A universal cooperative assembly-directed method for coating of mesoporous TiO nanoshells with enhanced lithium storage properties

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A universal cooperative assembly-directed method for coating of mesoporous TiO₂ nanoshells with enhanced lithium storage properties

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TiO₂ is exceptionally useful, but it remains a great challenge to develop a universal method to coat TiO₂ nanoshells on different functional materials. We report a one-pot, low-temperature, and facile method that can rapidly form mesoporous TiO₂ shells on various inorganic, organic, and inorganic-organic composite materials, including silica-based, metal, metal oxide, organic polymer, carbon-based, and metal-organic framework nanomaterials via a cooperative assembly-directed strategy. In constructing hollow, core-shell, and yolk-shell geometries, both amorphous and crystalline TiO₂ nanoshells are demonstrated with excellent control. When used as electrode materials for lithium ion batteries, these crystalline TiO₂ nanoshells composed of very small nanocrystals exhibit remarkably long-term cycling stability over 1000 cycles. The electrochemical properties demonstrate that these TiO₂ nanoshells are promising anode materials.

INTRODUCTION

Titanium dioxide (TiO₂) is probably the most studied metal oxide due to low cost, low toxicity, high thermal and chemical stabilities, and excellent optical and electronic properties (1). These favorable features render TiO₂ materials very attractive for sensing (2), catalysis (3–6), solar energy conversion (7–9), energy storage (10–13), and many other applications (14). To enrich the architecture and functionalities of nanomaterials, numerous methods have been developed to synthesize core@TiO₂ particles and their derived hollow nanostructures. Among the strategies for forming TiO₂ shells on materials, the sol-gel coating approach has often been used (15–23). However, unlike silica (SiO₂), it is very difficult to precisely control the sol-gel chemistry and crystallinity of TiO₂ on substrate surface. For example, a general method similar to the Stöber process for silica has been developed to synthesize porous TiO₂ shells for making multifunctional core-shell particles (24). To control the crystallization process of TiO₂ shells, a multistep “silica-protected calcination” strategy has been developed to synthesize high-quality TiO₂ hollow spheres with controlled nanosized TiO₂ grains in the shells (25). In our experience, the methods above still require delicate controls of the synthesis conditions. Meanwhile, the atomic layer deposition (ALD) method can deposit titania layers with a precisely (<1 nm) controlled thickness (26, 27). However, the ALD method is relatively time-consuming. In addition, it requires expensive ALD instruments, which increase the cost and hamper large-scale production. A universal recipe for the facile coating of mesoporous TiO₂ shells on functional nanomaterials at room temperature is not known. Therefore, it is highly desirable and technically very important to develop a universal method for synthesizing TiO₂-enhanced nano-composites for a diverse range of applications.

According to the hydrolysis polymerization reaction mechanism, TiO₂ has similar sol-gel reaction as SiO₂ (28, 29). In addition, TiO₂ precursors [for example, titanium isopropoxide (TIP)] also have similar molecular structures to commonly used SiO₂ precursors [for example, tetraethyl orthosilicate (TEOS)], and both TIP and TEOS can form three-dimensional -O-M-O-M-O- networks through the sol-gel process. Both TiO₂ and SiO₂ aerogels have been synthesized via the sol-gel process by using an acid or base catalyst (29). In the presence of ammonia as a catalyst, core@TiO₂ (24) and core@SiO₂ (30) nanospheres are synthesized by the Stöber process. Also, an inorganic-organic self-assembly method has been developed to synthesize ordered mesoporous TiO₂ (31), which is analogous to the synthesis of mesoporous SiO₂ by using triblock polymers as soft templates (32, 33).

The cooperative assembly-directed strategy has been widely used for the general coating of various functional materials with mesoporous SiO₂ shells (34–38). The synthesis usually involves self-assembled soft core particles, structure-directing agents [for example, cetyltrimethylammonium bromide (CTAB)], and SiO₂ precursors (for example, TEOS) in a water/ethanol mixture solution under alkaline conditions (for example, ammonia). By using this method, it is very easy to control the thickness (35), pore structure (39), and functionality (40) of the silica shells. However, this cooperative assembly-directed strategy rarely works for other materials (41).

Among its various potential applications, TiO₂ has been extensively studied as a promising anode material for lithium ion batteries (LIBs) (12, 42). It has been demonstrated that nanoshells with well-defined hollow cavity can stabilize the nanoparticles against agglomeration and keep electrically connected to other grains, leading to superior cycling performance (43, 44). Hence, enhanced lithium storage properties are generally expected from mesoporous TiO₂ nanoshells.

Here, we develop a universal method for growing mesostructured TiO₂ shells on diverse functional particles through a cooperative assembly-directed process at room temperature within 10 min. As a first demonstration, we show that high-quality TiO₂ hollow or yolk-shell spheres with tunable cavity size and shell thickness can be easily generated by alkaline etching of SiO₂ cores in SiO₂@TiO₂ or SiO₂ interlayers in core@SiO₂@TiO₂ particles. We further show that high-quality amorphous and crystalline mesoporous TiO₂ shells can also be grown on diverse functional particles, including metal and metal-oxide nanoparticles, mesoporous silica nanoparticles (MSNs), polymer...
nospheres (PNs), graphene oxide (GO), carbon nanospheres (CNs), and metal-organic framework (MOF) nanocrystals. Last, we demonstrate the potential use of these mesoporous TiO$_2$ nanoshells as anode materials for LIBs with long-term cycling stability.

RESULTS

The general synthesis procedure is very simple and illustrated in Fig. 1. The nanoparticles to be coated are homogeneously dispersed in ethanol by ultrasonication, followed by the addition of hexadecylamine (HDA) surfactants and ammonia under stirring. The HDA surfactants segregate to the surface of the nanoparticles. Then, TIP is added to the dispersion under stirring. The amino groups of the HDA molecules participate in hydrogen-bonding interactions with a TIP hydrolysis product (TiO$_2$) to form inorganic-organic composites that coat the nanoparticle, whereas the hydrophobic long carbon chains of HDA self-organize into rodlike micelles that will become pores in TiO$_2$ domains. This process generally completes at room temperature within 10 min. To remove the organic species, we perform a follow-up solvothermal treatment at 160°C. Depending on whether ammonia is used during the treatment, either amorphous TiO$_2$ (atTiO$_2$) or crystalline TiO$_2$ (cTiO$_2$) will remain as the nanoshell.

Synthesis of mesoporous atTiO$_2$ shells

In a typical synthesis, SiO$_2$ nanospheres with an average diameter of 220 nm (Fig. 2A and fig. S1A) are used as the core, and HDA is used as the surfactant for the formation of TiO$_2$ mesostructures. Figure 2B shows a transmission electron microscopy (TEM) image of the formed SiO$_2$@TiO$_2$/HDA core-shell spheres with a total diameter of 340 nm and shell thickness of 60 nm. The core-shell spheres are nearly monodisperse, and the surfaces are very smooth (fig. S1B). These SiO$_2$@TiO$_2$/HDA core-shell spheres are transformed into SiO$_2$@atTiO$_2$ yolk-shell nanospheres (Fig. 2, C and D) through a solvothermal treatment at 160°C in ammonia solution (0.5 M) for 16 hours. Each SiO$_2$@atTiO$_2$ yolk-shell nanosphere contains a small SiO$_2$ core with a diameter of about 70 nm, hollow cavity, and a uniform TiO$_2$ shell with a thickness of about 60 nm. The yolk-shell spheres obtained are still smooth and uniform without any cracks in the shells, in agreement with the field-emission scanning electron microscopy (FESEM) observation (fig. S1C).

To further characterize the uniform TiO$_2$ coating on the SiO$_2$ nanospheres, we characterize the hydrodynamic diameters of SiO$_2$ and SiO$_2$@TiO$_2$/HDA nanospheres with dynamic light scattering (DLS). The distributions in both DLS curves (fig. S2) are quite similar, with polydispersity index of only about 1%. The hydrodynamic diameter of SiO$_2$@atTiO$_2$/HDA nanospheres is larger than that of SiO$_2$ nanospheres by about 130 nm. The cooperative self-assembly of TiO$_2$ and HDA is evidenced by small-angle x-ray diffraction (XRD) analysis (fig. S3). The XRD pattern of SiO$_2$@TiO$_2$/HDA nanospheres shows one broad diffraction peak at about 2.0°, suggesting the formation of mesostructured TiO$_2$ shells. The status of the HDA molecules before solvothermal treatment is probed by Fourier transform infrared (FTIR) analysis (fig. S4). The bands of –NH$\_2$ stretching vibration near 3340 cm$^{-1}$ and N–H wagging vibration at 810 cm$^{-1}$ disappear, and the band of N–H deformation vibration shifts from 1570 to 1510 cm$^{-1}$. This indicates the strong interaction between HDA and TiO$_2$ in the mesostructured TiO$_2$ shell. The wide-angle XRD patterns (fig. S5) confirm the amorphous nature of the obtained SiO$_2$@TiO$_2$/HDA core-shell nanospheres. After the solvothermal treatment under alkaline condition, the obtained yolk-shell particles (SiO$_2$@atTiO$_2$) are still amorphous. The Brunauer-Emmett-Teller (BET) specific surface area of the SiO$_2$@TiO$_2$/HDA core-shell nanospheres is very small ($S_{\text{BET}} < 10$ m$^2$ g$^{-1}$) (fig. S6A). After the solvothermal treatment under alkaline condition, the HDA molecules are mostly removed (fig. S7) to generate mesopores with the diameter in the range from 2 to 3 nm (fig. S6B), which gives rise to a drastically increased BET surface area of 329 m$^2$ g$^{-1}$.

Hollow TiO$_2$ nanospheres with an amorphous shell can be obtained by the solvothermal treatment of SiO$_2$@TiO$_2$/HDA core-shell nanospheres at 160°C in ammonia solution (0.5 M) for 24 hours (fig. S8, A and B), which etches away the SiO$_2$ core completely. Compared with SiO$_2$@atTiO$_2$ yolk-shell spheres, the BET surface area of atTiO$_2$ hollow spheres increases to 342 m$^2$ g$^{-1}$ (fig. S9). The diameter, interior cavity size, and shell thickness of mesoporous TiO$_2$ hollow spheres can be precisely tailored at the nanoscale by tuning the amount of Ti precursor and the particle size of SiO$_2$ template nanospheres. The as-prepared TiO$_2$ hollow spheres are highly uniform with smooth surfaces (fig. S10). As shown in Fig. 3, the shell thickness can be easily varied.

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Fig. 1. Schematic illustration of the synthesis procedure for mesostructured TiO$_2$ shells.

Fig. 2. TEM characterizations of SiO$_2$@TiO$_2$/HDA core-shell spheres and SiO$_2$@atTiO$_2$ yolk-shell spheres. (A) SiO$_2$ template spheres. (B) SiO$_2$@TiO$_2$/HDA core-shell spheres. (C) and (D) SiO$_2$@atTiO$_2$ yolk-shell spheres.
from 8 to 54 nm, and the cavity size is tuned in the range from 270 to 475 nm.

**Synthesis of mesoporous TiO$_2$ shells with nanosized crystalline domains**

SiO$_2$@cTiO$_2$ core-shell nanospheres with a crystalline shell are obtained via a solvothermal treatment at 160°C without the addition of ammonia (fig. S11A). The HDA molecules are mostly removed to generate mesopores with the size in the range from 5 to 6 nm, which gives rise to a BET surface area of 186 m$^2$ g$^{-1}$ (fig. S12). The aTiO$_2$ in the precursor is transformed to anatase phase (fig. S13). The different degrees of crystallinity between the TiO$_2$ samples obtained under alkaline and neutral conditions might be due to the suppressing effect of silica on the crystallization process. Similar phenomena have also been observed in other SiO$_2$/TiO$_2$ reaction systems (25, 45). After the calcination in air (fig. S11B) and removal of silica template spheres, the cTiO$_2$ hollow spheres retain their morphology without apparent damage (Fig. 4, A and B). As can be seen from the rough surface of the nanosphere in the TEM image (Fig. 4C), the cTiO$_2$ nanoshell is composed of very small nanoparticles (~12 nm). At a high magnification, disordered intercrystallite mesopores and very small nanocrystals are clearly observed within the shell (Fig. 4D). A high-resolution TEM (HRTEM) image reveals lattice fringes of the nanocrystals, which can be correlated to the (101) planes of anatase TiO$_2$ (Fig. 4E). The distinct selected area electron diffraction (SAED) pattern also confirms the anatase phase of the sample (Fig. 4F). The BET surface

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**Fig. 3.** TEM characterizations of mesoporous aTiO$_2$ hollow spheres. (A to C) aTiO$_2$ hollow spheres with identical hollow core size of about 230 nm but varied shell thicknesses: 8 nm (A), 41 nm (B), and 54 nm (C). (D to F) aTiO$_2$ hollow spheres with average diameter (core size) of 300 (270) nm (D), 410 (325) nm (E), and 680 (475) nm (F).

**Fig. 4.** FESEM and TEM characterizations of mesoporous cTiO$_2$ hollow spheres. (A and B) FESEM (A) and TEM images (B) of cTiO$_2$ hollow nanospheres. (C and D) Magnified TEM images show an individual cTiO$_2$ hollow nanosphere (C) and the mesoporous shell (D). (E) HRTEM image of the cTiO$_2$ shell. (F) Corresponding SAED pattern of cTiO$_2$ hollow nanospheres.
area of cTiO2 hollow spheres is 176 m² g⁻¹ (fig. S14) and is comparable to many other reported porous TiO2 hollow particles (15, 24, 25, 45). No peaks corresponding to Si element are found in the energy-dispersive x-ray spectroscopy spectrum (fig. S15), indicating the purity of the cTiO2 nanoshells. Moreover, the pH value has some effect on the structure and crystallinity of the final products during the solvothermal process (fig. S16).

**Yolk-shell and core-shell particles with various functional core materials**

In addition to TiO2 hollow spheres, yolk-shell particles with mesoporous TiO2 shells can be easily prepared. It is very easy to coat a layer of silica on different materials to form core-shell structures. After that, a TiO2 shell can be further grown on the core-shell particles to generate three-layered core@SiO2@TiO2 structures. As a demonstration, two such structures are prepared with Au nanoparticles and Fe₂O₃ cubes as the inner cores. After selectively etching the SiO₂ interlayer, Au@TiO2 yolk-shell nanospheres and Fe₂O₃@TiO2 yolk-shell cubes can be obtained under alkaline conditions (fig. 5.A and B, and figs. S17 and S18). A double-shell TiO2-polymer hollow structure with two functional materials in the shell can also be obtained by coating a polymer layer on the hollow TiO2 spheres (fig. 5C and fig. S19).

We further demonstrate the versatility of our method by growing a layer of mesostructured TiO2 on many other commonly used materials, including MSNs, PNs, GO, CNs, and MOF nanocrystals (fig. 5.D to H, and figs. S20 to S22). This versatile method could even be applied to form mesostructured TiO2 layers on HNO₃-treated hydrophilic carbon nanotubes (CNTs) with many functional groups and untreated hydrophobic CNTs to synthesize smaller core-shell structures with a diameter of about 50 nm (fig. S23). Magnified TEM images and small-angle XRD patterns of representative samples further confirm the formation of mesostructured TiO2 shells on diverse materials (fig. S24). These results indicate that the formation of a mesostructured TiO2 layer by this assembly-directed method is facile and universal, independent of composition, surface functional groups, hydrophilicity, curvature, and size of the substrate particles.

**Electrochemical performance for lithium storage**

To demonstrate the potential use of the TiO2 nanoshells in electrochemical systems, we select cTiO2 hollow spheres as a representative sample to investigate their lithium storage properties as anode materials for LIBs. The cyclic voltammograms (fig. S25) exhibit the characteristic Li⁺ ion insertion/deinsertion behaviors for anatase TiO2, with two redox peaks recorded at approximately 1.6 and 2.2 V versus Li⁺/Li. Figure 6A shows typical discharge-charge voltage profiles within a cutoff voltage window of 1.0 to 3.0 V. There are two notable voltage plateaus at approximately 1.7 and 2.1 V versus Li⁺/Li, which respectively correspond to the Li⁺ ion insertion/deinsertion processes (23). The initial discharge and charge capacities are 184.1 and 142.8 mAh g⁻¹, respectively, with a high initial coulombic efficiency of 77.5%. After the first few cycles, the capacity quickly stabilizes, indicating that the electrochemical Li⁺ ion insertion/deinsertion reactions are highly stable and reversible in the electrode. Figure 6B shows the cycling performance of cTiO2 hollow spheres at a current density of 10 C (1 C = 173 mA g⁻¹). The capacity decays from initially 184.1 to 140.8 mAh g⁻¹ in the second cycle, then to 138.6 mAh g⁻¹ in the fifth cycle, and remains at 127.7 mAh g⁻¹ after 1000 cycles, corresponding to a very low capacity fading rate of <0.01% per cycle from the second cycle onward. The long-term cycling stability of these TiO2 hollow spheres is superior to that of other reported TiO2-based anode materials (11, 12, 46–48). Moreover, the cTiO2 hollow spheres can also be cycled with high stability at lower current rates of 1, 5, 10, 20, and 30 C (fig. S26). As shown in Fig. 6C, the cTiO2 hollow spheres also exhibit good rate capability at discharge-charge current rates ranging from 1 to 30 C. The average specific capacities are 196.2, 164.5, 127.4, 76.1, and 49.1 mAh g⁻¹ at current rates of 1, 5, 10, 20, and 30 C, respectively. After the high-rate discharge-charge cycling, a specific capacity of 199.5 mAh g⁻¹ can be restored when the current density is reduced back to 1 C. These results demonstrate that these mesoporous TiO2 nanoshells have excellent electrochemical kinetics and lithium storage properties as potential anode materials. Moreover, a postmortem study of the material after the cycling test reveals that the hollow structure is retained after discharging/charging at 10 C for 100 cycles (fig. S27).

**Fig. 5. TEM characterizations of TiO2 yolk-shell and double-shell hollow structures and nanocomposites. (A) Au@TiO2 yolk-shell nanospheres. (B) Fe₂O₃@TiO2 yolk-shell cubes. (C) TiO2-polymer double-shell nanospheres. (D) MSN@TiO2 core-shell nanospheres. (E) PN@TiO2 core-shell nanospheres. (F) GO@TiO2 composite nanosheets. (G) CN@TiO2 core-shell nanospheres. (H) MOF@TiO2 core-shell particles.**
indicating the excellent structural robustness of these $c\text{TiO}_2$ hollow spheres.

**DISCUSSION**

In summary, a universal cooperative assembly-directed method is developed to form mesoporous TiO$_2$ shells on different particles at room temperature. A key feature of this new method is that HDA molecules serve as the soft template for mesostructured TiO$_2$, which allows successful growth of a layer of mesoporous TiO$_2$ (both amorphous and crystalline) on many functional nanomaterials irrespective of composition, shape, and size. This provides the platform for making many designed TiO$_2$-based hollow nanostructures, including hollow and yolk-shell structures with tailored cavity size and shell thickness and hybrid structures for different applications. It is foreseen that the present recipe will open up vast opportunities to precisely control the structure of TiO$_2$ nanocomposites for a wide range of applications. As a demonstration of their potential applications, $c\text{TiO}_2$ hollow spheres consisting of very small nanocrystals are shown to manifest improved lithium storage properties with remarkably stable capacity retention over 1000 cycles.

**MATERIALS AND METHODS**

**Synthesis of SiO$_2$ nanospheres**

Briefly, SiO$_2$ nanospheres were synthesized by a modified Stöber method. In a typical reaction, 23.5 ml of water, 63.3 ml of 2-propanol, and 13 ml of ammonia (25 to 28%) were mixed and heated in an oil
bath to 35°C. Then, 0.6 ml of TEOS (99%) was added dropwise to this solution, and the reaction was continued for 30 min under vigorous stirring to form the silica seeds. Then, 5 ml of TEOS was added dropwise to the reaction system. The reaction mixture was kept for 2 hours at 35°C. The SiO2 nanospheres were isolated by centrifugation, washed with ethanol and water repeatedly, and finally dried in air.

**Synthesis of SiO2@TiO2 core-shell spheres with αTiO2 and cTiO2 shells**

For mesostructured TiO2 coating, 0.08 g of as-prepared SiO2 spheres was homogeneously dispersed in 9.74 ml of ethanol by ultrasonication, followed by the addition of 0.08 g of HDA (90%) and 0.2 ml of ammonia, and stirred at room temperature for 1 min to form uniform dispersion. Then, 0.2 ml of TIP (97%) was added to the dispersion under stirring, and the solution turned to white within 10 s. After reaction for 5 min, the product SiO2@TiO2/HDA core-shell particles were collected by centrifugation and then washed several times with water and ethanol. To prepare SiO2@αTiO2 yolk-shell spheres with mesoporous αTiO2 shells, a solvothermal treatment of the SiO2@TiO2/HDA spheres was performed. The SiO2@TiO2/HDA spheres (0.02 g) were dispersed in a mixture of 20 ml of ethanol and 10 ml of water with an ammonia concentration of 0.5 M. Then, the resulting mixture was sealed in a Teflon-lined autoclave (50 ml in capacity) and heated at 160°C for 16 hours. Prolongation of the reaction time to 24 hours will generate completely hollow TiO2 spheres with mesoporous αTiO2 shells. To prepare SiO2@cTiO2 core-shell spheres with mesoporous cTiO2 shells, a similar solvothermal treatment of the SiO2@TiO2/HDA spheres was performed but in the absence of ammonia. After that, the as-obtained SiO2@cTiO2 sample was calcined at 450°C for 2 hours in air and treated with a 10% HF solution to remove the silica template spheres and generate cTiO2 hollow spheres.

**Preparation of Au@TiO2 yolk-shell nanospheres**

Au@SiO2 core-shell nanoparticles were prepared according to the method reported by Arnal et al. (49). For TiO2 coating, 0.08 g of as-obtained Au@SiO2 spheres was homogeneously dispersed in ethanol (9.74 ml) by ultrasonication, followed by the addition of 0.08 g of HDA and 0.2 ml of ammonia, and stirred at room temperature for 1 min to form uniform dispersion. Further stirring for 10 min was necessary, and Au@SiO2@TiO2 nanospheres were collected by centrifugation and then washed with water and ethanol several times. To prepare Au@TiO2 yolk-shell nanospheres, a solvothermal treatment of the precursor beads was performed. The Au@SiO2@TiO2 spheres (0.02 g) were dispersed in a mixture of 20 ml of ethanol and 10 ml of water with an ammonia concentration of 0.5 M. Then, the resulting mixture was sealed in a Teflon-lined autoclave (50 ml in capacity) and heated at 160°C for 16 hours. After centrifugation and ethanol washing, 0.01 g of the obtained pink powder was dispersed in 30 ml of 0.05 M aqueous NaOH solution. Then, the resulting mixture was sealed in a Teflon-lined autoclave (50 ml) and heated at 85°C for 1.5 hours. The Au@TiO2 nanospheres were isolated by centrifugation, washed repeatedly with ethanol and water, and finally dried in air for characterization.

**Synthesis of Fe2O3@TiO2 yolk-shell cubes**

Uniform Fe2O3 cubes were synthesized by the method developed by Sugimoto et al. (50). Silica coating on Fe2O3 cubes was achieved by a modified Stöber method. Briefly, 0.15 g of Fe2O3 cubes was dispersed into 65 ml of ethanol and 6.5 ml of H2O through ultrasonication, followed by the addition of 6 ml of ammonia solution. TEOS (0.5 ml) dissolved in 4.5 ml of absolute ethanol was slowly added into the mixture at a rate of 1 ml min⁻¹ under magnetic stirring. The reaction was continued for 6 hours before the product was collected by centrifugation, followed by washing and drying at 70°C overnight. For TiO2 coating, 0.1 g of as-obtained Fe2O3@SiO2 cubes was homogeneously dispersed in ethanol (9.74 ml) by ultrasonication, followed by the addition of 0.08 g of HDA and 0.2 ml of ammonia, and then stirred at room temperature for 1 min to form uniform dispersion. Then, 0.01 ml of TIP was added to the dispersion under stirring. Stirring for another 10 min was necessary, and then Fe2O3@SiO2@TiO2 cubes were collected by centrifugation. To prepare Fe2O3@SiO2@TiO2 yolk-shell spheres, a solvothermal treatment of Fe2O3@SiO2@TiO2 cubes was performed. The Fe2O3@SiO2@TiO2 precursor cubes (0.02 g) were dispersed in a mixture of 20 ml of ethanol and 10 ml of water with an ammonia concentration of 0.5 M. Then, the resulting mixture was sealed in a Teflon-lined autoclave (50 ml) and heated at 160°C for 16 hours.

**Synthesis of TiO2-polymer double-shell hollow spheres**

Briefly, 0.1 g of as-obtained hollow TiO2 spheres was homogeneously dispersed in deionized water (7.04 ml) by ultrasonication, followed by the addition of 0.23 g of CTAB, 0.035 g of resorcinol, 2.82 ml of ethanol, and 0.01 ml of ammonia, and stirred at 35°C for 1 min to form uniform dispersion. Then, 0.05 ml of a formalin solution was added to the dispersion under stirring. The mixture was cooled to room temperature after 6 hours and then aged at room temperature overnight without stirring. The TiO2-polymer product was collected by centrifugation and washed with water and ethanol several times.

**Synthesis of MSNs and MSN@TiO2 nanospheres**

MSNs were synthesized by the method developed by Lu et al. (51). For TiO2 coating, 0.06 g of as-obtained MSNs was homogeneously dispersed in ethanol (9.74 ml) by ultrasonication, followed by the addition of 0.08 g of HDA and 0.2 ml of ammonia. The mixture was then stirred at room temperature for 1 min to form uniform dispersion. Then, 0.2 ml of TIP was added to the dispersion under stirring. After stirring for another 10 min, MSN@TiO2 nanospheres were collected by centrifugation and then washed with water and ethanol several times.

**Synthesis of PNs and PN@TiO2 nanospheres**

PNs were synthesized by the method developed by Liu et al. (52). For TiO2 coating, 0.04 g of as-obtained PNs was homogeneously dispersed in ethanol (9.74 ml) by ultrasonication, followed by the addition of 0.08 g of HDA and 0.2 ml of ammonia, and stirred for 1 min to form uniform dispersion. Then, 0.1 ml of TIP was added to the dispersion under stirring. After stirring for another 10 min, PN@TiO2 nanospheres were collected by centrifugation and then washed with water and ethanol several times.

**Synthesis of GO and GO@TiO2 nanosheets**

GO nanosheets were prepared according to Hummers method (53). For TiO2 coating, 0.005 g of as-obtained GO was homogeneously dispersed in ethanol (9.74 ml) by ultrasonication, followed by the addition of 0.08 g of HDA and 0.2 ml of ammonia, and then stirred at room temperature for 1 min to form uniform dispersion. Then, 0.04 ml of TIP was added to the dispersion under stirring. After stirring for
10 min, GO@TiO2 nanosheets were collected by centrifugation and then washed with water and ethanol several times.

**Synthesis of CNs and CN@TiO2 nanospheres**

CNs were synthesized according to Sun and Li's method (54). For TiO2 coating, 0.02 g of as-obtained CNs was homogeneously dispersed in ethanol (9.74 ml) by ultrasonication, followed by the addition of 0.08 g of HDA and 0.2 ml of ammonia, and then stirred at room temperature for 1 min to form uniform dispersion. Then, 0.04 ml of TIP was added to the dispersion under stirring. After stirring for 10 min, CN@TiO2 nanospheres were collected by centrifugation and then washed with water and ethanol several times.

**Synthesis of MOF and MOF@TiO2 nanocrystals**

MOF nanocrystals were synthesized according to the method by Lu et al. (55). For TiO2 coating, 0.08 g of as-obtained MOF crystals was homogeneously dispersed in ethanol (9.74 ml) by ultrasonication, followed by the addition of 0.08 g of HDA and 0.2 ml of ammonia, and then stirred at room temperature for 1 min to form uniform dispersion. Then, 0.2 ml of TIP was added to the dispersion under stirring. After stirring for 10 min, MOF@TiO2 nanocrystals were collected by centrifugation and then washed with water and ethanol several times.

**Materials characterization**

The crystal phase of the products was examined by XRD on a Bruker D2 Phaser x-ray diffractometer. A field-emission scanning electron microscope (FESEM; JEOl-6700F) and a transmission electron microscope (TEM; JEM, JEM-2010) were used for morphology characterizations. The nitrogen sorption measurement was carried on Autosorb-6B at liquid-nitrogen temperature. The particle size was measured by photon correlation spectroscopy using a Nano ZS90 laser particle analyzer (Malvern Instruments) at 25°C. FTIR spectra were recorded with an FTIR-Digilab FTS 3100 spectrometer.

**Electrochemical measurements**

Electrochemical measurements were carried out using CR2032 coin-type half-cells. The working electrode consisted of active material (that is, cTiO2 hollow spheres), carbon black (Super P Li), and polyvinylidene fluoride (polyvinylidene fluoride) in a weight ratio of 70:20:10. Lithium foil was used as both the counter electrode and the reference electrode. LiPF6 (1 M) in a 1:1 mixture of ethylene carbonate and diethyl carbonate was used as the electrolyte. Cell assembly was carried out in an Ar-filled glove box with moisture and oxygen concentrations below 1.0 ppm. The galvanostatic charge-discharge tests were performed on a Neware battery test system.

**REFERENCES AND NOTES**


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