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Supporting Information

Confining Sb_2Se_3 nanorod yolk in mesoporous carbon shell with an in-built buffer space for stable Li-ion batteries

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Experimental

Material Synthesis

All the materials and chemicals used in this study were of analytical grade and directly used as received from the Aladdin manufacturers.

Synthesis of Sb_2Se_3 nanorods.

Sb_2Se_3 nanorods were synthesized through a facile solvothermal method. Typically, 2 mmol of $SbCl_3$ was added into 60 mL of poly (ethylene glycol)-200 (PEG-200) and stirred for 2 h. Separately, the hydrazine hydrate-Se solution prepared by mixing 4 mmol of Se and 10 mL of hydrazine hydrate (N_2H_4•H_2O, 80wt%). The solution was added dropwise into the above organic mixture and continuously stirred for 4 h. Then, the mixed solution was transferred into a 100 mL Teflon-lined stainless-steel autoclave, sealed and maintained at 200 °C for 12 h. Finally, after cooling down to room temperature, the as-prepared product of Sb_2Se_3 nanorods, were collected by centrifugation and washed with deionized water and ethanol for three times before vacuum drying overnight at 60 °C.

Synthesis of Sb_2Se_3@SiO_2 core-shell nanorods

In a typical synthesis, 0.25 g of Sb_2Se_3 nanorods were dispersed into a mixture of isopropanol (97 mL), deionized water (9 mL), and ammonia (5 mL, 25wt%) by sonication. After ultrasonic dispersion for 10 min, 0.1 mL tetraethyl orthosilicate (TEOS) was added to the above solution. Then the dispersion was further stirred for 2 h at 40 °C. Afterwards, the core-shell Sb_2Se_3@SiO_2 nanorods were obtained after centrifugation and washing with ethanol several times.

Synthesis of Sb_2Se_3@Void@C yolk-shell nanorods

The 0.2 g of as-prepared Sb_2Se_3@SiO_2 nanorods and 0.115 g of cetyltrimethylammonium bromide (CTAB) were added into a mixture with 7 mL of deionized water and 14 mL of alcohol. After 0.5 h ultra-sonication and 0.5 h stirring, 0.0175 g of resorcinol and 0.05 mL of ammonia (25wt%) were added sequentially. The mixture in the beaker was stirred for an additional 0.5 h at room temperature and then 0.06 mL of formaldehyde was finally added. The above mixture was continually stirred for 12 h, the precipitates were obtained and washed with water and ethanol several times, and dried at 60 °C overnight. Sb_2Se_3@Void@C yolk-shell nanorods were obtained after carbonization at 500 °C under argon for 3 h and removal of silica by 8wt% hydrofluoric acid

(HF) solution for 12 h.

Synthesis of Sb_2Se_3@C core-shell nanorods

The Sb_2Se_3@C core-shell nanorods were also prepared for comparison in electrochemical performance. Similarly, 0.2 g of Sb_2Se_3 nanorods were directly reacted with resorcinol and formaldehyde, instead of SiO_2 pre-coating and afterwards HF etching.

Material characterization

Field-emission scanning electron microscopy (FE-SEM, JSM-7800F & TEAM Octane Plus, 10 kV, Japan) was used to characterize the morphology and size of the obtained samples. Transmission electron microscopy (TEM, JEM-2100 and X-Max 80, 200-300 kV, Japan) was performed to observe the internal structure of the sample, the lattice parameters and the elements. X-ray diffraction was performed on a PANalytical X'pert PRO X-ray diffractometer (XRD, PANalytical Empyrean, Netherlands) with a Cu-Ka radiation at 45 kV and 40 mA. The chemical states and elements in the samples were identified by X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha$^+$, UK). Thermogravimetric analysis (TGA, Q50, Germany) was performed in a temperature range of 30-800 °C with a heating rate of 10 °C min^{-1} in air. Raman spectroscopy (Renishaw inVia) is a technique to detect the confusion and defect degree of material. Specific surface area and pore size distributions were obtained by using the Brunauer-Emmett-Teller method (BET, NOVA1200e).

Electrochemical measurements

The active electrode material, acetylene black and carboxymethyl cellulose (CMC) were mixed in deionized water with a weight ratio of 8:1:1, which was coated directly on Cu foil and dried at 60 °C under vacuum overnight. The prepared electrode was cut into discs with diameter of 14 mm, and the typical mass loading is about 1.0 mg cm^{-2}. The electrochemical performance was investigated by using CR2032 coin-type cell. The metallic lithium foil and Celgard polymer membrane were used as the counter electrode and separator, respectively. The electrolyte was 1 M $LiPF_6$ in EC/DMC/EMC (1:1:1 by volume ratio). The charge-discharge tests were performed at a potential range of 0.01-3.0 V using a LAND CT2001A instrument (Wuhan, China). Cyclic voltammetry (CV) was measured at a scan rate of 0.2 mV s^{-1} between 0.01 and 3 V using an electrochemical station (CHI760E, China). The electrochemical impedance spectroscopy (EIS) was collected by CHI760E electrochemical station in the frequency range of 100 kHz to 0.01 Hz,

which was obtained at an AC potential amplitude of 5 mV around the open circuit before the electrochemical performance testing. The mass loading of the Sb_2Se_3@Void@C yolk-shell nanorods was calculated based on the total mass of the composite including the carbon shell.

In situ XRD measurements

In situ XRD measurements were performed in the Swagelok-type cell at current density of 100 mA g^{-1} within a potential window from 0.01 to 3.0 V. The active electrode material mixed with acetylene black and CMC in a weight ratio of 8:1:1, was coated directly on Beryllium (Be) foil and dried at 60 °C under vacuum overnight. The electrode was assembled in the glove-box with a Swagelok-type cell, which was connected to the LAND CT2001A battery testing system during the in situ XRD measurements.

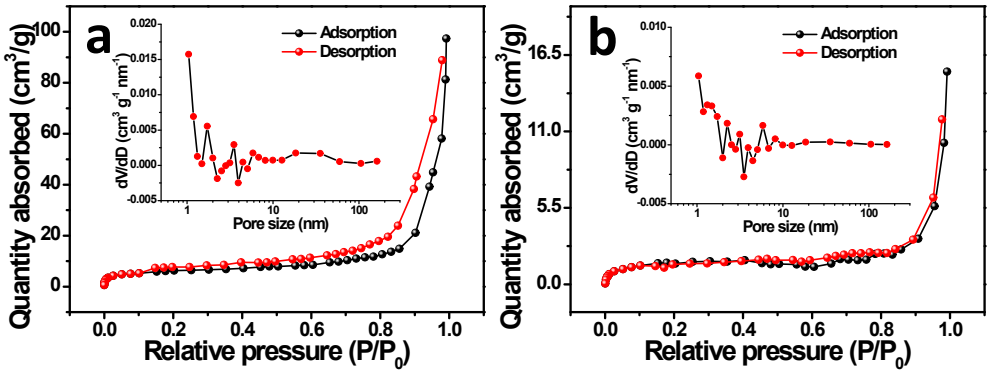

Figure S1. N_2 adsorption/desorption isotherms and the corresponding pore size distribution of (a) Sb_2Se_3@Void@C and (b) Sb_2Se_3.

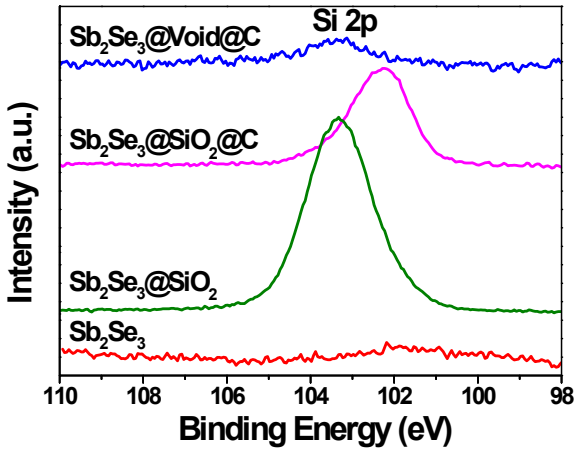

Figure S2. Si 2p core level XPS spectra of the pristine Sb_2Se_3, precursor Sb_2Se_3@SiO_2, intermediate Sb_2Se_3@SiO_2@C and final Sb_2Se_3@Void@C composite samples.

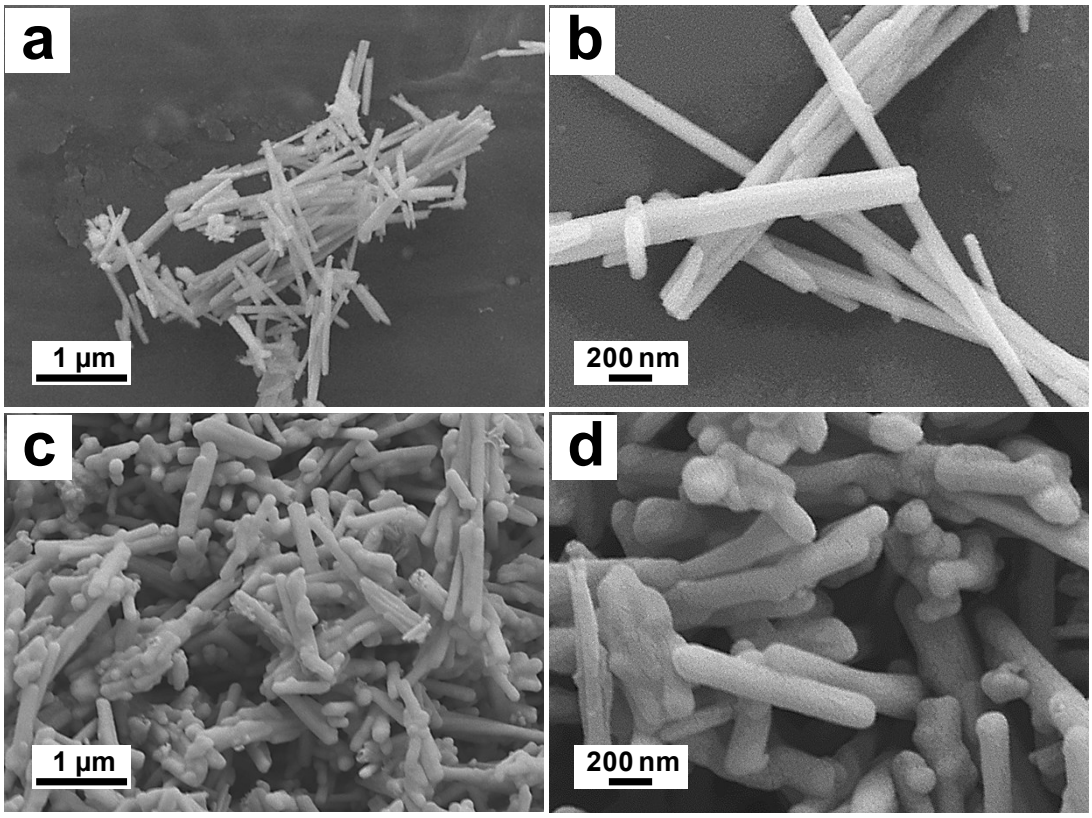

Figure S3. FESEM images of the obtained samples: (a, b) precursor Sb_2Se_3@SiO_2 and (c, d) intermediate Sb_2Se_3@SiO_2@C.

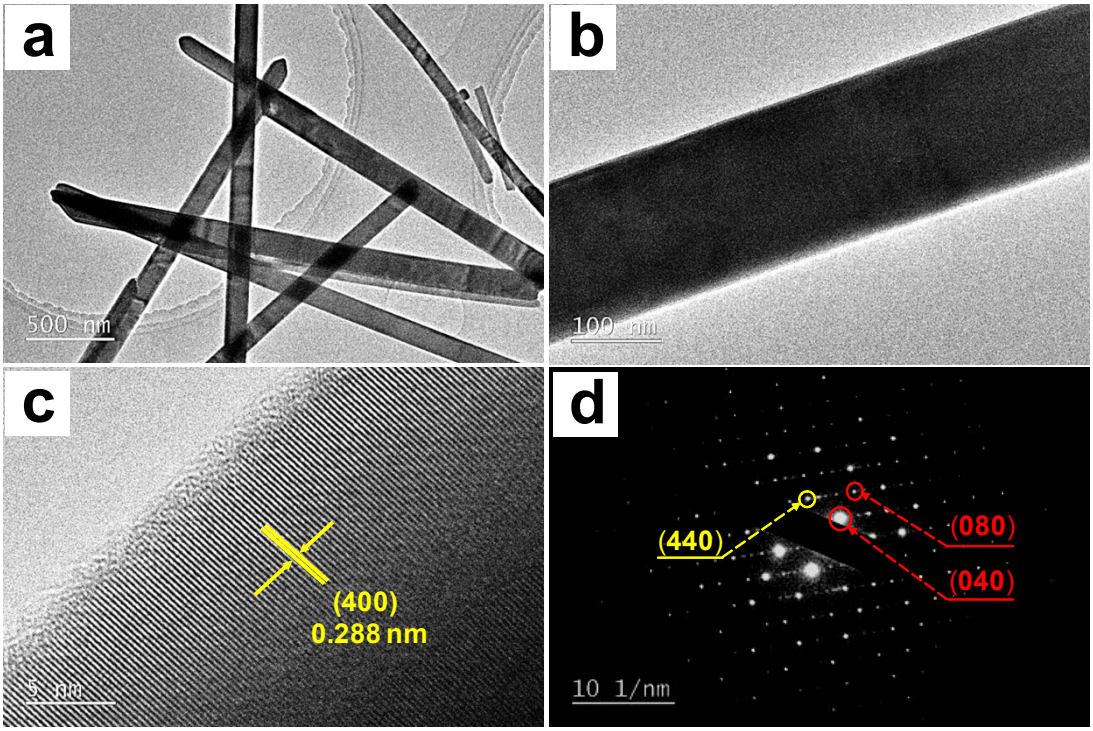

Figure S4. (a, b) TEM images and (c) HRTEM image for the Sb_2Se_3 sample; (d) the corresponding selected area electron diffraction (SAED) pattern.

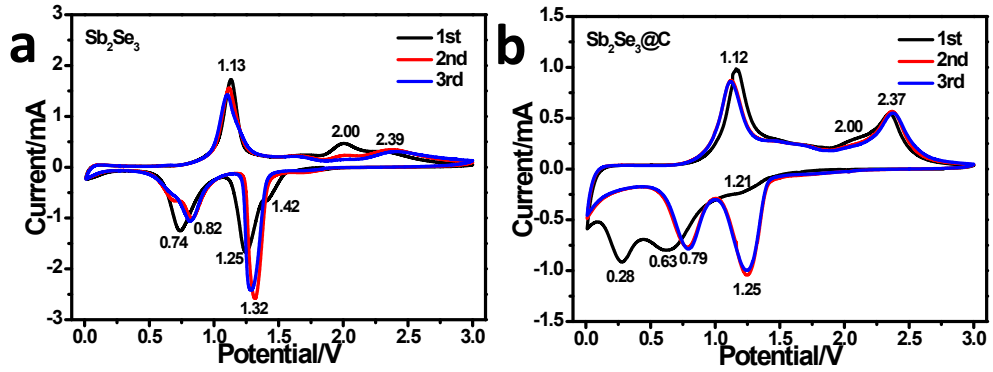

Figure S5. CV curves for the first 3 cycles at a scan rate of 0.2 mV s^{-1} in the voltage range of 0.01-3.0 V for the pristine Sb_2Se_3 (a) and comparative Sb_2Se_3@C (b) samples.

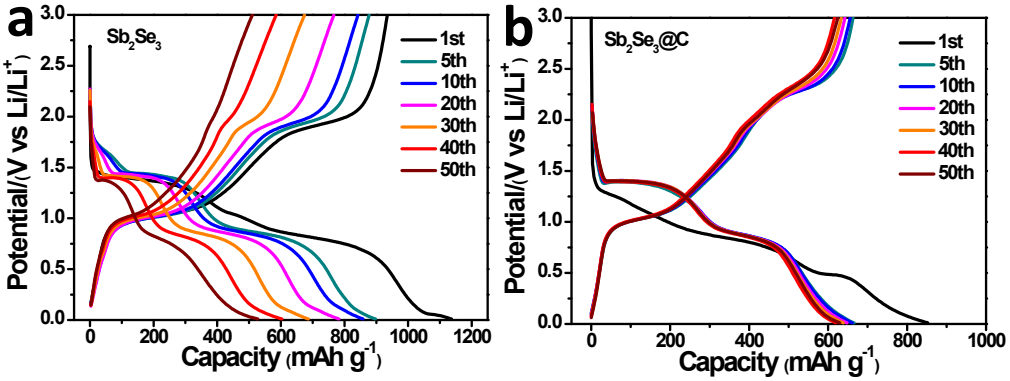

Figure S6. Charge/discharge profiles at a current density of 0.2 A g^{-1} for the pristine Sb_2Se_3 (a) and comparative Sb_2Se_3@C (b) samples.

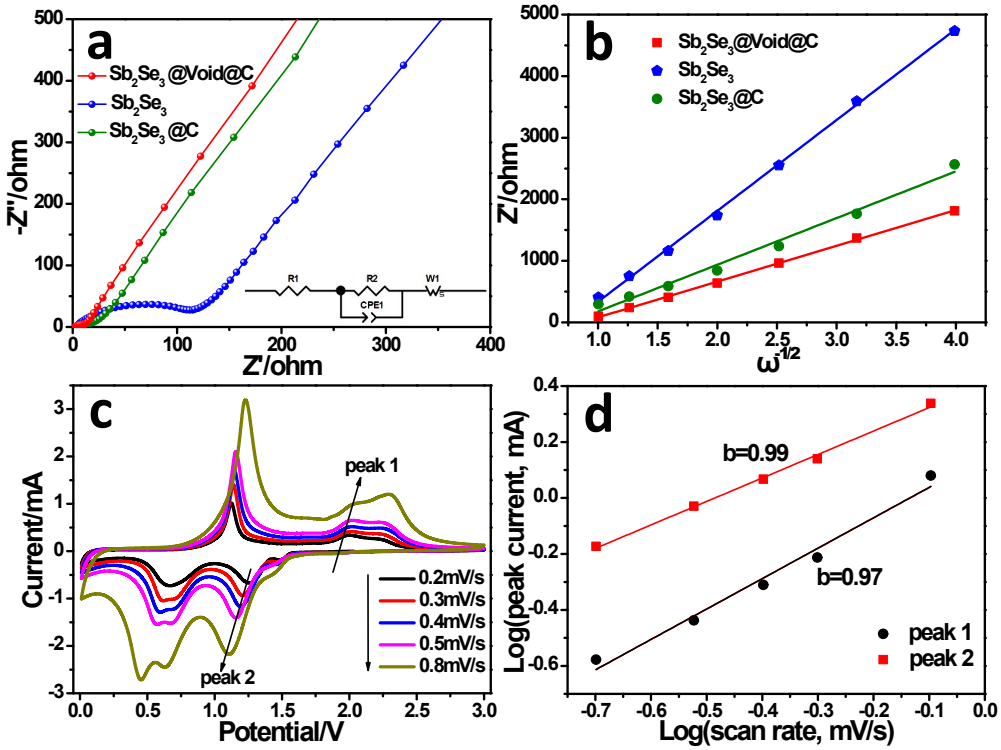

Figure S7. (a) Nyquist plots and (b) Z' vs $\omega^{-1/2}$ in the low-frequency regions of Sb_2Se_3@Void@C, Sb_2Se_3 and Sb_2Se_3@C; (c) CV curves at different scan rates and (d) plots for log(i) versus log(v) (peak current, i; scanning rate, v) for Sb_2Se_3@Void@C.

Table S1. Comparison of the performance between yolk-shell Sb_2Se_3 nanorods with other reported Sb_2Se_3 studies as anode materials for LIBs

Samples	Cycling current ($A\ g^{-1}$)	Cycles	Cycling capacity ($mA\ h\ g^{-1}$)	Rate current ($A\ g^{-1}$)	Rate capacity ($mA\ h\ g^{-1}$)	Ref.
Sb_2Se_3@Void@C	0.2	100	658.6	2.0	625.3	This work
				3.0	594.7	
Sb_2Se_3/rGO	0.1	100	430	1.0	247	[1]
Sb_2Se_3 nanowires	0.1	50	650.2	2.0	389.5	[2]
Amorphous Sb_2Se_3/C	0.1	100	662	1.95	623	[3]
Sb_2Se_3 nanowire membrane	0.1	50	584	1.6	255	[4]
Sb_2Se_3 nanorods	0.067	100	230	0.67	120	[5]
$Ge_2Sb_2Se_5$ glass	0.424	100	626	0.848	554	[6]
Sb_2Se_3@C nanofibers	0.1	100	625	2.0	400	[7]

Table S2. $R2$, σ and D_{Li+} values for the Sb_2Se_3@Void@C, Sb_2Se_3 and Sb_2Se_3@C electrodes

	$R2$ (Ω)	σ ($\Omega\ cm^2 s^{-0.5}$)	D_{Li+}($cm^2 s^{-1}$)
Sb_2Se_3@Void@C	16	580.8	4.8×10^{-16}
Sb_2Se_3	134.4	1476.4	7.6×10^{-17}
Sb_2Se_3@C	29	758.1	2.8×10^{-16}

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