Supporting Information

Hydrogenated Dual-Shell Sodium Titanate Cubes for Sodium-Ion Batteries with Optimized Ion Transportation

Fangxi Xie,^a Lei Zhang,^a Yan Jiao,^a Anthony Vasileff,^a Dongliang Chao*^a and Shi-Zhang Qiao*^a

^aSchool of Chemical Engineering, The University of Adelaide, Adelaide, SA 5005, Australia.

* E-mail: dongliang.chao@adelaide.edu.au (D. Chao); s.qiao@adelaide.edu.au (S.Z. Qiao)

Preparation of Materials

*The preparation of Fe*₂*O*₃ *cubes*: The Fe₂O₃ sub-microcubes were first synthesized by a previously reported method (Colloids Surf., A 1998, 134, 265; Angew. Chem. Int. Ed., 2015, 54: 4001). Typically, 50 mL of 5.4 M NaOH solution was added to the same volume of 2 M FeCl₃ solution in 5 min under continuous stirring at 75 °C. The resulting Fe(OH)₃ gels were continuously stirred at the same temperature for 5 min, and afterward aged at 100 °C in a preheated oven for 96 hours. After the reaction, the red products were collected by filtration and washed three times with deionized water and ethanol before drying in a vacuum oven overnight.

The preparation of hollow silica boxes: 1.5 g of iron oxide cubes were dispersed in a mixed solution of 130 ml ethanol and 13 ml water using ultrasonication (10 min). Subsequently, 12 ml of ammonium hydroxide solution was added in the as-prepared solution. After that, a mixed solution of 9.7 ml ethanol and 0.3 ml TEOS was added dropwise at 1.0 ml per minute under continuous stirring. After 6 hours reaction time, the sediment was collected by centrifugation. The precipitate was re-dispersed in 500 ml of 0.5 M oxalic acid to react for 18 hours at 90°C. In this time, the color of the solution turns a chartreuse yellow. All the sediments were collected by centrifugation.

The preparation of titanate coated hollow silica boxes: 30 mg of silica boxes was dispersed in a mixed solution of 120 ml of ethanol and 1.2 ml of distilled water using ultrasonication (10 min). 0.3g of hydroxypropyl cellulose (average $M_w = ~80,000$, Sigma-Aldrich) was added to the solution. After stirring for 30 minutes, a mixed solution of 2.0 ml of titanium butoxide and 10.0 ml of ethanol were added to the mixed solution at a rate of 1.5 ml min⁻¹. Next, the temperature of the oil bath was increased to 80 °C and maintained for 100 minutes. The as-prepared titanate coated hollow silica boxes were collected by centrifugation and washed with ethanol three times.

Preparation of sodium titanate dual-shell structured boxes: The as-prepared titanate coated hollow silica boxes were re-dispersed ultrasonically in 19 ml of distilled water. This as-prepared suspension was added to a 50 ml autoclave with an additional 1.0 ml of 5 M sodium hydroxide aqueous solution. After sealing, the autoclave was kept at 120 °C in a preheated oven for 6 hours. Finally, the as-prepared sample was collected by centrifugation and washed with ethanol three times.

Preparation of H-DSNTO and P-DSNTO: The as-prepared sodium titanate dual-shell boxes is calcined in a tube furnace with the gas of 5% hydrogen and 95% Argon at 500°C for 5 h with a ramping rate of 1 °C per minute, which will be denoted as H-DSNTO. As the comparison, the sample calcined in a muffle furnace with the same condiction will be denoted as P-DSNTO.

Characterization

X-Ray Powder Diffraction (XRD) spectra were collected on Rigaku MiniFlex 600 X-Ray Diffractometer. The field-emission scanning electron microscope (SEM) images were acquired on a FEI Quanta 450 FEG scanning electron microscope. The transmission electron microscope (TEM) images and the high-resolution transmission electron microscope (HRTEM) images were taken on JEOL JEM 2100F. X-ray photoelectron spectroscopy (XPS) measurements were conducted on an X-ray microprobe from Thermo (Escalab 250Xi) with monochromatic Al K α radiation. The synchrotron-based XANES measurements were carried out on the soft X-ray spectroscopy beamline at the Australian Synchrotron, which is equipped with a hemispherical electron analyzer and a microchannel plate detector that enables simultaneous recording of the total electron yield and partial electron yield.

Electrochemical Measurements

The electrochemical performance tests were carried out in 3025 type coin cells at room temperature. The working electrode consisted of active material (i.e., P-DSNTO, H-DSNTO), carbon black (Super P from VWR, supplied by Alfa Aesar) and binder (CMC, average M_w = ~700,000, Sigma-Aldrich) in a mass ratio of 60:30:10 and a mass loading of about 1.0 mg cm², while copper foil was employed as the current collector. The electrolyte was composed of 1.0 M NaClO₄ in a mixture of ethylene carbonate and diethyl carbonate (1:1 by volume) with 5% Fluoroethylene carbonate. Galvanostatic tests were performed on a Land CT2001A.

Computational Details

Density functional theory calculations were performed using the Vienna Ab Initio Simulation Package (VASP).^[1] The exchange-correlation interaction was described by generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional.^[2] The Monkhorst-Pack k-point mesh was set to $2 \times 3 \times 4$. The convergence criteria on the total energy for each ionic step was set to be 1.2×10^{-5} eV. Atoms were relaxed until the residual forces were less than 0.01

eV Å $^{-1}$ in each system. For the density of state calculations, the k-points was set to be $6 \times 9 \times 12$.

Supporting Figures



Fig. S1 SEM images of iron oxide cubes at different magnifications: a) low magnification; b) high magnification.



Fig. S2 a) SEM image, b) TEM image of hollow silica cubes with ultrathin shells.



Fig. S3 High resolution transmission electron microscope images of a) H-DSNTO; b) P-DSNTO.





Fig. S4 The STEM elemental mapping images of different elements (Na, Ti and O) of H-DSNTO.

Fig. S5 The STEM elemental mapping images of different elements (Na, Ti and O) of P-DSNTO.



Fig. S6 XPS survey spectrum of H-DSNTO.



Fig. S7 XPS survey spectrum of P-DSNTO.



Fig. S8. High-resolution Ti 2p XPS spectra of H-DSNTO and P-DSNTO



Fig. S9 Cyclic voltammetry profiles of H-DSNTO.



Fig. S10 Initial cycle curves of P-DSNTO.



Fig. S11 Discharging and charging curves of H-DSNTO under various current densities.



Fig. S12 Discharging and charging curves of P-DSNTO under various current densities.



Fig. S13 CV curves of P-DSNTO at various sweep rates.



Fig. S14 The corresponding Coulombic efficiency during the long cycling test of H-DSNTO.



Fig. S15 Diagram of capacitive contribution to the total capacity of P-DSNTO.



Fig. S16 Comparison of electrochemical impedance spectroscopy of H-DSNTO and P-DSNTO.

Supplementary References

- [1] G. Kresse, J. Furthmüller, *Phys. Rev. B* **1996**, 54, 11169-11186.
- [2] J. P. Perdew, *Phys. Rev. Lett.* **1996**, 77, 3865-3868.