Surfactant-templating strategy for ultrathin mesoporous TiO₂ coating on flexible graphitized carbon supports for high-performance lithium-ion battery

Yong Liu^a, Ahmed A. El zatahry^b, Wei Luo^{a,c}, Kun Lan^a, Pengfei Zhang^{a,d}, Jianwei Fan^{a,e}, Yong Wei^a, Chun Wang^a, Yonghui Deng^a, Gengfeng Zheng^a, Fan Zhang^a, Yun Tang^a, Liqiang Mai^d and Dongyuan Zhao^{a*}

^a Department of Chemistry, Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, State Key Laboratory of Molecular Engineering of Polymers, Laboratory of Advanced Materials, iChEM (Collaborative Innovation Center of Chemistry for Energy Materials), Fudan University, Shanghai, 200433, China.

^b Materials Science and Technology Program, College of Arts and Sciences, Qatar University, P.O. Box 2713, Doha, Qatar

^c State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Materials Science and Engineering, Donghua University, Shanghai 201620, P. R. China

^d State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Hubei, Wuhan 430070 P. R. China

^e College of Environmental Science and Engineering, State Key Laboratory of Pollution Control and Resource Reuse, Tongji University, Shanghai 200092, P. R. China.

E-mail: dyzhao@fudan.edu.cn

Homepage: <http://www.mesogroup.fudan.edu.cn/>

Abstract

The electrochemical performance of nanocomposites could greatly be improved by rationally designing flexible core-shell heterostructures. Typically, the uniform coating of a thin mesoporous crystalline transition metal oxide shell on flexible graphitized carbon supports can provide both

fast ion and electron transport pathways, which is an ideal material for high-performance lithium-ion batteries. Herein, we report a surfactant-templating assembly coating method to deposit an ultrathin mesoporous crystalline TiO_2 shell on flexible graphitized carbon supports by using amphiphilic triblock copolymer Pluronic F127 as a template. Taking multi-wall carbon nanotubes (CNTs) as an example support, the obtained flexible CNTs@mTiO_2 hybrid mesoporous nanocables exhibit an ultra-high surface area ($\sim 137 \text{ m}^2/\text{g}$), large internal pore volume ($\sim 0.26 \text{ cm}^3/\text{g}$), uniform accessible mesopores ($\sim 6.2 \text{ nm}$) and ultrathin highly-crystalline mesoporous anatase shells ($\sim 20 \text{ nm}$ in thickness). As an anode material for lithium battery, the flexible CNTs@mTiO_2 hybrid mesoporous nanocables show high-rate capacity ($\sim 210 \text{ mA h g}^{-1}$ at 20 C , $1 \text{ C} = 170 \text{ mA g}^{-1}$), high Coulombic efficiency (nearly 100 % during 1000 cycles at 20 C) and ultralong-cycling life (keeping $\sim 210 \text{ mAh g}^{-1}$ after 1000 cycles at 20 C). The strong synergistic coupling effect between CNT cores and thin mesoporous TiO_2 shells, high surface area, accessible large pores and highly crystalline thin mesoporous shells result in excellent performance in lithium batteries. This versatile surfactant-templating assembly coating method can be easily extended to deposit an ultrathin mesoporous TiO_2 layer on flat graphene (GR) to form a uniform sandwich-like flexible GR@mTiO_2 nanoflakes, which opens up a new opportunity for depositing thin mesoporous transition-metal oxides on graphitized carbon supports for advanced applications in energy conversion and storage, photocatalysis, sensors and drug delivery, etc.

Keywords: Surfactant templating strategy; Mesoporous TiO_2 shell Coating; Graphitized carbon supports; Lithium-ion Battery.

Introduction

Development of high-performance lithium-ion batteries (LIBs) with a capacitor-like high rate and battery-like high capacity is highly demanded for the next generation electronic devices¹⁻¹⁶. In this

regard, improvement of both ion and electron transport kinetics in batteries is greatly needed¹⁷⁻²¹. From the materials perspective, a flexible coaxial core-shell heterostructures formed by coating an ultrathin mesoporous crystalline TiO₂ shell on flexible graphitized carbon supports can meet both criteria^{22, 23}. In this unique flexible coaxial core-shell hybrid architecture, each component synergistically serves a specific purpose. The graphitized carbon core can provide superior electronic conductivity and excellent mechanical flexibility^{10, 24-27}. Meanwhile, the ultrathin mesoporous crystalline TiO₂ shells can in turn shorten Li⁺ ions diffusion length and facilitate fast penetration of the electrolyte²⁸⁻³⁰, which guarantee sufficient transport of both ions and electrons in high rate and capacity performance in lithium-ion batteries. Previously, many efforts have been directed toward synthesis of various CNT/TiO₂ hybrid materials. Typically, Wan et al. have reported a wet-chemical synthetic route to deposit disordered nanoporous TiO₂ shells onto CNT surface for efficient lithium storage²⁸. Wang and co-workers have developed a PEO-aided self-assembly method to grow TiO₂ nanoparticles onto CNT surface as a high-rate anode. In addition, Lou and co-workers have developed a new hydrothermal method to direct grow TiO₂ nanosheets@CNTs coaxial nanocables with excellent lithium-storage performance²⁹. We have also confirmed a sol-gel design strategy for ultra-dispersed TiO₂ nanoparticles on graphene for high-performance lithium ion batteries^{30, 31}. Though there are many papers concerning CNT/TiO₂ composites, very few work has succeeded in coating well ordered mesoporous TiO₂ shells on the surface of CNTs, yet. It is highly desirable for achieving fast rate and high capacity performance in lithium ion batteries.

Typically, direct coating of ultrathin mesoporous anatase TiO₂ shells with a highly crystalline framework and large-pore size on the entire surface of graphitized carbon supports is difficult to achieve, which attributes to two reasons primarily: (i) The large lattice mismatch and high interfacial energy on the curved interfaces between graphitized carbon supports and titanium crystals often allow the depositing of island-like TiO₂ domains on the surface of graphitized carbon, rather than a continuous and conformable mesoporous TiO₂ shell³⁶⁻³⁹. (ii) The high coordination number of titanium endows its

precursor high reactivity, which makes it difficult to control the hydrolysis rate for heterogeneous nucleation and corresponding cooperative assembly with surfactants to grow a thin mesoporous shell with a highly-crystalline framework⁴⁰⁻⁴². Therefore, it is of great importance and interest to develop a new method to controllably grow an ultrathin mesoporous anatase TiO₂ shell with large and accessible mesopores on the graphitized carbon supports by a surfactant-based coating process, so as to achieve the double goal of capacitor-like high rate and battery-like high capacity performance in lithium-ion batteries.

Taking CNTs as an example support, here we demonstrate a novel surfactant-templating assembly coating method to synthesize uniform CNTs@mTiO₂ core-shell hybrid mesoporous nanocables with flexible multi-wall CNT cores and ultrathin crystalline mesoporous anatase TiO₂ shells. To the best of our knowledge, it is the first time to synthesize uniform flexible CNTs@mTiO₂ hybrid mesoporous nanocables through a layer-by-layer spherical micelles depositing process within surfactant-templating assembly coating process. This method is also very simple and reproducible, yet important, which allows direct coating a uniform ordered mesoporous TiO₂ shell with spherical mesopores on various flexible graphitized carbon supports, highly desirable for achieving fast rate and high capacity performance in lithium ion batteries. Triblock copolymer Pluronic F127 (PEO₁₀₆PPO₇₀PEO₁₀₆) here is used as a template, tetrabutyl titanate (TBOT) as a titania precursor, ammonia as hydrolysis catalyst and ethanol/dimethyl formamide (DMF) as mixed solvent. The obtained flexible CNTs@mTiO₂ coaxial nanocables possess a high surface area (~ 137 m²/g), large internal pore volume (~ 0.26 cm³/g), highly-open large ordered mesopore (~ 6.2 nm) and thin crystalline anatase TiO₂ mesoporous shell (~ 20 nm in thickness). Lithium battery measurements show that the flexible CNTs@mTiO₂ hybrid mesoporous nanocable anodes can synergistically enhance Li⁺ ion and electron transport kinetics, resulting in unusual superior electrochemical performance with high-rate capacity (213 mA h g⁻¹ at 20 C), high Coulombic efficiency (nearly 100 % during 1000 cycles at 20 C) and superior cycling stability (keeping reversible capacity about 210 mAh g⁻¹ after 1000 cycles at 20 C).

Experimental section

Chemicals.

The oxidized CNTs were purchased from Chengdu Organic Chemicals Co., LTD). Triblock copolymer Pluronic F127 ($M_w = 12600$, $\text{PEO}_{106}\text{PPO}_{70}\text{PEO}_{106}$) were purchased from Aldrich Corp. Concentrated HNO_3 , KNO_3 , KMnO_4 , H_2O_2 (30 wt %), tetrabutyl titanate (TBOT), concentrated HCl , anhydrous ethanol and N, N-dimethyl formamide (DMF) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Concentrated ammonia solution (28 - 30 wt %) and graphite were purchased from Sigma-Aldrich. All chemicals were used as received without further purification. Deionized water was used for all experiments.

Preparation of the oxidized CNT supports.

The oxidized CNTs were prepared as follows: 0.1 g of raw multi-wall CNTs were suspended in 50 ml of concentrated nitric acid (68 wt. %) and refluxed at $120\text{ }^\circ\text{C}$ in an oil bath for 5 h. (*Caution:* Concentrated nitric acid is a corrosive solution, and appropriate safety precautions should be utilized including the use of acid resistant gloves and adequate shielding). After the mixture was cooled down to room temperature, it was filtered through a filter membrane with a pore diameter of $0.2\text{ }\mu\text{m}$ and washed with deionized water until the pH value of the filtrate was around 7.0. Then the product was dried at $60\text{ }^\circ\text{C}$ for 12 h. This acid-pre-treatment could remove the caps of the carbon nanotubes as well as amorphous carbon. At the same time, surface oxygen groups such as carbonyl, carboxylic and ether could be produced onto the surfaces of the CNTs.

Synthesis of Graphene Oxide (GO).

The GO was synthesized from graphite via a modified Hummers method. Briefly, the commercial graphite (5.0 g) was added into a solution of concentrated H_2SO_4 (115 mL) cooled in an ice-water bath. KNO_3 (2.5 g) and KMnO_4 (15 g) were added very slowly (with a period more than 15 min) into the

mixture. All the operations were carried out very slowly in a fume hood. The solution was allowed to stir in an ice-water bath for 2 h, then at 35 °C for 1 h. Then, 115 mL of water was added to the flask. After 1 h, 700 mL of water was added. After 15 min, the solution was removed from the oil bath and 50 mL of 30 % H_2O_2 were added to end the reaction. This suspension was stirred at room temperature for 5 min. The suspension was then repeatedly centrifuged and washed twice with 5% HCl solution and then dialyzed for a week.

Synthesis of the mesoporous CNTs@mTiO₂ hybrid core-shell nanocables.

The flexible mesoporous CNTs@mTiO₂ hybrid core-shell nanocables were prepared via surfactant-templating assembly coating method. Briefly, 20 mg of the oxidized CNTs obtained above was dispersed in a mixed solution containing 0.18 g of Pluronic F127, 30 ml of ethanol/DMF mixed solvent (20 ml of ethanol and 10 ml of DMF) and 0.07 ml of concentrated ammonia aqueous solution (28 wt %) to form a uniform dispersion. After stirring at room temperature for 3 h, 0.1 g of TBOT was added dropwise to the dispersion with continuous stirring. After the reaction for 6 h, the product was collected by centrifugation (8500 rpm for 15 min), leaving a colourless supernatant. The collected product was then washed with ethanol and water for three times, respectively. Finally, the dried mesostructured CNTs@ F127 micelles/TiO₂ hybrid nanocables were calcined under Ar at 400 °C for 2 h to remove the Pluronic F127 template, and the mesoporous CNTs@mTiO₂ hybrid nanocables were obtained. The sandwich-like flexible GR@mTiO₂ hybrid nanoflakes were prepared *via* the same surfactant templating assembly coating method strategy described above.

Materials characterization.

Transmission electron microscopy (TEM) experiments were conducted on a JEOL JEM-2100F (UHR) microscope (Japan) operated at 200 kV. Energy-dispersive X-ray (EDX) and high-angle annular dark-field scanning TEM (HAADF-STEM) analyses were performed with a FEI Talos F200X electron microscope at 200 kV with an EDX detector system. The samples for TEM and EDX measurements were suspended ultrasonically in ethanol and supported onto a carbon-coated copper grid. X-ray

diffraction (XRD) patterns were recorded with a Bruker D8 powder X-ray diffractometer (Germany) using Cu K α radiation (40 kV, 40 mA). Small angle X-ray scattering (SAXS) measurements were taken on a Nanostar U small angle X-ray scattering system (Bruker, Germany) using Cu K α radiation (40 kV, 35 mA). The d -spacing values were calculated by the formula $d = 2\pi/q$. Nitrogen sorption isotherms were measured at 77 K with a Micromeritics Tristar 3020 analyzer. All of the samples were degassed under vacuum at 180 °C for at least 8 h prior to the measurement. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas using adsorption data in a relative pressure range from 0.05 to 0.25. The pore size distributions (PSD) were derived from the adsorption branch of the isotherms using the Barrett-Joyner-Halenda (BJH) model. The total pore volume (V_t) was estimated from the adsorbed amount at a relative pressure P/P_0 of 0.995. X-ray photoelectron spectroscopy (XPS) was recorded on an AXIS ULTRA DLD XPS System with MONO Al source (Shimadzu Corp.). Photoelectron spectrometer was recorded by using monochromatic Al K α radiation under vacuum at 5×10^{-9} Pa. All of the binding energies were referenced to the C $_{1s}$ peak at 284.6 eV of the surface adventitious carbon. Atomic force microscopy (AFM) measurements were taken using a Multimode in the tapping mode. The samples were deposited on a freshly cleaved mica surface. Raman spectra were collected by using Raman microscopes (Renishaw, UK) under 632.8 nm excitation.

Electrochemical Tests.

The electrochemical properties were evaluated by assembly of 2025 coin cells in an argon-filled glove box ($O_2 \leq 1$ ppm and $H_2O \leq 1$ ppm). Lithium pellets (China Energy Lithium Co., Ltd.) were used as the anode. The solution of LiPF $_6$ (1 M) in ethylene carbon (EC)/dimethyl carbonate (DMC) was used as electrolyte. The cathodes were obtained with 70 % active material, 20 % acetylene black and 10 % poly(tetrafluoroethylene) (PTFE). Then the mixed clay was rolled using a roller mill to form the freestanding film. And the film was cut into disk with a diameter of 8 mm. The loading of the active materials was 2-3 mg cm $^{-2}$. **The specific capacity of the CNT@mTiO $_2$ hybrid mesoporous nanocables is calculated based on the total electrode mass.** Galvanostatic charge/discharge cycling was studied with a

multichannel battery testing system (LAND CT2001A). Cyclic voltammetric (CV) tests were conducted from 3.00 to 1.00 V using an electrochemical analyser (Germany Instruments, Inc). The electrochemical impedance spectroscopy (EIS) was conducted using an electrochemical station (CHI 660).

Results and discussion

The procedure for the preparation of the flexible CNTs@mTiO₂ hybrid mesoporous nanocables is shown in Figure 1. First, the multi-wall CNTs were functionalized with abundant carboxyl and hydroxyl groups by boiling in nitric acid, making them dispersible well in ethanol/DMF mixed solvent. Then, the spherical PEO-PPO-PEO/titania-oligomer composite micelles are formed via the hydrolysis and condensation of TBOT in a low content of concentrated ammonia (0.2 vol %), which are further deposited on the surface of the oxidized multi-wall CNTs through a layer-by-layer micelles depositing process. Transmission electron microscopy (TEM) images taken from the preparation solution show that these spherical composite micelles have a diameter of 8 - 10 nm, which is a typical core-shell structure with PEO-PPO-PEO as the core and titania oligomers as the shell (Figure. S1). Finally, F127 templates were removed by calcination at 400 °C for 2 h in Ar atmosphere to form a mesoporous thin TiO₂ shell with a large pore size and highly crystalline anatase framework, resulting in well-defined flexible CNTs@mTiO₂ hybrid mesoporous nanocables.

The CNTs support after being functionalized by boiling in nitric acid have a diameter of ~ 20 nm and length of dozens of micrometres (Figure S2), indicating that the nitric acid-pre-treatment does not change their morphology and flexibility. Then, a thin mesoporous TiO₂ shell with a thickness of about 20 nm are uniformly coated on entire functionalized CNTs via the surfactant-templating assembly coating process, resulting in uniform mesoporous core-shell CNTs@mTiO₂ hybrid nanocables (Figure 2a). The feature of the ultrathin mesoporous TiO₂ shells is clearly revealed in the broken tips of nanocables in the SEM image (Figure 2a, indicated by arrows). A high-resolution SEM (HRSEM) image of a single CNTs@mTiO₂ hybrid nanocable shows rough and porous surface with a diameter of

approximately 80 nm (Figure 2b). The ordered spherical mesopores are uniformly distributed on the entire rough surface of hybrid nanocables, and the average pore size is estimated to be ~ 5.8 nm. TEM images of the CNTs@mTiO₂ hybrid mesoporous nanocables (Figure 2c) exhibit distinct core-shell hybrid structure with outer shell comprising numerous close-packed spherical mesopores. Such a pore arrangement model is further visually described in upper-left inset of Figure 2c.

The high-resolution TEM image (HRTEM) recorded on the cross section of a single core-shell CNTs@mTiO₂ nanocable shows that the highly crystallized mesoporous TiO₂ shells are closely integrated with CNTs (Figure 2d and 2e). The cross-section TEM image also clearly reveals that the thickness of the mesoporous TiO₂ shells is as thin as ~ 20 nm. The spacing of 0.338 nm estimated in the core area of the coaxial nanocables corresponds to the (002) crystalline plane of the multi-wall CNTs (Figure 2e)³¹. Meanwhile, another spacing of 0.352 nm estimated in the mesoporous TiO₂ shells corresponds to the (101) planes of anatase (Figure 2e)^{43,44}. The HRTEM image taken along the CNTs@mTiO₂ mesoporous nanocables (Figure 2f and Figure S3) also clearly show the (101) and (002) anatase planes with an interfacial angle of 68.3°^{45,46}. The selected-area electron diffraction (SAED) pattern recorded on a single core-shell CNTs@mTiO₂ nanocable (Figure 2g) shows a series of clear spotty diffraction rings, which corresponds to the highly crystalline anatase phase⁴⁷. The above SAED and HRTEM results well confirm that the mesoporous TiO₂ shells are highly crystalline anatase phase after calcination at 400 °C in Ar atmosphere.

The small-angle X-ray scattering (SAXS) pattern of the as-made CNTs@amorphous F127/TiO₂ hybrid nanocables (Figure 2h) clearly shows three well-resolved diffraction peaks at q values of 0.070, 0.099 and 0.123 nm⁻¹, which can be indexed to the 110, 200 and 211 reflections of a body-centred cubic *Im3m* mesostructure, indicating that the spherical composite micelles are successfully coated on the surface of the oxidized CNTs *via* the surfactant-templating assembly coating method. After the removal of Pluronic F127 templates by calcination at 400 °C for 2 h in Ar, the CNTs@mTiO₂ hybrid mesoporous nanocables still shows three weak and broad scattering peaks at higher q values of 0.075,

0.106 and 0.130 nm⁻¹, obviously indicating that the cubic mesostructure is still retained. Nitrogen adsorption-desorption isotherms of the CNTs@mTiO₂ hybrid nanocables show characteristic type IV curves with distinguishable capillary condensation step (Figure 2i). A distinct capillary condensation step at $P/P_0 = 0.4-0.7$ reflects characteristic mesopores. The pore size distribution calculated using the Barrett-Joyner-Halenda (BJH) model (inset of Figure 2i) show two sets of pores. The primary pore size distribution centred at 6.2 nm is ascribed to the mesoporous TiO₂ shells, and the secondary pore size at 2.3 nm is probably attributed to CNTs (Inset of Figure 2g). The Brunner-Emmet-Teller (BET) surface area and pore volume of the flexible CNTs@mTiO₂ hybrid mesoporous nanocables are calculated to be as high as ~ 137 m²/g and 0.26 cm³/g, respectively.

Wide-angle X-ray diffraction (WAXRD) of the pure CNTs shows four broad peaks of the 002, 101, 004 and 110 reflections, typical for crystalline graphite (Figure 3a). After coating with the mesostructured F127/TiO₂ hybrid shells, the diffraction peaks corresponded to CNTs are seriously weakened, which is possibly attributed to the lower atomic number (Z) of carbon as well as the uniform amorphous F127/TiO₂ shell coating. After calcination at 400 °C for 2 h in Ar, the WAXRD pattern of the CNTs@mTiO₂ hybrid mesoporous nanocables exhibits the characteristic broad diffraction peaks at $2\theta = 25.4, 37.8, 48.0, 53.9, \text{ and } 62.8^\circ$, which are indexed to the 101, 004, 101, 200, 105, and 204 diffractions of anatase (space group *I4₁/amd*)^{40,41,44}, respectively. The average crystal size is calculated to be ~ 6.5 nm, in agreement with the domain size of the nanocrystals estimated from the HRTEM images. The high resolution X-ray photoelectron spectra (XPS) spectrum of C element (Figure 3b) shows two sets of peaks. The main peak at the binding energy of 284.6 eV is assigned to adventitious carbon (C-C)^{48,49}. The sharp peak located at 285.6 eV is assigned to be defect-containing *sp*²-hybridized carbon (C=C) from CNTs^{49,50}, which is possibly attributed to the functionalization of the CNTs by boiling in nitric acid before the mesoporous TiO₂ shells are coated. The O1s XPS spectra (Figure 3c) show three chemical states of oxygen. The sharp peak at 530.6 eV is assigned to the O-Ti bonds of mesoporous

TiO₂ shells, indicating that the chemical state of oxygen in the mesoporous TiO₂ shells is mainly lattice oxygen. The other two peaks at 531.4 and 532.3 eV are assigned to O-H and O-C absorbed on the mesoporous TiO₂ shell surface⁴⁷. The Ti2p XPS spectrum (Figure 3d) reveals two sets of peaks at 465.2 eV (Ti2p_{1/2}) and 459.4 eV (Ti2p_{3/2}), which are slightly shifted to higher binding energy compared to those of bulk anatase. This shift implies a strong electron interaction between the mesoporous TiO₂ shells and CNT cores, and even partial formation of Ti-O-C bonds⁵¹. High-angle annular dark-field scanning TEM (HAADF-STEM) image of a single CNTs@mTiO₂ hybrid mesoporous nanocable clearly reveals the core-shell mesostructure with a CNT core and mesoporous TiO₂ shell (Figure 3e). The elemental mapping from the HAADF-STEM image shows that only Ti, O and C elements are uniformly distributed on the whole hybrid nanocable (Figure 3f-h and Figure S4), further confirming that a pure mesoporous anatase TiO₂ shell is coated on the curved surface of CNTs.

In this surfactant-templating coating strategy, it is found that the amphiphilic Pluronic F127 and ammonia content here play significant roles in uniform mesoporous TiO₂ shell coating. Without amphiphilic triblock copolymer F127 template, only a layer of the anatase TiO₂ nanoparticle (NPs) are deposited on the surface of the multi-wall CNTs (designated as CNTs@TiO₂ NPs) (Figure S5). The TEM and HRTEM images reveal that each shell of the CNTs@TiO₂ NPs is composed of numerous close-packed anatase TiO₂ NPs with a size of ~ 20 nm (Figure S5b and S5c), no apparent mesopores can be observed between the compact anatase TiO₂ NPs. For the ammonia parameter, when the concentration of ammonia below 0.2 vol %, no obvious mesoporous TiO₂ shell are formed on the surface of CNTs (Figure S6). Once the content of 0.2 vol % ammonia is reached, uniform thin mesoporous TiO₂ shells are coated on the surface of CNTs (Figure 1). As the ammonia concentration increases to 0.3 vol %, the thickness of mesoporous TiO₂ shell increases to be about 60 nm (Figure S7). This reveals that the higher ammonia concentration can increase the hydrolysis and condensation rate of TBOT, thus resulting in an increase of spherical PEO-PPO-PEO/titania oligomer micelles for TiO₂ shell coating^{52, 53}. However, when ammonia concentration is further increased to 0.4 vol %, some irregular

mesoporous TiO₂ nanospheres organized from TiO₂ nanoparticles are formed in the reaction system (Figure S8).

Based on the above observations, we propose a surfactant templating assembly coating process for the uniformly coating of the ultrathin mesoporous anatase TiO₂ shells on the functionalized surface of multi-wall CNTs (Figure 1). At a low concentration of weak base (0.2 vol % ammonia), TBOT molecules can slowly be hydrolysed and cross-linked to form titania oligomers. The oligomers can assemble with amphiphilic Pluronic F127 into uniform spherical PEO-PPO-PEO/titania oligomer micelles at the mixture solvent of ethanol and DMF^{40,54,55}. After the surface functionalization, the CNTs surface is chemically active and can be well dispersed in the ethanol/DMF mixed solution. At a low concentration, the tendency of the spherical F127/TiO₂ composite micelles heterogeneous nucleation on the surface of the functionalized CNTs is more favourable than the spontaneous stacking of micelles by homogeneous nucleation. Therefore, in the beginning sol-gel process, the initially formed spherical micelles as subunits can slowly be diffused and selectively anchored at the oxygen functional group sites of the oxidized CNTs owing to their strong hydrogen-bonding interaction. Once the spherical micelles deposition occurs, the new hydrolysed spherical micelles continuously diffuse and layer-by-layer deposit on the functionalized CNTs surface owing to deduction of high interfacial energy, thus resulting in a thin and continuous composite micelle layer on the surface of CNTs. Upon increasing ammonia content (0.3 vol % ammonia), the hydrolysis and condensation of TBOT can be promoted. In this case, the plentiful of spherical F127/TiO₂ composite micelles are formed, making the TiO₂ shells rapidly grow in thickness through a layer-by-layer coating. However, with a much higher content (> 0.4 vol %) or lower content (< 0.2 vol %) of ammonia, the balance between the production and consumption of spherical composite micelles is broken, thus resulting in isolated TiO₂ nanospheres or non-uniform TiO₂ coating. Without F127 templating assembly, only heterogeneous nucleation of TiO₂ nanoparticles takes place on the surface of CNTs, resulting in continuous TiO₂ nanoparticles coating layer on the surface of CNTs (CNTs@TiO₂ NPs).

We further demonstrate that ultrathin mesoporous TiO_2 shells can also be uniformly coated on the planar surfaces of the graphene (GR) *via* this surfactant-templating assembly coating method (Figure 4a). The graphene nanoflakes can be uniformly coated by two ultrathin mesoporous TiO_2 layers (top and bottom) with an average thickness of ~ 11 nm, resulting in a uniform sandwich-like flexible GR@m TiO_2 nanoflakes (Figure 4b and 4c). The average spherical pore size is estimated to be ~ 8 nm. The HRTEM and SAED pattern confirm that the mesoporous TiO_2 shells are well crystallized in anatase phase (Figure 4d). The Raman spectrum indicates the characteristic peaks of anatase TiO_2 at 154 cm^{-1} and the D band (1342 cm^{-1}) and G band (1586 cm^{-1}) of graphene (Figure 4e). The atomic force microscopy (AFM) and thickness analyses reveal that the total thickness of the sandwich-like GR@m TiO_2 nanoflakes is about 23 nm (Figure 3f and g), indicating that each mesoporous TiO_2 layer exhibits a thickness of about 11 nm, which is consistent with the SEM results.

As a proof of concept, the electrochemical performances of the flexible CNTs@m TiO_2 hybrid mesoporous nanocables are investigated as anode materials for LIBs. The charge-discharge voltage profiles of the flexible CNTs@m TiO_2 hybrid mesoporous nanocables electrode at a rate of 20 C ($1\text{ C} = 170\text{ mA g}^{-1}$) show the first discharge capacity are 260 mAh g^{-1} (Figure 5a). The discharge capacity drops to 158 mAh g^{-1} in the first 10 cycles, which is attributed to the irreversible interfacial reaction between anatase TiO_2 and the electrolyte⁴³. After 50 cycles, the discharge capacity gradually increases to 200 mAh g^{-1} with a corresponding charge capacity of 199 mAh g^{-1} , suggesting a possible activating process in the flexible CNTs@m TiO_2 hybrid mesoporous nanocables. The discharge and charge capacities show almost no change during the subsequent 1000 cycles, confirming excellent stability and high reversibility for the CNTs@m TiO_2 hybrid mesoporous nanocables at a high rate (20 C). The discharge and charge profiles deliver a high discharge and charge capacity of about 213 mAh g^{-1} after 1000 cycles, resulting in a high Coulombic efficiency of nearly 100 %. **It is worth mentioning that the weight percentage of TiO_2 in the CNT@m TiO_2 hybrid nanocables is dependent on the thickness of the**

mesoporous TiO₂ layers, which can be tuned in the range of 50 ~ 80 %. For the best performance on lithium battery, we have optimized the ratio of TiO₂ to be 70 % (~ 20 nm in TiO₂ shell thickness).

To investigate the rate capability, the flexible CNTs@mTiO₂ hybrid mesoporous nanocables electrode was discharged and charged at various current rates. The discharge capacity was found to be about 320, 300, 290, 270, 210, 180 and 150 mA h g⁻¹ at current rates of 0.4, 2, 4, 6, 20, 40 and 60 C (Figure 5b), respectively, confirming the excellent electronic/ionic transport properties and improved reaction kinetics. When the current rate was abruptly switched back to 0.4 C, a stable high capacity of about 320 mAh g⁻¹ was recovered, confirming the excellent stability and reversibility of the CNTs@mTiO₂ hybrid mesoporous nanocables. Even at ultra-high rate of 60 C (Figure 5b), the capacity of this lithium-ion cell can reach around 160 mAh g⁻¹. The cyclic voltammogram (CV) curve of the CNTs@mTiO₂ hybrid electrode shows two peaks at 1.73 V (cathodic) and 1.97 V (anode), which are associated with Li⁺ insertion/extraction in the anatase lattice (Figure 5c) ²⁶. The CV curves show an ideal rectangular shape in the range of 1.0-1.7 V, which is the characteristic of pseudocapacitive storage behaviour contributed from the ultrathin mesoporous TiO₂ shells. The CV measurements at different scan rates of 0.1–1.0 mV/s (the inset of Figure 5c) also clearly show that the peak current varies linearly with the scan rate, which further confirms the fast pseudocapacitive charge storage process in the CNTs@mTiO₂ hybrid electrode. For charge transfer resistance (R_{ct}) comparison, a CNTs-free-mTiO₂ sample is prepared by removing CNT cores of CNTs@mTiO₂ hybrid mesoporous nanocables via calcination in air at 400 °C for 3 h. Nyquist plots of the flexible CNTs@mTiO₂ hybrid mesoporous nanocables and CNTs-free-mTiO₂ nanocubes after removal of the CNTs by calcination at 500 °C in air show a semicircle in the moderate frequency region and a straight line in the high frequency region (Figure 5d), which are relevant to a charge transfer process and Warburg diffusion process ²⁷, respectively. Compared to CNTs-free-mTiO₂ nanocubes (R_{ct} , 86 Ω), the flexible CNTs@mTiO₂ hybrid mesoporous nanocables show much lower charge transfer resistance (R_{ct} , 27 Ω) in the moderate

frequency region, confirming that the lithium ions and electrons' transfer can be dramatically increased in the CNTs@mTiO₂ hybrid nanocables.

The flexible CNTs@mTiO₂ hybrid mesoporous nanocable electrode exhibits superior cycling capacity (about 210 mAh g⁻¹) over 1000 cycles at a high rate of 20 C accompanied with nearly 100 % Coulombic efficiency (Figure 5e). The SEM image of flexible CNTs@mTiO₂ hybrid mesoporous nanocables after cycling at 20 C for 500 cycles shows no notable variation in morphology or collapse of the hybrid structure (Figure S9), confirming its excellent tolerance of ultrafast lithium ions insertion and extraction for long-life LIBs. Compared to the flexible CNTs@mTiO₂ hybrid mesoporous nanocables, it is worth noting that the CNTs@TiO₂ NPs hybrid nanocables obtained without Pluronic F127 template show much lower rate capability of only about 80 mA h g⁻¹ at a current rate of 20 C (Figure S10). The lower rate capability of the CNTs@TiO₂ NPs hybrid nanocables is possibly attributed to their lower BET surface area (87 m²/g) and pore volume (0.17 cm³/g). For further comparison, Figure S10 shows the rate-capability performance of the CNTs@mTiO₂ hybrid mesoporous nanocables (our work) and some other CNT/TiO₂ composites reported previously. It should be noted that the rate capability from our nanocables is much higher than that for other hybrid nanostructures, such as CNT/TiO₂ nanocrystals³², CNT/TiO₂ nanosheets⁵⁶, CNT/TiO₂ nanoparticles⁵⁷ and CNT@ nanoporous TiO₂ coaxial nanocables³³ under similar testing conditions. In addition, the discharge capacity of the obtained mesoporous GR@mTiO₂ nanoflakes was measured to be about 310, 290, 275, 265, 205, 165 and 145 mA h g⁻¹ at current rates of 0.4, 2, 4, 6, 20, 40 and 60 C (Figure S10), respectively. It is a little lower than that of the CNTs@mTiO₂ hybrid mesoporous nanocables, but still higher than the values from other CNT/TiO₂ hybrid nanocomposites (such as CNT/TiO₂ nanocrystals³², CNT/TiO₂ nanosheets⁵⁶, CNT/TiO₂ nanoparticles⁵⁷ and CNT@ nanoporous TiO₂ coaxial nanocables³³) reported previously.

The remarkable high-rate capability and superior cycling stability of the flexible CNTs@mTiO₂ hybrid mesoporous nanocable can mainly be attributed the synergistic coupling effects between graphitic CNTs, high surface area, accessible large pores and highly crystalline thin mesoporous shells.

The thin mesoporous crystalline TiO_2 shells with a large surface area and accessible large mesopore (~ 6.2 nm) can not only provide large active surface sites, but also greatly reduces Li^+ diffusion length and guarantees the fast kinetics for Li^+ insertion and de-insertion, leading to a high-rate capacity. On the other hand, the graphitic CNTs core can significantly improve the electronic conductivity between the mesoporous anatase TiO_2 shells and current collectors, thus giving rise to high-rate capacity. The robust core-shell mesostructure effectively prevents the undesirable aggregation and volume expansion upon the lithiation and delithiation, which give rise to a long cycle life performance. Additionally, the highly crystalline nature of the mesoporous anatase TiO_2 shells can also contribute to the electrical conductivity and crystal lattice robustness during repeated charge-discharge cycling. The above outstanding features probably promote the electrochemical process and lead to high specific rate capability and superior cyclability.

Conclusions

In summary, well-defined, uniform flexible CNTs@mTiO₂ hybrid mesoporous nanocables with thin crystalline anatase shell and accessible mesopores have successfully been synthesized by a novel surfactant templating assembly coating approach. This surfactant templating assembly coating approach experiences a controlled layer-by-layer spherical F127/TiO₂ composite micelles coating process, and the thickness of the mesoporous TiO₂ shell can be well tuned from ~ 20 to ~ 60 nm by adjusting the spherical composite micelles content and ammonia concentration. Typically, the flexible CNTs@mTiO₂ hybrid mesoporous nanocable with ~ 20 nm shell thickness show an ultra-high surface area (~ 137 m²/g), large internal pore volume (~ 0.26 cm³/g), uniform accessible mesopores (~ 6.2 nm) and highly crystalline mesoporous anatase shells frameworks. Owing to their above unique features as well as synergistic coupling effect, the CNTs@mTiO₂ shows ultrahigh-rate capacity (~ 210 mAh g⁻¹ at 20 C), perfect coulombic efficiency (nearly 100 %) and superior cycling stability (keeping high capacity of ~ 210 mAh g⁻¹ after 1,000 cycles at 20 C). This surfactant templating assembly coating approach can be

easily extended to deposit an ultrathin mesoporous TiO₂ layer on flat graphene, which opens up a new design for depositing thin mesoporous transition-metal oxides on graphitized carbon supports for advanced applications in energy conversion and storage, photocatalysis, sensors and drug delivery, etc.

Acknowledgements

Y. L., A. A. E., W. L., P. F. Z., and K. L. contributed equally to this work. This work is supported by the State Key Research Program of China (2013CB934104 and 2012CB224805), the National Science Foundation (21210004), Science & Technology Commission of Shanghai Municipality (14JC1400700), China Postdoctoral Science Foundation (2015M580295), Shanghai Leading Academic Discipline Project (B108) and King Abdulaziz City for Science and Technology (project no. 29-280)

References

- [1] Y. Tang, Y. Zhang, J. Deng, J. Wei, H. L. Tam, B. K. Chandran, Z. Dong, Z. Chen, X. Chen, *Adv. Mater.* 26 (2014), 6111-6118.
- [2] C. K. Chan, H. Peng, G. Liu, K. McIlwrath, X. F. Zhang, R. A. Huggins, Y. Cui, *Nat. Nanotechnol.* 3 (2008), 31-35.
- [3] J. Jiang, Y. Li, J. Liu, X. Huang, C. Yuan, X. W. D. Lou, *Adv. Mater.* 24 (2012), 5166-5180.
- [4] B. Kang, G. Ceder, *Nature* 458 (2009), 190-193.
- [5] D. Dubal, O. Ayyad, V. Ruiz, P. Gómez-Romero, *Chem. Soc. Rev.* 44 (2015), 1777-1790.
- [6] N. Li, Z. Chen, W. Ren, F. Li, H.-M. Cheng, *Proc. Natl. Acad. Sci.* 109 (2012), 17360-17365.
- [7] P. Simon, Y. Gogotsi, *Nat. Mater.* 7 (2008), 845-854.
- [8] J. W. Long, M. B. Sassin, A. E. Fischer, D. R. Rolison, A. N. Mansour, V. S. Johnson, P. E. Stallworth, S. G. Greenbaum, *J. Phys. Chem. C.* 113 (2009), 17595-17598.

- [9] Z. S. Wu, W. Ren, D. W. Wang, F. Li, B. Liu, H. M. Cheng, *ACS nano* 4 (2010), 5835-5842.
- [10] C. X. Guo, M. Wang, T. Chen, X. W. Lou, C. M. Li, *Adv. Ener. Mater.* 1 (2011), 736-741.
- [11] J. S. Chen, Y. L. Cheah, Y. T. Chen, N. Jayaprakash, S. Madhavi, Y. H. Yang, X. W. Lou, J. *Phys. Chem. C.* 113 (2009), 20504-20508.
- [12] H. Liu, D. Su, G. Wang, S. Z. Qiao, *J. Mater. Chem.* 22 (2012), 17437-17440.
- [13] H. Liu, S. Chen, G. Wang, S. Z. Qiao, *Chem. Eur. J.* 19 (2013), 16897-16901.
- [14] L. Xia, S. Wang, G. Liu, L. Ding, D. Li, H. Wang, S. Qiao, *Small*, 12 (2016). 853-859
- [15] S. Chen, G. Liu, H. Yadegari, H. Wang, S.Z. Qiao, *J. Mater. Chem. A*, 3 (2015). 2559-2563.
- [16] H. Liu, D. Su, R. Zhou, B. Sun, G. Wang, S.Z. Qiao, *Adv. Energy Mater*, 2 (2012). 970-975.
- [17] Y. Tang, Y. Zhang, W. Li, B. Ma, X. Chen, *Chem. Soc. Rev.* 44 (2015), 5926-5940.
- [18] Q. Zhang, E. Uchaker, S. L. Candelaria, G. Cao, *Chem. Soc. Rev.* 42 (2013), 3127-3171.
- [19] Van der Ven, J. Bhattacharya, A. A. Belak, *Accounts. Chem. Res.* 46 (2012), 1216-1225.
- [20] H. Zhang, X. Yu, P. V. Braun, *Nat. Nanotechnol.* 6 (2011), 277-281.
- [21] L. Zhou, D. Zhao, X. W. Lou, *Adv. Mater.* 24 (2012), 745-748.
- [22] D. Wang, D. Choi, J. Li, Z. Yang, Z. Nie, R. Kou, D. Hu, C. Wang, L. V. Saraf, J. Zhang, *ACS Nano*. 3 (2009), 907-914.
- [23] J. S. Chen, H. Liu, S. Z. Qiao, X. W. D. Lou, *J. Mater. Chem.* 21 (2011), 5687-5692.
- [24] J. Zhu, T. Zhu, X. Zhou, Y. Zhang, X. W. Lou, X. Chen, H. Zhang, H. H. Hng, Q. Yan, *Nanoscale* 3 (2011), 1084-1089.
- [25] J. S. Chen, Y. Zhang, X. W. Lou, *ACS Appl. Mater. Interfaces* 3 (2011), 3276-3279.
- [26] S. Ding, J. S. Chen, *Adv. Funct. Mater.* 21 (2011), 4120-4125.
- [27] H. Liu, W. Li, D. Shen, D. Zhao, G. Wang, *J. Am. Chem. Soc.* 137 (2015), 13161-13166.
- [28] B. Wang, H. Xin, X. Li, J. Cheng, G. Yang, F. Nie, *Sci. Rep.* 4 (2014), 3729;
- [29] L. He, C. Wang, X. Yao, R. Ma, H. Wang, P. Chen, K. Zhang, *Carbon* 75 (2014), 345-352.
- [30] J. Wang, R. Ran, M. O. Tade, Z. Shao, *J. Power Sources* 254 (2014), 18-28.

- [31] F. F. Cao, Y. G. Guo, S. F. Zheng, X.L. Wu, L. Y. Jiang, R. R. Bi, L. J. Wan, J. Maier, *Chem. Mater.* 22 (2010), 1908-1914.
- [32] J. Wang, R. Ran, M.O. Tade, Z. Shao, *J. Power. Sources.* 254 (2014), 18-28.
- [33] S. Ding, J. S. Chen, X. W. Lou, *Adv. Funct. Mater.* 21 (2011), 4120-4125.
- [34] W. Li, F. Wang, S. Feng, J. Wang, Z. Sun, B. Li, Y. Li, J. Yang, A. A. Elzatahry, Y. Xia, D. Y. Zhao, *J. Am. Chem. Soc.* 135 (2013), 18300-18303.
- [35] W. Li, F. Wang, Y. Liu, J. Wang, J. Yang, L. Zhang, A. A. Elzatahry, D. Al -Dahyan, Y. Xia, D. Y. Zhao, *Nano Lett.* 15 (2015), 2186-2193.
- [36] X. Huang, X. Qi, F. Boey, H. Zhang, *Graphene-based composites. Chem. Soc. Rev.* 41 (2012), 666-686.
- [37] Q. Xiang, J. Yu, M. Jaroniec, *Chem. Soc. Rev.* 41 (2012), 782-796.
- [38] X. Li, W. Qi, D. Mei, M. L. Sushko, I. Aksay, J. Liu, *Adv. Mater.* 24 (2012), 5136-5141.
- [39] D. Wang, R. Kou, D. Choi, Z. Yang, Z. Nie, J. Li, L. V. Saraf, D. Hu, J. Zhang, G. L. Graff, *ACS Nano* 4 (2010), 1587-1595.
- [40] Y. Liu, R. Che, G. Chen, J. Fan, Z. Sun, Z. Wu, M. Wang, B. Li, J. Wei, Y. Wei, G. Wang, G. Z. Guan, A. A. Elzatahry, A. A. Bagabas, A. M. Al-Enizi, Y. H. Deng, H. S. Peng, D. Y. Zhao, *Sci. Adv.* 1 (2015), e1500166.
- [41] Y. Liu, Y. Luo, A. A. Elzatahry, W. Luo, R. Che, J. Fan, K. Lan, A. M. Al-Enizi, Z. Sun, B. Li, Z. W. Liu, D. K. Shen, Y. Ling, C. Wang, J. X. Wang, W. J. Gao, C. Yao, K. P. Yuan, H. S. Peng, Y. Tang, Y. H. Deng, G. F. Zheng, G. Zhou, D. Y. Zhao, *ACS Cent. Sci.* 1 (2015), 400-408.
- [42] Y. Liu, K. Lan, A. A. Bagabas, P. Zhang, W. Gao, J. Wang, Z. Sun, J. Fan, A. A. Elzatahry, D. Zhao, *Small.* 12 (2016), 860-867.
- [43] J. S. Chen, Y. L. Tan, C. M. Li, Y. L. Cheah, D. Luan, S. Madhavi, F. Y. C. Boey, L. A. Archer, X. W. Lou, *J. Am. Chem. Soc.* 132 (2010), 6124-6130.

- [44] E. J. Crossland, N. Noel, V. Sivaram, T. Leijtens, J. A. Alexander-Webber, H. J. Snath, *Nature* 495 (2013), 215-219.
- [45] H. G. Yang, C. H. Sun, S. Z. Qiao, J. Zou, G. Liu, S. C. Smith, H. M. Cheng, G. Q. Lu, *Nature* 453 (2008), 638-641.
- [46] H. G. Yang, G. Liu, S. Z. Qiao, C. H. Sun, Y. G. Jin, S. C. Smith, J. Zou, H. M. Cheng, G. Q. Lu, *J. Am. Chem. Soc.* 131 (2009), 4078-4083.
- [47] Y. Liu, L. Chen, J. Hu, J. Li, R. Richards, *J. Phys. Chem. C* 114 (2010), 1641-1645.
- [48] B. Liu, H. C. Zeng, *Chem. Mater.* 20 (2008), 2711-2718.
- [49] Y. Cong, X. Li, Y. Qin, Z. Dong, G. Yuan, Z. Cui, X. Lai, *Appl. Catal. B-Environ* 107 (2011), 128-134.
- [50] J. Li, S. Tang, L. Lu, H. C. Zeng, *J. Am. Chem. Soc.* 129 (2007), 9401-9409.
- [51] L.-C. Chen, Y.-C. Ho, W.-S. Guo, C.-M. Huang, T.-C. Pan, *Electrochim. Acta* 54 (2009), 3884-3891.
- [52] D Y. Deng, Y. Cai, Z. Sun, J. Liu, C. Liu, J. Wei, W. Li, C. Liu, Y. Wang, D. Y. Zhao, *J. Am. Chem. Soc.* 132, 8466-8473 (2010).
- [53] Y. Deng, D. Qi, C. Deng, X. Zhang, D. Zhao, *J. Am. Chem. Soc.* 130 (2008), 28-29.
- [54] M. Wang, X. Wang, Q. Yue, Y. Zhang, C. Wang, J. Chen, H. Cai, H. Lu, A. A. Elzatahry, D. Zhao, *Chem. Mater.* 26 (2014), 3316-3321.
- [55] M. Wang, Z. Sun, Q. Yue, J. Yang, X. Wang, Y. Deng, C. Yu, D. Zhao, *J. Am. Chem. Soc.* 136 (2014), 1884-189
- [56] L. He, C. Wang, X. Yao, R. Ma, H. Wang, P. Chen, K. Zhang, *Carbon*, 75 (2014), 345-352.
- [57] Z. Chen, D. Zhang, X. Wang, X. Jia, F. Wei, H. Li, Y. Lu, *Adv. Mater.*, 24 (2012), 2030-2036.

Figure 1. Schematic representation of the surfactant-templating assembly coating approach for the preparation of the flexible CNTs@mTiO₂ hybrid mesoporous nanocables with a thin mesoporous anatase shell.

Figure 2. (a, b) SEM image of the flexible CNTs@mTiO₂ hybrid mesoporous nanocables. Inset of (a) is the mesoscopic structure model of the surface of a single CNTs@mTiO₂ hybrid mesoporous nanocable. (c), TEM image of flexible CNTs@mTiO₂ hybrid mesoporous nanocables. Inset of (c) is the pore arrangement model. (d, e, f), HRTEM images recorded on a single flexible CNTs@mTiO₂ hybrid mesoporous nanocable. Insets of (d) and (f) are the mesoscopic structure models. The dotted red circles in (f) represent open pores exposed on the surface of CNTs@mTiO₂ hybrid nanocable. (g), SAED pattern recorded on a single flexible CNTs@mTiO₂ hybrid mesoporous nanocable. (h) SAXS patterns of the as-made CNT@amorphous F127/TiO₂ hybrid nanocables before calcination and the flexible CNTs@mTiO₂ hybrid mesoporous nanocables after calcination at 400 °C in Ar for 2 h. (i), Nitrogen adsorption-desorption isotherms and pore size distributions (inset) of the flexible CNTs@mTiO₂ hybrid mesoporous nanocables.

Figure 3. (a), WXRd patterns of the multi-wall CNTs, the as-made CNT@amorphous F127/TiO₂ hybrid nanocables before calcination and the flexible CNTs@mTiO₂ hybrid mesoporous nanocables prepared after calcination at 400 °C in Ar for 2 h. (b), C1s, (c), O1s and (d) Ti_{2p} XPS core-level spectra for the flexible CNTs@mTiO₂ hybrid mesoporous nanocables (e), STEM image of a single flexible CNTs@mTiO₂ hybrid mesoporous nanocable. (f-h), EDX elemental mapping images of a single flexible CNTs@mTiO₂ hybrid mesoporous nanocable. White, green, and orange indicate oxygen, titanium and carbon atoms, respectively.

Figure 4. (a) Schematic representation of the surfactant-templating coating approach for the preparation of the sandwich-like mesoporous GR@mTiO₂ hybrid nanoflakes. (b, c) SEM images of GR@mTiO₂ hybrid nanoflakes. Inset of (b) is the mesoscopic structure model of the surface of a single GR@mTiO₂ hybrid nanoflakes. (d), HRTEM images recorded on the surface of a single GR@mTiO₂ hybrid nanoflakes. Inset of (d) is the corresponding SAED pattern. (e), Raman spectra of the graphene oxide (GO), reduced graphene (GR) and GR@mTiO₂ hybrid nanoflakes. (f), AFM topography images of the GR@mTiO₂ nanoflakes on a mica substrate and (g) the corresponding height-profile analysis along the line in (f).

Figure 5. Electrochemical performance characterization of the flexible CNTs@mTiO₂ hybrid mesoporous nanocables. (a), Charge-discharge voltage profiles at a current rate of 20 C. **(b),** Rate capacity at different current rates from 0.2 C to 60 C. **(c),** Cyclic voltammogram curves of the CNTs@mTiO₂ hybrid mesoporous electrode at a scan rate of 0.2 mV/s. Inset is the plot of peak reduction current with respect to scan rates from 0.1 ~ 1.0 mV/s. **(d),** Nyquist plots of the flexible CNTs@mTiO₂ hybrid mesoporous nanocables and CNTs-free-mTiO₂ nanotubes at room temperature. **(e),** cycle performance at a constant current rate of 20 C. **(f),** Schematic representation of the lithiation and delithiation processes of the flexible CNTs@mTiO₂ hybrid mesoporous nanocables.

Vitae

Dr. Yong Liu received his Ph.D. degree from Fudan University in 2015. Now, he is a postdoctoral fellow with Prof. Dongyuan Zhao in Laboratory of Advanced Materials, Fudan University. His research interests focus on the synthesis of oriented mesoporous semiconductors for energy storage and conversion.

Mr. Kun Lan received his Master degree from Lanzhou University in 2013. Now, he is a Ph.D. candidate in Laboratory of Advanced Materials, Fudan University. His research interests include synthesis of mesoporous semiconductors for energy storage and conversion.

Dr. Ahmed A. Elzatahry now is an associate professor in materials science and technology program, college of arts and sciences, Qatar University. He received the award for The State Prize of Egypt in Advanced science and technology (Chemistry) in 2010. In 2006, he moved to

the United States-Virginia Commonwealth University (VCU) as a research scholar to take advantage of work in nanotechnology and its application in catalysis field. In 2007, He received his Ph.D. from al-Azhar University, Egypt. In 2008 and 2009 he undertook postdoctoral work in porous and mesoporous materials at VCU, USA.

Dr. Jianwei Fan is an associate professor in College of Environmental Science and Engineering at Tongji University. He completed his Post-doctoral research in Laboratory of Advanced Materials in 2014, Fudan University. His current research interests focus on the novel materials for energy and environmental science.

Dr. Wei Luo received his Ph.D. degree from Fudan University in 2013. He works as a lecturer in College of Materials Science and Engineering, Donghua University. His research interests mainly focus on the synthesis and application for ordered mesoporous materials.

Mr. Wei Yong received his Master degree from Fudan University in 2010. Now, he is a Ph.D. candidate in Laboratory of Advanced Materials, Fudan University. His research interests mainly focus on the synthesis and application for ordered mesoporous materials.

Mr. Pengfei Zhang received his Master degree from Wuhan University of Technology in 2015. Now, he is a Ph.D. candidate in Laboratory of Advanced Materials, Fudan University. His research interests focus on the synthesis of mesoporous semiconductors for energy storage.

Mr. Chun Wang received his Master degree from Fudan University in 2013. Now, he is a Ph.D. candidate in Department of Chemistry, Fudan University. His research interests mainly focus on the synthesis and application for ordered mesoporous materials.

Prof. Yonghui Deng received his BS in chemistry from Nanchang University (2000) and PhD in polymer chemistry & physics from Fudan University (2005). He worked as a postdoctoral researcher with Prof. Dongyuan Zhao (2005–

2007), and was promoted as associate (2007) and full professor (2011) in Fudan University. He has coauthored over 60 scientific papers and filed 12 patents. His research interests include core-shell nanomaterials, functional porous materials, and their applications in catalysis, and separation, etc.

Prof. Gengfeng Zheng obtained his BS degree (2000) at Fudan University in China, and Master (2004) and PhD (2007) degrees in Chemistry at Harvard University in USA, under the guidance of Prof. Charles Lieber. He was a postdoctoral fellow working with Prof. Chad Mirkin at Northwestern University in

USA (2007–2009). He became a full professor at the Department of Chemistry and Laboratory of Advanced Materials at Fudan University in 2010. He is also a Co-Editor of the Journal of Colloid and Interface Science, and an Advisory Board member of the Journal of Materials Chemistry A. His research interests include low-dimensional semiconducting nanomaterial-based synthesis and surface chemistry, biosensing, interfacing with cells, photoelectrochemical conversion, photocatalysis and energy storage.

Prof. Fan Zhang received his PhD in 2008 from Fudan University followed by more than 2 years postdoctoral experience in University of California at Santa Barbara before joining as an associate professor in the Chemistry Department of Fudan University in 2010. He became a full professor in Fudan University in 2013. His current

research interests include the development of multifunctional nanostructured materials and nanotechnology for applications in biomedical analysis, drug delivery and cancer therapy.

Dr. Yun Tang received his PhD degree in 2009 in chemical physics, University of Maryland, college park, USA. He became a research fellowship in Fudan University in 2014. His current research interests include the development of tailed zero-dimensional nanostructures for biological applications.

Prof. Liqiang Mai is Chair Professor of Materials Science and Engineering at Wuhan University of Technology and Executive Director of WUT-Harvard Joint Nano Key Laboratory. He received his Ph.D. from Wuhan University of Technology in 2004. He carried out his postdoctoral research in the laboratory of

Prof. Zhonglin Wang at Georgia Institute of Technology in 2006-2007 and worked as advanced research scholar in the laboratory of Prof. Charles M. Lieber at Harvard University in 2008-2011. His current research interests focus on nanowire materials and devices for energy storage.

Prof. Dongyuan Zhao is a Chair Professor of Materials and Chemistry (Cheung Kong and Hao Qing Professorship), and a Director of the Laboratory of Advanced Materials at Fudan University (China). He is also the Co-Director of the 2011 Collaborative Innovation Center of Chemistry for Energy

Materials (iChEM). He received his BS (1984) and PhD (1990) from Jilin University. He carried out postdoctoral research at the Weizmann Institute of Science (1993–1994), University of Houston (1995–1996), and University of California at Santa Barbara (1996–1998). He was elected as an academican of the Chinese Academy of Science in 2007, and a member of The World Academy of Science (TWAS) in 2010. His research interests are focused on the interfacial assembly and macroscopic control of ordered mesoporous materials for applications in catalysis, energy, water purification and biomedicine.