EXPERIMENTAL SECTION

Materials. Tin(V) isopropoxide, 99% (metals basis), 10% w/v in isopropanol liquid was purchased from Beijing InnoChem Science and Technology Co., Ltd. Formaldehyde solution (37%–40%), Urea (A.R.), Hydrochloric Acid (36%–40%, A.R.), Commercial SnO$_2$ nanoparticles were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were used as received without further purification. Milli-Q water (typically 18.2 MΩ·cm at 25 °C) was used for all experiments.

Synthesis of SnO$_2$ sol. The synthetic procedure followed here is referenced as TiO$_2$ sol reported as previously. In a typical synthesis, 30 ml of deionized water and 1 ml of hydrochloric acid were stirred at 60 °C in oil bath. Then, 10 mmol of Tin(IV) isopropoxide was added and stirred for 60 min. Subsequently, the transparent yellow sol was cooled down to room temperature and stored for further use.

Synthesis of SnO$_2$-UF microspheres. 2 mmol SnO$_2$ sol and 17 mmol urea were dispersed into 30 ml deionized water. The pH of the solution was controlled at 1–1.5 by concentrated hydrochloric acid and then 2 ml formaldehyde (37 wt%) was added under stirring violently. Finally, keep the reaction solution static for 3 h at room temperature. The precipitate was collected by centrifugation, washed with water and ethanol for three times, respectively and dried in 80 °C overnight for further characterization.

Synthesis of SnO$_2$-C hollow composite. The prepared SnO$_2$-UF powder was transferred into tube furnace heated to 500 °C in H$_2$/Ar atmosphere. SnO$_2$-C hollow composite was subsequently formed as a dark powder.

Synthesis of solid SnO$_2$-C. The synthesis process is similar to that for SnO$_2$-C hollow composite, the only difference is a much higher amount of SnO$_2$ sol, namely 5 mmol, was used for the PICA process. The SnO$_2$-UF was also heated in H$_2$/Ar flow to prepare solid SnO$_2$-C.

Materials Characterization. The field emission electron microscopy (FESEM) images and Energy-dispersive x-ray (EDX) analysis were acquired on a JEOL JSM-6701F microscope. The transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) images were recorded on JEOL-2100F microscope. The SEM images of cross section were collected by focused ion beam (FIB) technique. X-ray diffraction (XRD) patterns were
collected on a Rigaku D.MAX-2500 with Cu Kα radiation ($\lambda = 1.5406$ Å) at a voltage of 50 kV and a current of 250 mA. Thermogravimetric analysis (TGA) curves were carried out with a SII WXSTAR6000-TGA6300 over the range 20-800 °C in air flow, at a heating rate of 10 °C /min.

**Electrochemical Characterization.** Electrochemical performances were evaluated with CR2032 coin cells. The electrodes were made by mixing 70 wt% of active material, 20 wt% carbon black (Super-P), 5 wt% carboxymethyl cellulose (CMC) sodium and 5 wt% styrene butadiene rubber(SBR) in deionized water by using mixing machines(Planetary Mixer/Deaerator). The obtained slurry was spread onto pure Cu foil (99.9%, Goodfellow) and then dried in a vacuum oven at 80 °C for 8 hours. The assembling procedure of the cells was performed in a recirculating argon glovebox, and the electrolyte was a 1 mol L$^{-1}$ LiPF6 solution in a mixture of ethylene carbonate/dimethyl carbonate (1:1 v/v). The galvanostatical charge−discharge tests were carried out in a Land-CT2001A system within the potential range of 0.01−3 V vs Li/Li$^+$. Electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) measurements were taken on an electrochemical workstation (Autolab). AC impedance spectra were obtained in a frequency range from 100 kHz to 0.01 Hz at a scan rate of 5.0mV s$^{-1}$. The cyclic voltammograms were obtained over the potential range of 0.01−3 V vs Li/Li$^+$ at a scan rate of 0.1 mV s$^{-1}$.

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Fig. S1 TEM image of SnO$_2$ sol and HRTEM image of SnO$_2$ sol (inset). The TEM image shows that SnO$_2$ sol is irregular colloids and HRTEM image shows it is low crystallinity.
Fig. S2 SEM image for broken species of SnO$_2$-UF microspheres

Fig. S3 TGA curve of SnO$_2$-UF microspheres over range of 20-800°C in air with a heating rate of 10°C/min. The TGA curve shows that there is a sharply weight loss (82.82 wt%) of the SnO$_2$-UF precursor sample.

Fig. S4 TGA curve of SnO$_2$-C hollow sample over the range of 30-800°C in air at a heating rate of 10 °C/min.

Fig.S4 TGA curve of SnO$_2$-C hollow sample over the range of 30-800°C in air at a heating rate of 10 °C/min.
Fig. S5 CV curves of the first five cycles for SnO$_2$-C hollow sample.

Fig. S6 TEM image of solid SnO$_2$-C sample (a) clearly shows that it is solid in the core. TEM image of SnO$_2$ nanoparticle (b) shows it is nanosphere with diameter around 50 nm.
Fig. S7  SEM images(a, b) about the surface of electrode before and after 100 cycles, TEM images(c, d) about the hollow SnO2-C microsphere before and after 100 cycles.