Electronic Supplementary Information (ESI) for

Mesoporous hydrogenated TiO₂ microspheres for high rate capability lithium ion batteries

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Experimental section

Synthesis of mesoporous TiO₂ precursor

All reagents were used without further purification. The mesoporous TiO₂ precursor was prepared via a combined sol-gel and solvothermal process as previous report with a little modification. In a typical procedure, 4 g hexadecylamine and 1.6 g deionized water was dissolved in 400.0 mL anhydrous ethanol and stirred for ten minutes. Then 10 mL butyl titanate was added into the above solution. After aging for 20 hours, the white precipitates were separated by centrifugation and washed with ethanol for several times, and then dried at 80 °C for 24 h. 0.6 g obtained precipitates were dispersed into a 30 mL mixed solution in which the volume ratio of ethanol to water was 2. The white suspension was sealed within a Teflon-lined autoclave (40 mL) and kept at 160 °C for 16 h. After cooling down to room temperature, the mesoporous TiO₂ precursor was collected by centrifugation, washed with ethanol, and dried at 80 °C for 24 h.

Synthesis of A-TiO₂ microspheres

The mesoporous TiO₂ precursor was put into a 200 °C electric oven to remove the absorbed water and other evaporable impurities for 24 hours. After cooling down to room temperature, the preheated sample was put into an tubular furnace and calcined at 500 °C for 2 h in air with a heating rate of 5 °C min^{-1}. A-TiO₂ microspheres were successfully

synthesized after the furnace was cooled down to room temperature.

Synthesis of H-TiO$_2$ microspheres

The A-TiO$_2$ microspheres were put into a tubular furnace filled with static hydrogen atmosphere. The hydrogen thermal treatment was performed by calcining the A-TiO$_2$ microspheres under ambient pressure at 400 °C for 1 h with a heating rate of 5 °C min^{-1}. The H-TiO$_2$ microspheres were obtained after the furnace was completely cooled down to room temperature.

Characterization

The phase composition and crystallite size of the samples were determined by X-ray diffraction (XRD Rigaku D-max-γA XRD with Cu K$_\alpha$ radiation, λ = 1.54178 Å) from 10° to 80°. The XRD peak widening enabled estimation of the crystallite size via the Scherrer equation: d = (kλ)/(β × cosθ). In which β is the full-width at half-maximum for the peak at 2θ = 25.5; k is 0.89; λ is the X-ray wavelength (1.54178 Å for Cu K$_\alpha$); d is the average crystallite size; and θ is the angle of the diffraction peak. The morphologies and diameters of the samples were investigated by a field-emission scanning electron microscopy (FE-SEM, JSM 6700F) and a transmission electron microscopy (TEM, JEOL 2100F). The UV–vis adsorption spectra of the samples were characterized in reflection mode using a Cary 500 UV–vis–NIR spectrophotometer. Nitrogen sorption isotherms of the samples were measured at 77 K with a micrometrics ASAP 2020 analyzer. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface area using adsorption data in a relative pressure range from 0.05 to 0.3. The pore size distributions were derived from the adsorption branch of the isotherms using the Barrett-Joyner-Halenda (BJH) model.

Electrochemical test

The electrochemical measurements were carried out using CR2032-type coin cell at room temperature. The working electrodes were prepared by mixing the samples, carbon black (Super-P), and poly(vinyl difluoride) (PVDF) at a weight ratio of 70:10:20 and pasting onto pure Cu foil. Pure lithium foil was used as the counter electrode and separated by a Celgard 2500 membrane separator. The electrolyte consisted of a solution of 1 mol L^{-1} LiPF$_6$ in ethylene carbonate/dimethyl carbonate (1:1 by volume). The cells were assembled in a glove box filled with high purity argon gas. The galvanostatic discharge-charge experiments were performed over a voltage range of 1.0–3.0 V (vs. Li$^+$/Li) at different rates using a LAND CT2001A battery tester. Electrochemical impedance spectroscopy (EIS) measurements were carried out on an Autolab PGSTAT302N electrochemical workstation by applying a sine wave with the amplitude of 10.0 mV over the frequency range from 100 kHz to 10 mHz. Cyclic voltammetry (CV) curves were performed using

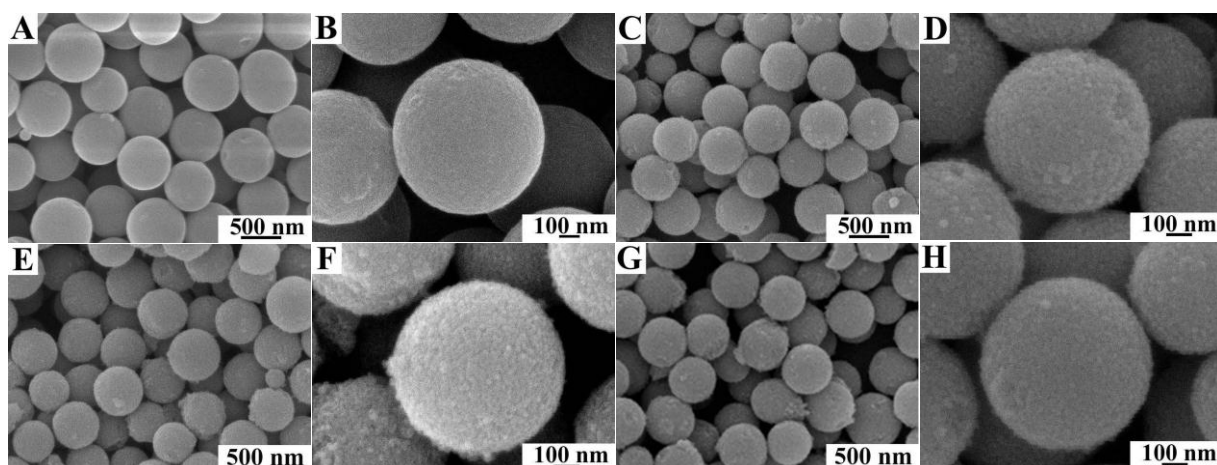the same workstation as EIS measurements at a scanning rate of 0.5 mV s^{-1}.

Fig. S1 SEM images of the white precipitates (A and B) obtained by the sol-gel process and the TiO$_2$ precursor (C and D). The white precipitates obtained by the sol-gel process (A, B) are monodisperse amorphous TiO$_2$ microspheres with smooth surfaces and diameters of 500 ± 20 nm. After hydrothermal treatment, the amorphous TiO$_2$ microspheres are changed to anatase TiO$_2$ precursor with a little shrinkage in size (460 ± 20 nm) due to the crystallization and the effect of Oswald ripening (C, D). SEM images of H-TiO$_2$ microspheres (E, F) and A-TiO$_2$ microspheres (G, H).

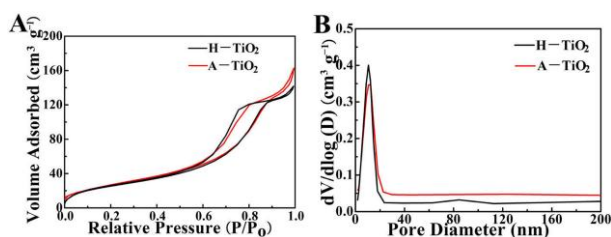Fig. S2 N$_2$ adsorption–desorption isotherms (A) and BJH pore-size distributions (B) of H-TiO$_2$ microspheres and A-TiO$_2$ microspheres.
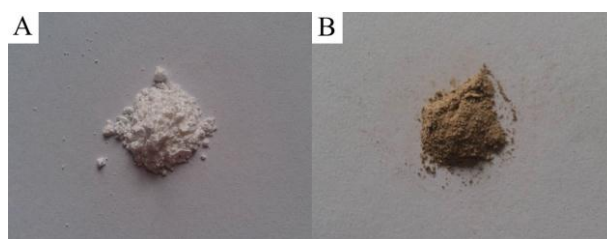

Fig. S3 Photos of the A-TiO$_2$ (A) microspheres and H-TiO$_2$ (B) microspheres.
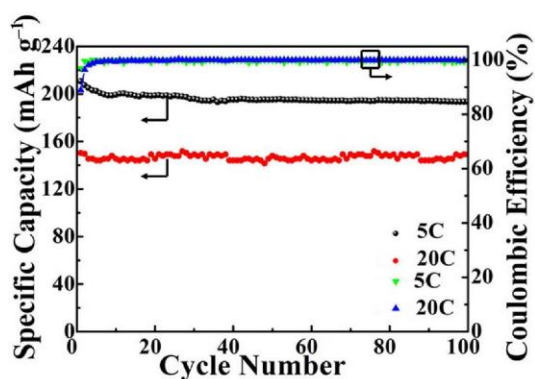
Fig. S4 The long-term cycling performances and Couloumbic efficiency of H-TiO$_2$ microspheres at 5 and 20 C.
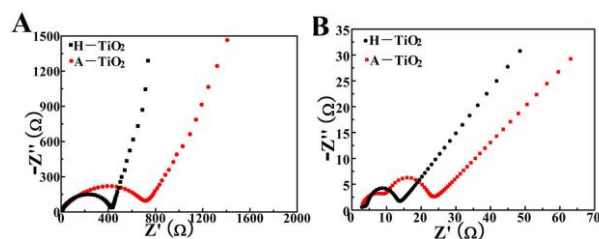

Fig. S5 Electrochemical impedance spectra (EIS) of the fresh cells (A) and after 70th cycles of rate capabilities test (B) of H-TiO$_2$ microspheres and A-TiO$_2$ microspheres.

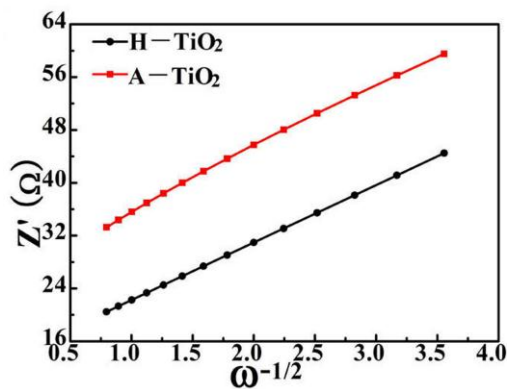

Fig. S6 The relation of Z' (real) and $\omega^{-1/2}$ at low frequency. With the Warburg impedance at lower frequency ranges, the Warburg factor σ is determined by plotting in the complex plane Z' (real) = σ × $\omega^{-1/2}$ against $\omega^{-1/2}$ where ω is angular frequency. The diffusion coefficient (D$_{Li}$) of lithium ions are calculated based on the determined σ.

Tab. S1 Space group, lattice parameters and crystallite size of the TiO_2 precursor, A-TiO_2 microspheres, and H-TiO_2 microspheres.

	TiO_2 precursor	A-TiO_2	H-TiO_2
Space group	I41/amd	I41/amd	I41/amd
Lattice parameters a/c [A]	3.785/9.514	3.781/9.490	3.783/9.532
Crystallite size (nm)	7.0 ± 0.5	8.0 ± 0.3	8.2 ± 0.3