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_2SO_4 ($c(H^+)$ =1 mol L^{-1}) were added in 800 mL deionized water at 35 ℃. 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 ℃ overnight. Finally, the precursors were obtained by annealing at 400 ℃ 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 $LiPF_6$ 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 ℃.

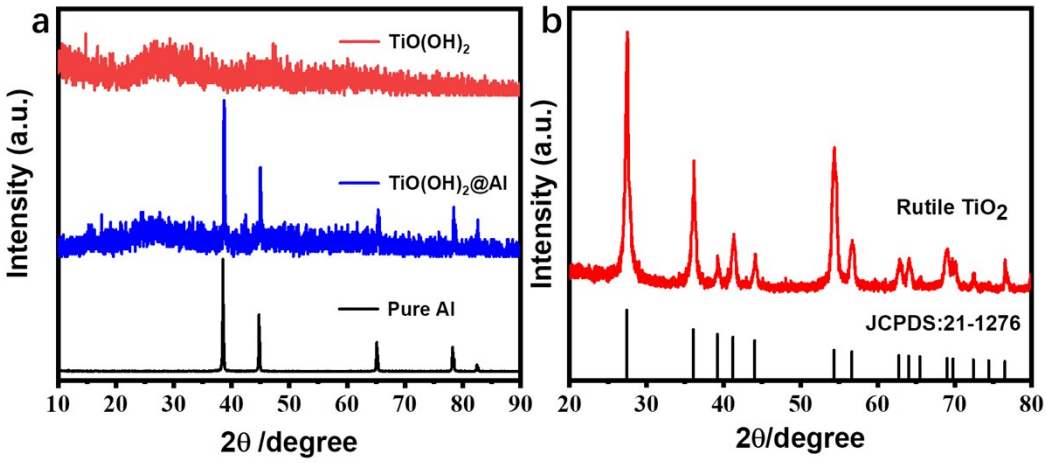

Fig. S1 XRD patterns of precursors at different stages (a) and TiO_2 (b) annealed at 700 °C.

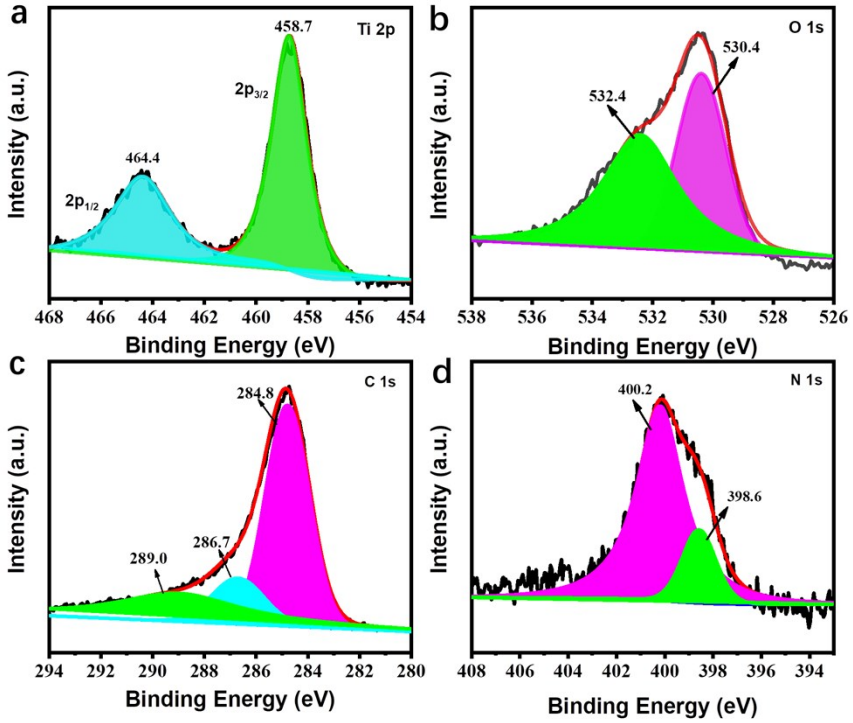

Fig. S2 High resolution XPS spectra of Ti 2p (a), O 1s (b), C 1s (c), N 1s (d) in TiO_2@C, respectively.

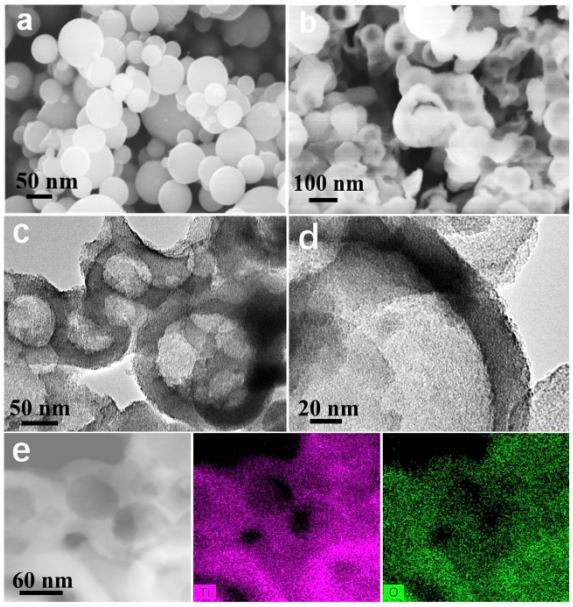

Fig. S3 SEM images of (a) Al powers, (b)$TiO(OH)_2$@Al; (c)-(d) TEM images of pure TiO_2; (e) elemental mapping images of Ti and O of TiO_2 hollow spheres.

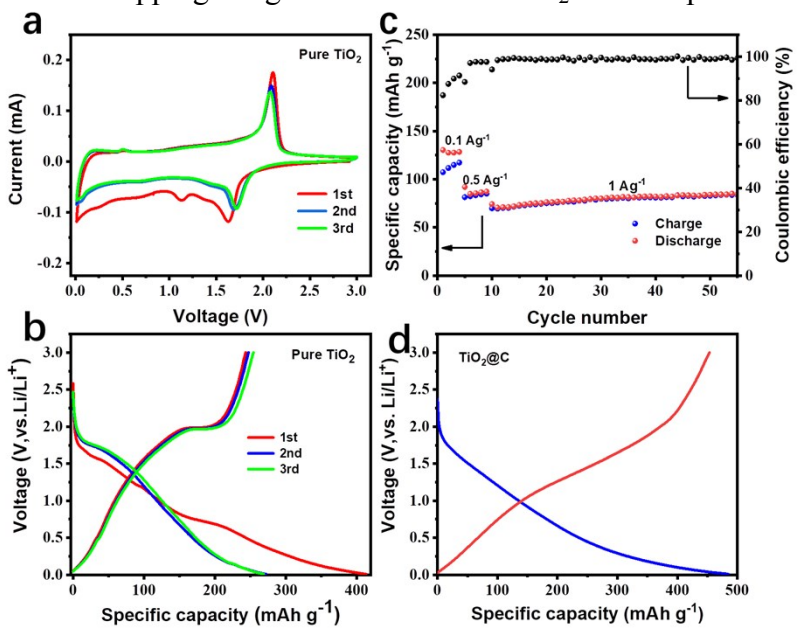

Fig. S4 (a) Cyclic voltammogram of pure TiO_2 at a scanning rate of 0.2 mV s^{-1}; (b) Charge/discharge curves of pure TiO_2 at 0.1 A g^{-1}; (c) the rate capability and the cycle performances of rutile TiO_2; (d) the initial charge-discharge curve of TiO_2@C after chemical prelithiation.

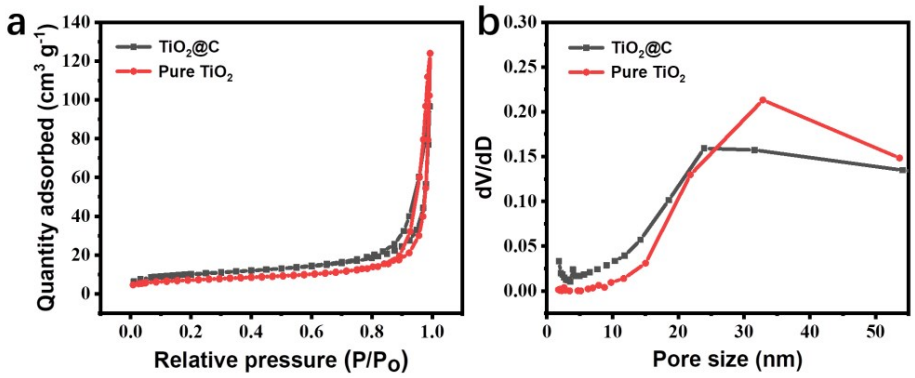

Fig. S5 (a) Nitrogen adsorption/desorption isotherms of TiO_2 and TiO_2@C; (b) Barrett-Joyner-Halenda (BJH) pore size distribution curves for TiO_2 and TiO_2@C.

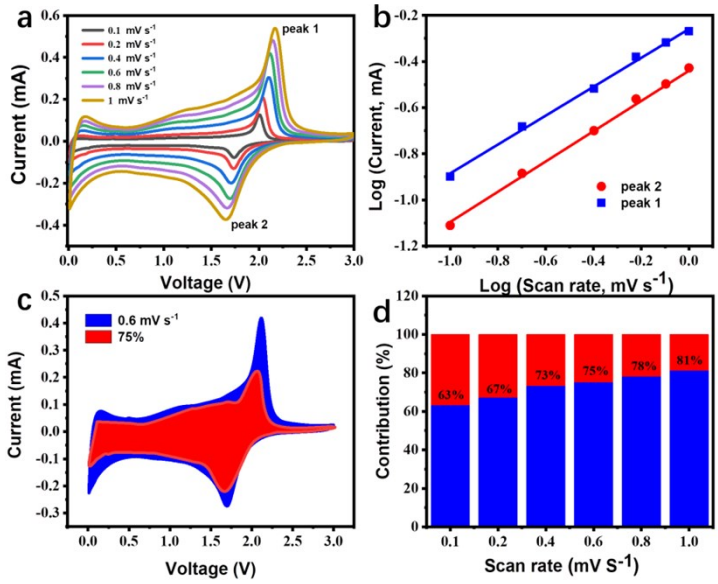

Fig. S6 (a) CV curves of TiO_2 at different scan rates; (b) Log (*i*) versus log (*v*) plots at different cathodic/anodic peaks for TiO_2; (c) Contribution of the surface-driven process at 0.6 mV s^{-1} in TiO_2; (d) Capacitance contribution of TiO_2 at different scan rates.

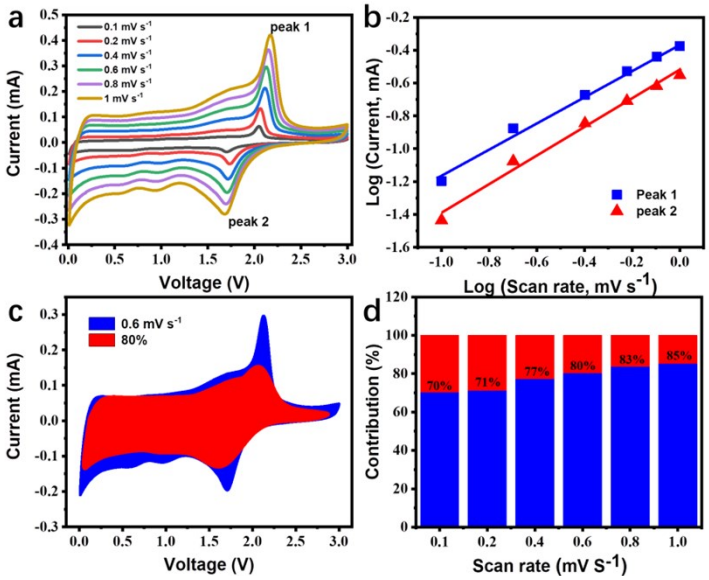

Fig. S7 (a) CV curves of TiO_2@C at different scan rates; (b) Log (*i*) versus log (*v*) plots at different cathodic/anodic peaks for TiO_2@C; (c) Contribution of the surface-driven process at 0.6 mV s^{-1} in TiO_2@C; (d) Capacitance contribution of TiO_2@C at different scan rates.

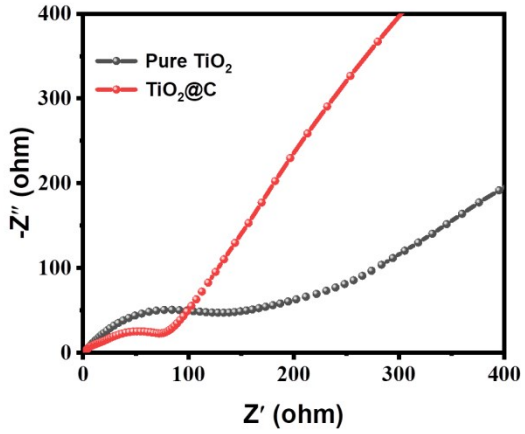

Fig. S8 EIS of pure TiO_2 and TiO_2@C after 3 cycles at 0.1 A g^{-1}.

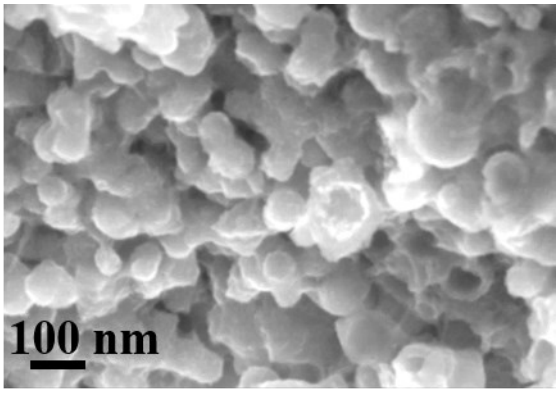

Fig. S9 SEM image of TiO_2@C composites after 2000 cycles.

Reference

1 F. Wu, Z. Wang, X. Li, L. Wu, X. Wang, X. Zhang, Z. Wang, X. Xiong, H. Guo, *J. Alloys Compd.,* 2011, **509**, 596-601.