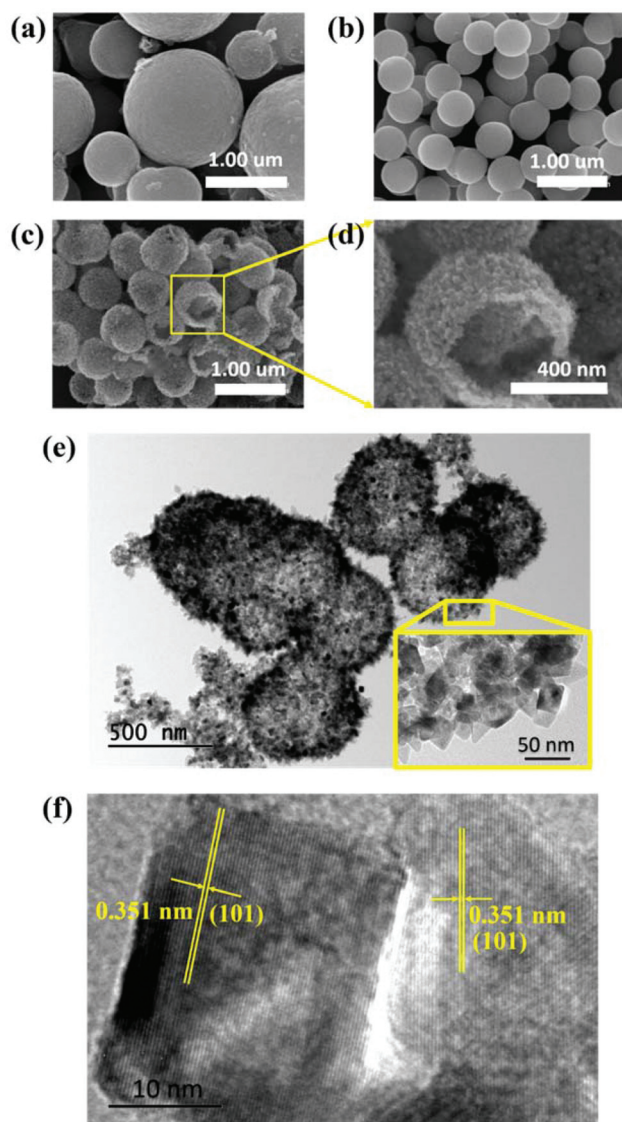


Fig. 1 (a and b) SEM image of solid TiO₂ mesospheres synthesized with (a) sodium chloride acetone solution, and (b) ethylene glycol, respectively. (c–f) SEM (c), TEM (d), and HRTEM (e and f) images of hollow TiO₂ mesospheres prepared by the hydrothermal treatment of the product in (b). Average diameters of solid and hollow mesospheres are 406 and 522 nm, respectively (Table 1).

spheres converted into solid TiO₂ spheres composed of small nanocrystals in the absence of ammonium fluoride. The morphology of small grains was examined by HRTEM (Fig. 2b and c), where the lattice fringes are clearly evident, signifying a crystalline nature. The lattice spacing of 0.351 nm corresponded to the (101) planes of the anatase. The addition of ammonium fluoride led to the formation of hollow mesospheres and the area of hollow interior increased with the increased ammonium fluoride concentration (Fig. 2d and e). Interestingly, comparing the HRTEM images in Fig. 1e and 2b, we noted that for the molar ratio $R = 1$ of F[−] to Ti⁴⁺ ions, the crystals on the surface had a relatively larger size than that at

$R = 0$ (*i.e.*, in the absence of ammonium fluoride). The reason may be that the Coulomb repulsion between Ti⁴⁺ and (Ti–OH)³⁺ ions is weakened by the hydrogen bond interaction between F[−] and Ti⁴⁺ (or (Ti–OH)³⁺) ions, which was beneficial for the growth of TiO₂ crystals.

The comparison of the crystal structure of mesospheres before and after the subsequent hydrothermal reaction was carried out by XRD measurements (Fig. 2f). No obvious diffraction peak could be detected for the solid mesosphere sample before the hydrothermal reaction for the scattering angle, 2θ from 20° to 80°, signifying an amorphous nature of solid mesospheres. In contrast, strong diffraction peaks were observed for the solid and hollow samples after the hydrothermal treatment. The peaks at scattering angles of 25.31°, 37.91°, 48.10°, 53.96°, 55.11°, and 62.72° can be assigned to the diffraction from (101), (004), (200), (105), (211), and (204) crystal planes of anatase TiO₂, respectively. All peaks can be perfectly indexed as an anatase phase of TiO₂ (JCPDS card no. 21-1272) with lattice constants $a = 3.7852$ Å and $c = 9.5139$ Å.

The controllable synthesis of hollow TiO₂ mesospheres was carried out at the 1 : 1 molar ratio of ammonium fluoride to Ti(OBu)₄. It is not surprising that the diameter of hollow TiO₂ mesospheres was dictated by solid amorphous mesospheres that served as scaffolds, which can be easily controlled by varying the molar concentration of Ti(OBu)₄ in acetone. Table 1 summarizes the diameters of mesospheres prepared at different molar concentrations of precursor Ti(OBu)₄ before and after the subsequent hydrothermal treatment. Clearly, the diameter of mesospheres increased after the hydrothermal reaction. The largest hollow mesospheres with an average diameter of 760 nm were obtained at the concentration of Ti(OBu)₄, $c = 1.21$ mM. However, when the concentration was lower than 1.21 mM, the diameter decreased with the decreased precursor concentration; whereas when it was larger than 1.21 mM, the diameter decreased with the increased precursor concentration (Table 1). This may be due to the fact that the nucleation rate is greater than the growth rate of solid mesospheres when the molar concentration of Ti(OBu)₄ was above a certain value (*i.e.*, 1.21 mM in this study). In order to achieve uniform mesospheres, in the hydrolysis reaction of Ti(OBu)₄, the concentrations of Ti(OBu)₄ and H₂O were maintained to be rather low (H₂O concentration was lower than 0.5%). When the concentration of Ti(OBu)₄ exceeded a certain value, the reactant collision probability increased, thereby increasing its nucleation rate. On the other hand, the growth rate of mesospheres was suppressed due to the lack of water, and thus the number of mesospheres increased, whereas the diameter decreased. SEM images of the hollow mesospheres prepared at different concentrations are shown in Fig. 3. At $c = 0.68$ and 1.03 mM, the as-synthesized TiO₂ hollow mesospheres exhibited a good uniformity. The size distribution of hollow mesospheres was evaluated based on the SEM images for the samples prepared at $c = 0.68$ mM and 1.03 mM. The hollow mesospheres have an average diameter of 364 nm and 384 nm, respectively, with a reasonably narrow standard deviation as depicted in Fig. 3e and f. With a further increase

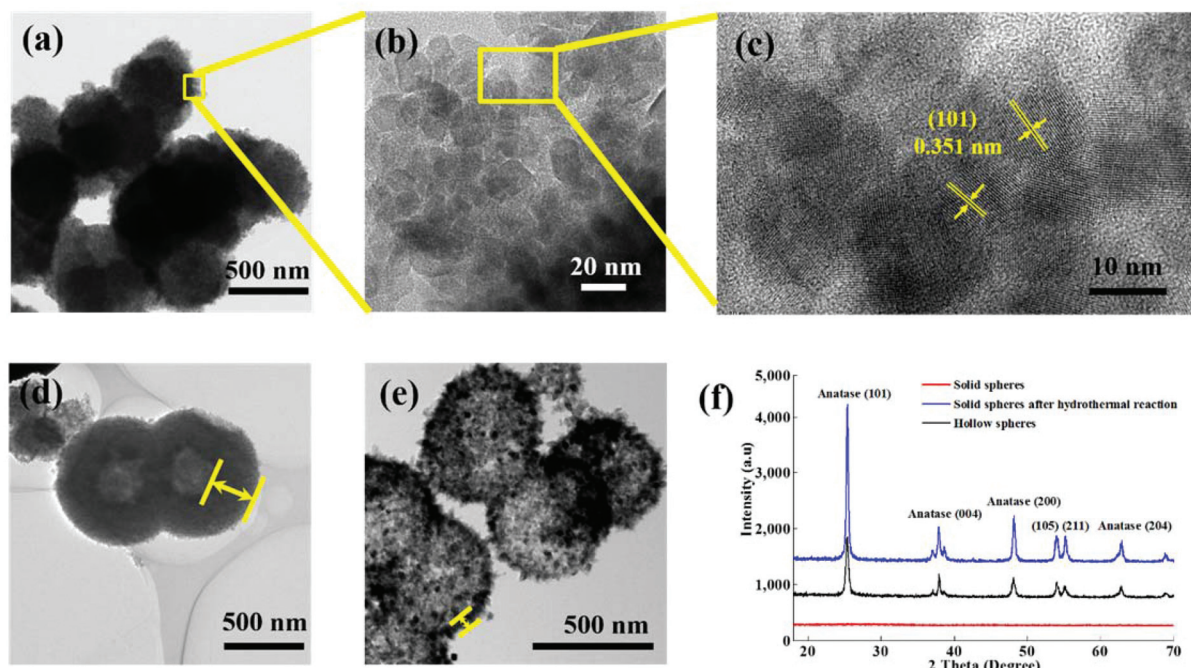


Fig. 2 (a–e) TEM and HRTEM images of TiO_2 mesospheres synthesized by hydrothermal reaction with various concentrations of ammonium fluoride at 180°C for 15 h. The molar ratios of ammonium fluoride to $\text{Ti}(\text{OBu})_4$, R , were varied: (a) $R = 0$, (d) $R = 0.5$, (e) $R = 1.0$. (b and c) HRTEM images of (a) and (b), respectively. (f) XRD pattern of solid colloidal mesospheres (red curve; as-prepared), solid TiO_2 mesospheres (blue curve; after hydrothermal treatment), and hollow TiO_2 mesospheres (black curve; after hydrothermal treatment).

Table 1 A summary of diameters of mesospheres obtained by varying the molar concentration of precursor $\text{Ti}(\text{OBu})_4$ in acetone, c

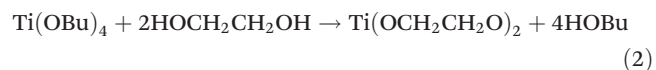
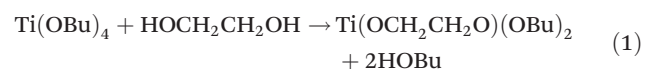
c (mM)	0.68	1.03	1.21	2.30	3.50
Average diameter of solid mesospheres (nm)	316	340	660	406	250
Average diameter of hollow mesospheres (nm)	364	384	760	522	308

in the concentration, mesospheres appeared to aggregate with one another.

The crystal size can be estimated from the full width at half maximum of XRD peaks using the Scherrer equation, yielding 12.4–20.0 nm crystals based on the analysis of (101), (004) and (200) peaks (Table 2 and Fig. S1 in the ESI†). Interestingly, the crystal size increased with the increased precursor $\text{Ti}(\text{OBu})_4$ concentration due likely to the increased titanium ion contents in solid mesospheres, thereby promoting the growth of the TiO_2 crystal during the hydrothermal reaction. The specific surface area and the average pore diameter of hollow mesospheres were also measured and summarized in Table 2. Based on the measurements on nitrogen adsorption-desorption of samples, the specific surface area was determined by the multipoint Brunauer-Emmett-Teller (BET) method and the pore dimensions of the hollow mesospheres were obtained. Notably, the small-sized TiO_2 nanocrystals possessed a high surface area. The pore size was calculated using the

Barrett-Joyner-Halenda (BJH) pore-size distribution method. When the precursor concentration was lower than 1.21 mM, the pore sizes are small but comparable. As the concentration increased to 3.5 mM, the pore size increased significantly, which may be that the gaps between adjacent hollow mesospheres were also included in the measured value due to their aggregation at this concentration. The chemical composition of solid and hollow TiO_2 mesospheres was revealed by Raman spectroscopy measurements, as shown in Fig. 4. For hollow mesospheres (red curve), one peak with strong intensity at 142 cm^{-1} , three peaks with moderate intensity at 396, 513 and 636 cm^{-1} and a weak peak at 768 cm^{-1} were seen. These measured peaks are in good agreement with E_g , B_{1g} , and $A_{1g}(B_{2g})$ modes of anatase TiO_2 .²¹ In contrast, no obvious Raman peak could be detected for the solid mesosphere sample, which is indicative of poor crystallinity.

On the basis of the morphological characterization and chemical reaction analysis discussed above, we propose a possible mechanism for the formation of hollow mesospheres. $\text{Ti}(\text{OBu})_4$ and ethylene glycol were mixed to react and produce glycolates or alkoxide/glycolate derivatives, which can be described by the following equations.²²



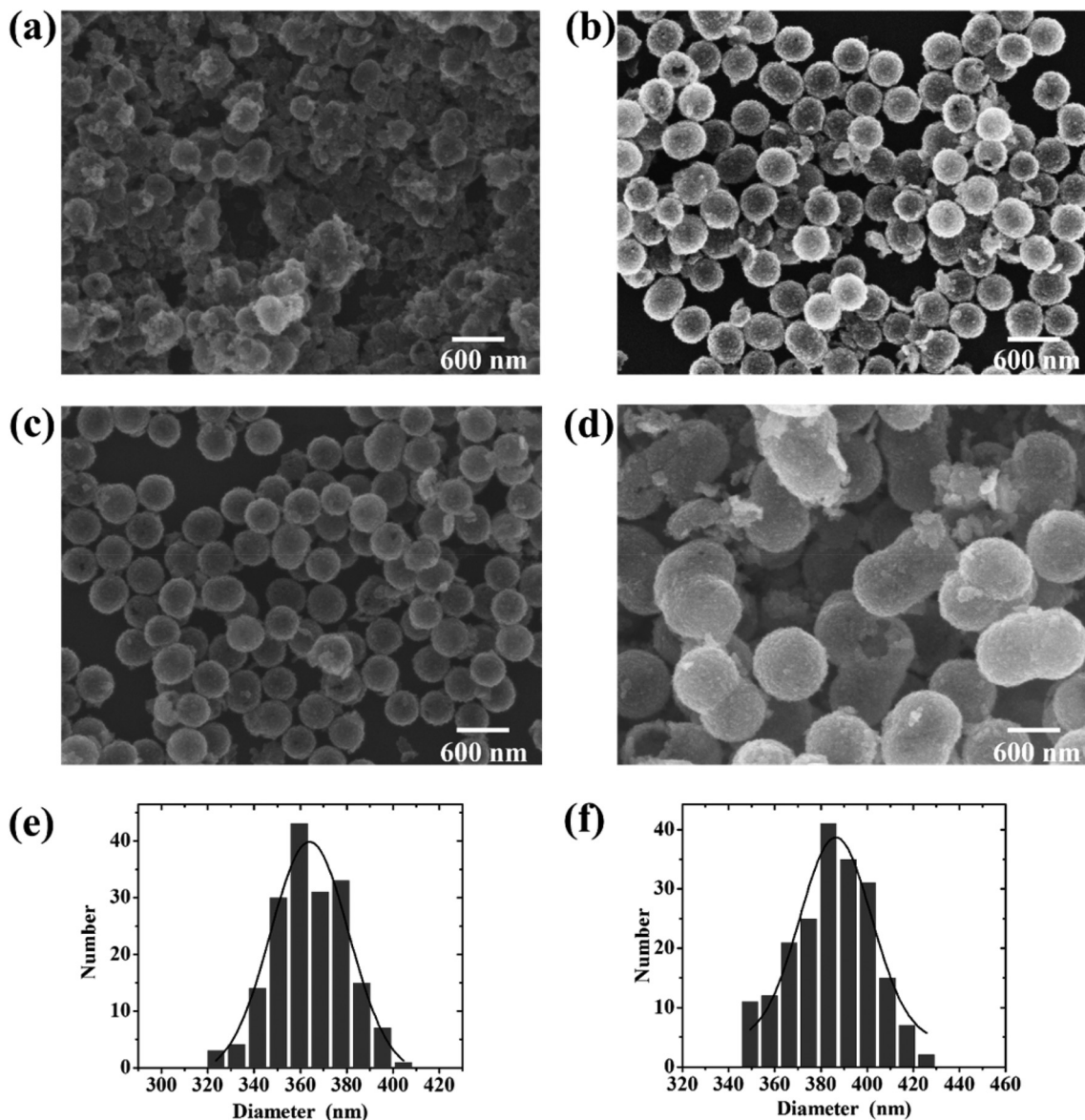


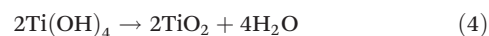
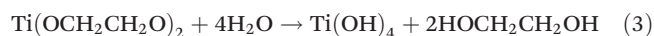
Fig. 3 SEM images of hollow mesospheres after hydrothermal reaction at 180 °C for 15 h. The diameters of mesospheres can be varied by tuning the precursor concentration, *c*: (a) *c* = 3.5 mM, (b) *c* = 0.68 mM, (c) *c* = 1.03 mM, and (d) *c* = 1.21 mM. (e) and (f) size distributions of hollow mesospheres in (b) and (c), respectively.

Table 2 Crystal size, BET surface area, and average pore dimension of hollow mesospheres obtained by varying the molar concentration of the precursor $\text{Ti}(\text{O}i\text{Bu})_4$ in acetone, *c*

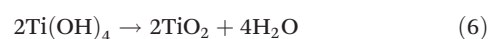
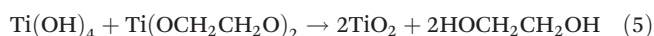
<i>c</i> (mM)	Crystal size (nm)	BET surface area ($\text{m}^2 \text{g}^{-1}$)	Average pore diameter (nm)
0.68	12.4	414.22	7.3
1.03	15.2	355.66	7.4
1.21	19.0	290.48	7.2
3.50	20.0	131.53	15.1

When $\text{Ti}(\text{O}i\text{Bu})_4$ and ethylene glycol were added into the acetone bath that may contain a trace amount of water, the reaction solution changed from colorless to white, signifying

the formation of solid titania in large quantities through a homogeneous nucleation and growth process.



During the hydrothermal process, the plausible reactions for forming hollow TiO_2 nanospheres in the presence of ammonium fluoride and water can be given as follows:²⁰



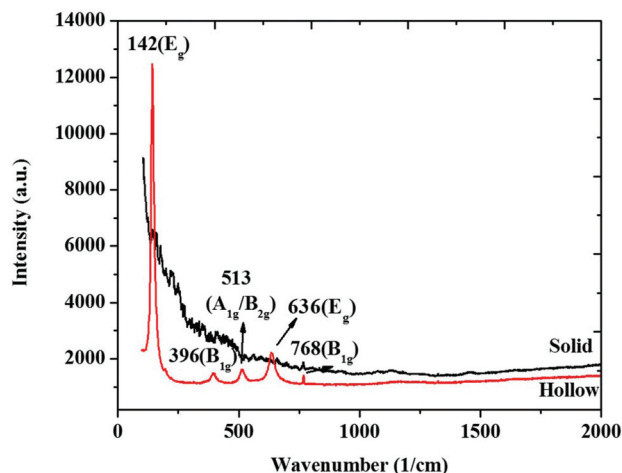
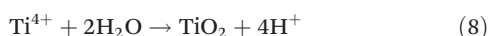
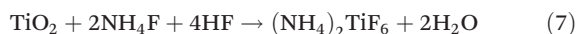


Fig. 4 Raman spectra of solid TiO₂ mesospheres (black curve) and hollow TiO₂ mesospheres (red curve), respectively.



In the hydrothermal process, amorphous solid mesospheres gradually hydrolyze and form TiO₂ crystals. If the solution does not contain fluoride ions, the hydrothermal reaction process would produce solid crystalline TiO₂ mesospheres rather than hollow anatase TiO₂ mesospheres (Fig. 2a). When a certain amount of ammonium fluoride is added into the reaction solution, the dissolution of TiO₂ crystals occurs and ultimately poorly crystallized solid mesospheres transform into hollow ones. This transformation is a direct consequence of two competing processes, that is, the dissolution and growth of TiO₂ crystals. TiO₂ grains gradually grow in mesospheres during the hydrothermal reaction. The grain size of the inner layer was much smaller than that of the outer layer, which can be seen from a broken hollow mesosphere (Fig. 1c), suggesting that the inner grains have high surface energy, and thus are easy to dissolve. At the same time, the titanium ions diffuse outwards and react with water. As a result, the recrystallization and growth of TiO₂ occur on the surface of mesospheres. Taken together, the diameter of hollow mesospheres is larger than that of their scaffold, as shown in Table 1.

3.2 Photocatalytic activity

These intriguing hollow anatase TiO₂ mesospheres were then exploited as three-dimensional photocatalysts in the photocatalytic degradation of methylene blue (MB) at room temperature. Fig. 5 shows the photodegradation curves of MB by capitalizing on hollow TiO₂ mesospheres prepared at the different concentrations of the precursor, Ti(OBu)₄. At the concentration of Ti(OBu)₄, *c* = 1.21 mM, the concentration of MB was degraded to 41% under UV irradiation for 20 min. In contrast, at the concentration of Ti(OBu)₄, *c* = 0.68 mM, it was reduced to 81%. The improved photocatalytic ability was due

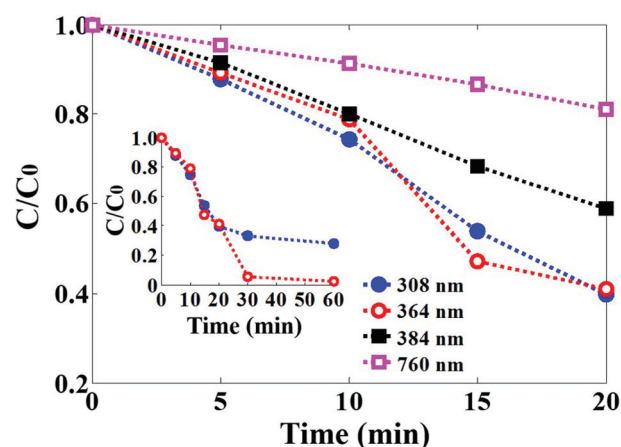


Fig. 5 Photocatalytic degradation of methylene blue (MB) using hollow TiO₂ mesospheres of different sizes (*i.e.*, different concentrations of Ti(OBu)₄ precursor yielded different sizes; see Table 1). The inset compares the photodegradation of MB for 60 min using hollow mesospheres with the size of 308 nm and 364 nm, respectively.

primarily to a high surface area (Table 2). On the other hand, the morphology of hollow mesospheres also influenced their photocatalytic activity. When the concentration of Ti(OBu)₄ increased to 3.5 mM, the resulting hollow mesospheres had a small diameter of 308 nm but with slight aggregation (Fig. 3a), and their uniformity was not as good as those prepared with the low concentration Ti(OBu)₄ solution. Consequently, the surface area of 308 nm mesospheres was lower than that of 364 nm mesospheres. The inset in Fig. 5 compares their photocatalytic abilities.

Moreover, the influence of the hydrothermal reaction time at a fixed precursor concentration on the photocatalytic performance of hollow TiO₂ mesospheres was also scrutinized (Fig. 6a). The sample prepared by the hydrothermal reaction for 15 h (the concentration of Ti(OBu)₄, *c* = 0.68 mM) showed a high photocatalytic ability and can completely decompose MB within one hour (Fig. 6b). Fig. 6c compares the XRD profiles of three samples prepared by the hydrothermal reaction for 12 h, 15 h and 18 h, respectively. Clearly, the 15 h sample had the most intense peaks, signifying that nanoparticles on the shell of the hollow mesosphere possessed the best crystallinity and maximum size. The high crystallinity reduced the recombination rate of photogenerated electrons and holes, thereby resulting in enhanced photoactivity in the 15 h sample. It is also interesting to note that the photocatalytic ability of all hollow TiO₂ samples was better than that of P25.

4. Conclusions

In summary, hollow TiO₂ mesospheres with a uniform size were crafted by a one-step external template-free hydrothermal reaction *via* capitalizing on solid amorphous mesospheres as scaffolds that were prepared by controlled hydrolysis of

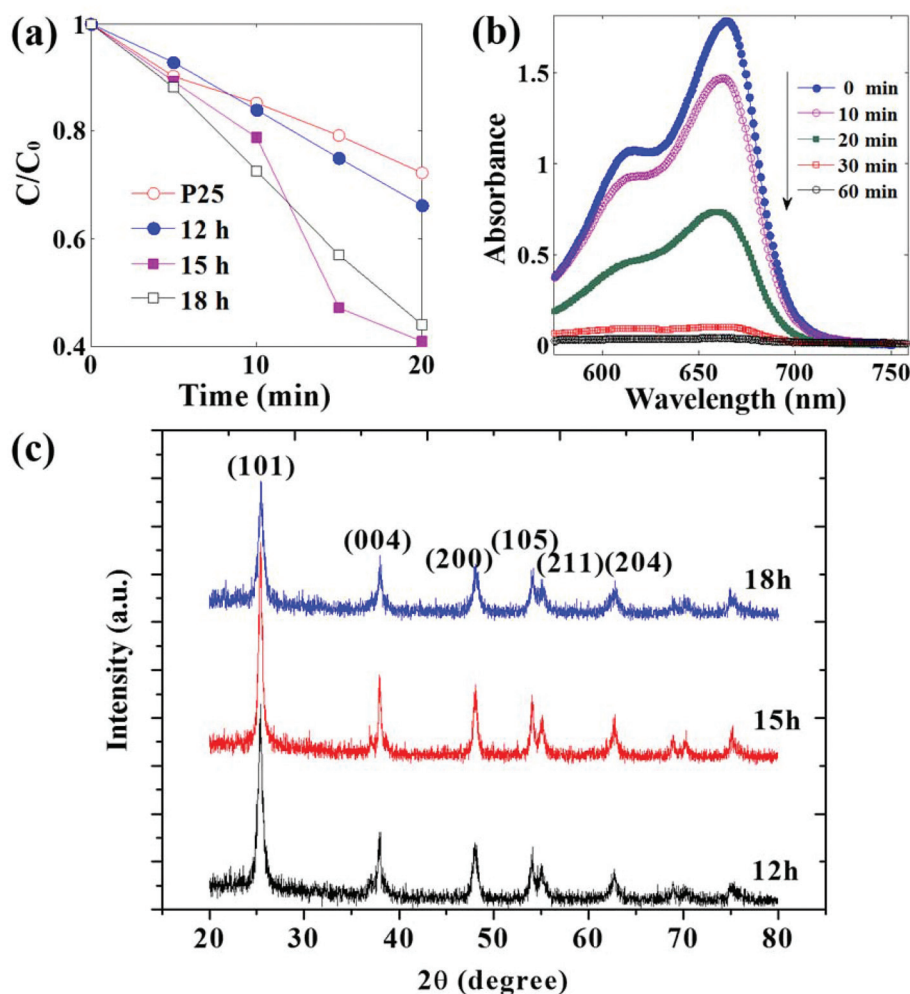


Fig. 6 (a) The photodegradation of MB by P25 and hollow TiO_2 mesospheres prepared by hydrothermal reaction for different times (12 h, 15 h and 18 h) at a fixed precursor concentration, $c = 0.68$ mM. (b) UV-vis spectra of MB in the presence of hollow TiO_2 mesospheres prepared by hydrothermal treatment for 15 h. (c) The XRD patterns of the samples noted in (a).

Ti-containing precursors. The optimization of synthetic protocol was performed by investigating the effect of buffer reagents and fluoride ions on the formation of hollow TiO_2 spheres and the formation mechanism of hollow TiO_2 mesospheres was experimentally explored. The diameter of hollow TiO_2 mesospheres, ranging from 308 to 760 nm, can be readily tailored by changing the precursor concentration. The shell of hollow mesospheres comprised anatase TiO_2 nanocrystals with a much smaller grain size of the inner layer than that of the outer layer. The diameter of the hollow mesospheres was larger than their scaffolds. These hollow TiO_2 mesospheres possessed a large surface area and were thus employed in the photocatalytic degradation of methylene blue under UV irradiation. Interestingly, the synthetic conditions, including the precursor concentration and hydrothermal time, were found to exert a profound influence on the photocatalytic ability of hollow TiO_2 mesospheres. The study revealed that hollow TiO_2 mesospheres prepared by first using precursors at a concentration of 0.68 mM to yield solid amorphous meso-

spheres, and then being hydrothermally reacted for 15 h, exhibited the optimal photocatalytic performance.

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