Supplementary Information

Facile synthesis of Uniform N-doped Carbon-Coated TiO$_2$ Hollow Spheres with Enhanced Lithium Storage Performances

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1. Experimental

1.1. Method

Synthesis of TiO$_2$ hollow spheres: TiO$_2$ hollow spheres are synthesized through the ‘wet conversion’ method. In our experiment, 1 ml industrial titanyl sulfate solution ($c$(TiOSO$_4$) = 480 g L$^{-1}$, $c$(Fe$^{2+}$) = 48 g L$^{-1}$, $c$(Mn$^{2+}$) = 0.77 g L$^{-1}$) used in our previous work$^1$, and 18 g H$_2$SO$_4$ ($c$(H$^+$) = 1 mol L$^{-1}$) were added in 800 mL deionized water at 35 °C. Then, 0.1 g Al powder (50-200 nm in diameter, Hongwu New Material) was added and stirred for 3 hours until the solution turned from dark gray to light gray. After filtrating and drying, the sample was added to the 50 mL NaOH (0.2 mol L$^{-1}$) in 500 mL deionized water and stirred overnight. Finally, TiO$_2$ hollow sphere was obtained by filtration and drying process.

Synthesis of TiO$_2$@C materials: TiO$_2$ precursors were dispersed in Tris-buffer solution (0.1 M, 100 mL) by sonication, and then 0.1 g dopamine hydrochloride were added and stirred for 3 hours at room temperature. After centrifuging and washing with deionized water and ethanol for three times, respectively, the sample was collected and further dried at 60 °C overnight. Finally, the precursors were obtained by annealing at 400 °C for 3 h in an Ar/H$_2$ atmosphere.

1.2. Material characterization

The X-ray diffraction measurements were conducted on Rigaku D/max 2500 using
Cu Ka radiation and the 2θ range of tests was from the range of 10°-90°. Raman and XPS measurement were performed by Renishaw RM1000 micro spectroscopic system and Thermo K-Alpha XPS spectrometer respectively. Thermogravimetric analysis (TGA) was performed in the air with the temperature range from 30 °C to 800 °C. The materials morphologies were measured by FESEM (Hitachi S-4800) and TEM (JEM-2010 JEOL, 200 kV). Brunauer-Emmett-Teller (BET) specific surface areas were obtained using a JW-BK200C Surface Area and Pore size Analyzer (Beijing JWGB Sci. & Tech. Co., Ltd) at the liquid-nitrogen boiling point (77 K).

1.3. Electrochemical measurements

The lithium storage performances of all samples were characterized by fabricating CR2032 coin-type half-cells in an Ar glove box. The anode electrode was prepared by mixing the active material with super P and polyvinylidene fluoride (PVDF) according to a mass ratio of 6:2:2 in N-methyl-2-pyrrolidone. The obtained slurry was cast onto a copper (Cu) foil and then dried at 110 °C under vacuum for 12 h. Generally, the mass loading of the active material is about packing density of ∼0.5 mg cm⁻². A solution of 1 M LiPF₆ in EC: DMC: EMC=1:1:1 Vol% is selected as the electrolyte. CV measurements were carried out by a CHI660E electrochemical workstation. LAND-BT2013A measurement system is responded for testing cycling performance and rate capacity at 25 °C.
Fig. S1 XRD patterns of precursors at different stages (a) and TiO$_2$ (b) annealed at 700 °C.

Fig. S2 High resolution XPS spectra of Ti 2p (a), O 1s (b), C 1s (c), N 1s (d) in TiO$_2$@C, respectively.
Fig. S3 SEM images of (a) Al powers, (b) TiO(OH)\(_2\)@Al; (c)-(d) TEM images of pure TiO\(_2\); (e) elemental mapping images of Ti and O of TiO\(_2\) hollow spheres.

Fig. S4 (a) Cyclic voltammogram of pure TiO\(_2\) at a scanning rate of 0.2 mV s\(^{-1}\); (b) Charge/discharge curves of pure TiO\(_2\) at 0.1 A g\(^{-1}\); (c) the rate capability and the cycle performances of rutile TiO\(_2\); (d) the initial charge-discharge curve of TiO\(_2\)@C after chemical prelithiation.
**Fig. S5** (a) Nitrogen adsorption/desorption isotherms of TiO_2 and TiO_2@C; (b) Barrett-Joyner-Halenda (BJH) pore size distribution curves for TiO_2 and TiO_2@C.

**Fig. S6** (a) CV curves of TiO_2 at different scan rates; (b) Log (i) versus log (v) plots at different cathodic/anodic peaks for TiO_2; (c) Contribution of the surface-driven process at 0.6 mV s\(^{-1}\) in TiO_2; (d) Capacitance contribution of TiO_2 at different scan rates.
Fig. S7 (a) CV curves of TiO$_2$@C at different scan rates; (b) Log ($i$) versus log ($v$) plots at different cathodic/anodic peaks for TiO$_2$@C; (c) Contribution of the surface-driven process at 0.6 mV s$^{-1}$ in TiO$_2$@C; (d) Capacitance contribution of TiO$_2$@C at different scan rates.

Fig. S8 EIS of pure TiO$_2$ and TiO$_2$@C after 3 cycles at 0.1 A g$^{-1}$.

Fig. S9 SEM image of TiO$_2$@C composites after 2000 cycles.

Reference