

Supporting Information for

Urchin-like TiO₂@C core-shell microspheres: coupled synthesis and application in lithium-ion batteries

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Experimental Section

Titanium tetrachloride was bought from Beijing Jingxiang Chemical Reagent Company, and the others were purchased from Beijing Chemical Reagent Company. All chemicals were of analytical grade and used without further purification.

Synthesis of TiO₂@C microspheres

In a typical procedure, 1.0 g glucose was added to a solution consisted of 10.0 mL of alcohol and 20.0 mL of acetic acid in a 40.0 mL Teflon flask. 2.0 mL of titanium tetrachloride was added to the solution. The Teflon flask was sealed in a stainless steel autoclave and then heated at 140 °C for 10 h. After reaction, the reactor was cooled down to room temperature naturally. The products was centrifuged, washed by water and ethanol for three times and dried at 80 °C overnight. The materials were calcined at 700 °C for 2 h under Ar protection before electrode fabrication.

Characterization

Scanning Electron Microscopy (SEM, Zeiss SUPRA 55) was operated at an acceleration voltage of 5 kV. Transmission Electron Microscopy (TEM) was performed on Hitachi 800 running at an accelerating voltage of 200 kV. X-ray diffraction (XRD) patterns were obtained on a Shimadzu XRD-6000 diffractometer, using Cu K_α radiation ($\lambda=1.5418 \text{ \AA}$) at 40 kV, 30 mA. Raman spectra were recorded on a LabRAM HR Raman microprobe (HORIBA Jobin Yvon). The carbon contents of the materials were determined by thermogravimetry analysis (TGA) and

differential thermoanalysis (DTA) on a HCT-2 differential thermal analyzer (Beijing Scientific Instrument Factory) from 50 °C to 600 °C at a heating rate of 10 °C min⁻¹ under air flow. Chemical compositions were determined by elemental analysis (vario EL cube V2.0.1) and X-ray photoelectron spectroscopy (PHI Quantera).

Electrode fabrication and electrochemical tests

Coin-type half cells were assembled to evaluate the anodic performances of the TiO₂@C microspheres. The assembly was carried out in an Ar-filled glove box with less than 0.1 ppm each of oxygen and water vapor. The active material is mixed with acetylene black and PTFE, using ethanol as dispersant. The weight ratio of TiO₂@C or TiO₂-air, acetylene black and PTFE in the final dry cathode is 80:10:10. The mixture is rolled into a film with thickness of ca. 60 μm, cut into disks with diameter of 11 mm and pressed onto nickel foam current collectors. Li metal foil was used as the counter and reference electrode, and 1 M LiPF₆ dissolved in a 1 : 1 (by volume) mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) was employed as the electrolyte. Charge–discharge tests were performed in the range of 1 to 3 V (vs. Li⁺/Li).

Supplementary Figure and Table

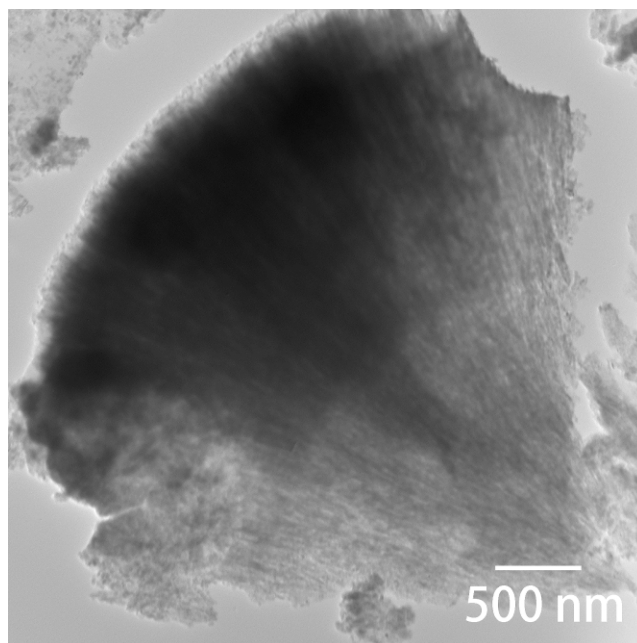


Fig. S1 Low magnification TEM image of TiO₂@C microspheres prepared with 1 g glucose at 140 °C before annealing.

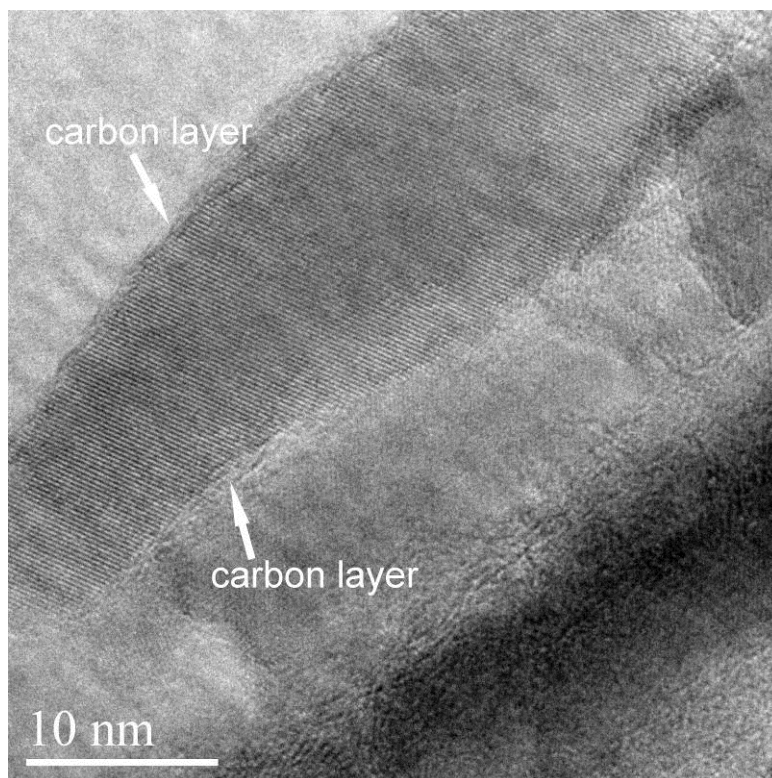


Fig. S2 HRTEM image of TiO₂@C microsphere prepared with 1 g glucose at 140 °C before annealing.

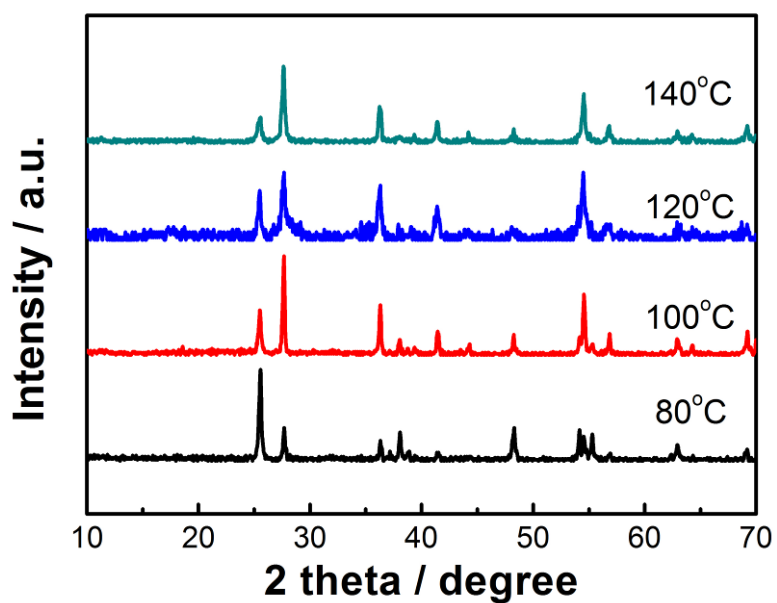


Fig. S3 XRD patterns of TiO₂@C microspheres prepared with 1 g glucose at various temperatures before annealing.

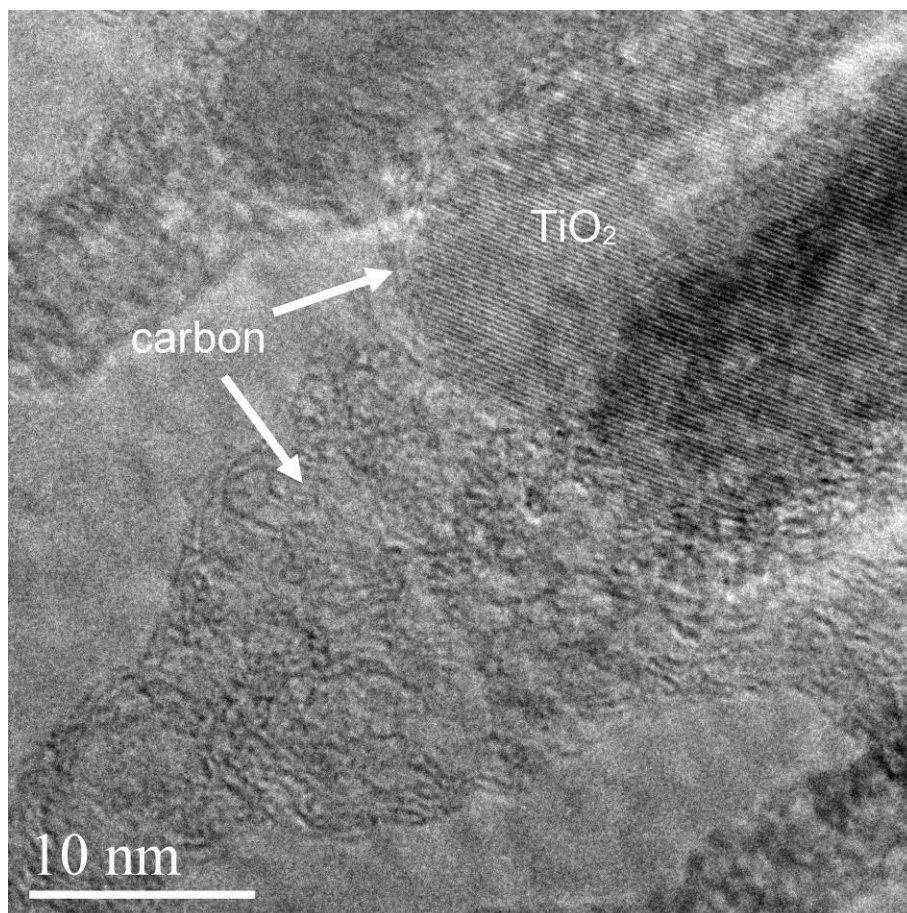


Fig. S4 HRTEM image of TiO₂@C-700.

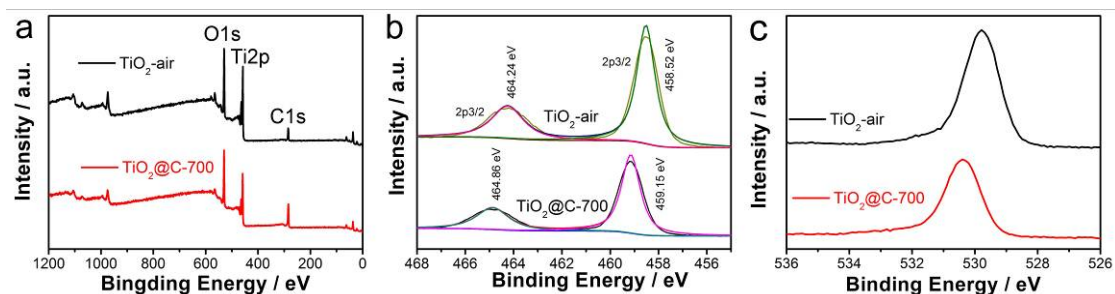


Fig. S5 XPS spectra of TiO₂-air and TiO₂@C-700: (a) survey, (b) Ti2p and (c) O1s

The Ti2p spectra (Fig. S5b) for the TiO₂@C-700 comprises two symmetrical peaks with binding energies (BEs) of 459.15 eV and 464.86 eV, which are attributable to Ti2p_{3/2} and Ti2p_{1/2}, respectively, and are slightly larger than those of the TiO₂-air. These binding energies (and their corresponding spin-orbital splitting) are highly comparable to those reported in the literature for TiO₂.¹⁻³

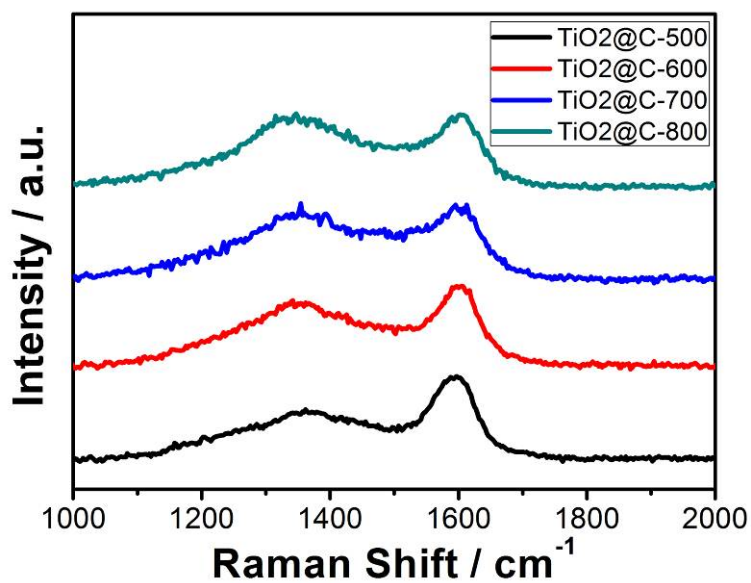


Fig. S6 Raman spectra of TiO₂@C microspheres annealed at different temperatures.

Tab. S1 Yield, carbon content and TiO₂ yield prepared with different amounts of glucose.

Glucose /g	Yield /g	carbon content /wt%	TiO ₂ yield /%
0.25	0.90±0.23	~1.7	60.7
0.50	1.04±0.20	~5	67.8
0.75	1.30±0.25	~8	82.1
1.00	1.52±0.24	~9	94.9

Tab. S2 Carbon content of TiO₂@C microspheres treated at different temperatures measured by organic element analysis

Sample	Carbon content / wt%
TiO ₂ @C-500	6.76
TiO ₂ @C-600	6.46
TiO ₂ @C-700	6.78
TiO ₂ @C-800	6.61

Tab. S3 D/G peak area ratio of TiO₂@C microspheres treated at different temperatures

Sample	I _D /I _G
TiO ₂ @C-500	1.194779
TiO ₂ @C-600	1.036763
TiO ₂ @C-700	1.022253
TiO ₂ @C-800	1.014979

References:

1. J. Yu, G. Dai, Q. Xiang and M. Jaroniec, *J. Mater. Chem.*, 2011, **21**, 1049-1057.
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3. Z. Yang, G. Du, Z. Guo, X. Yu, Z. Chen, T. Guo and H. Liu, *J. Mater. Chem.*, 2011, **21**, 8591-8596.