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Supporting Information

Solvent-Free Synthesis of Uniform MOF Shell-Derived Carbon Confined SnO$_2$/Co Nanocubes for Highly Reversible Lithium Storage

Qiu He, Jinshuai Liu, Zhaohuai Li, Qi Li,* Lin Xu, Baoxuan Zhang, Jiashen Meng, Yuzhu Wu, and Liqiang Mai*

Supporting Information

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Experimental section

All the reagents are of analytical grade and used as-received without further purification.

Synthesis of hollow CoSn(OH)$_6$ nanocubes

A simple co-precipitation method was used to fabricate hollow CoSn(OH)$_6$ nanocubes. In a typical synthesis, 5 mL of ethanol containing 1 mmol SnCl$_4$·5H$_2$O was added into 35 mL of a mixed aqueous solution containing 1 mmol CoCl$_2$·6H$_2$O and 1 mmol sodium citrate under stirring, followed by adding 5 mL of NaOH aqueous solution (2 M) drop by drop at room temperature. After 1 h, 20 mL of NaOH aqueous solution (8 M) was successively added into the resulting pink suspension containing CoSn(OH)$_6$ nanocubes and allow for reaction for 0.5 h. The resultant white precipitate was collected by several wash and centrifugation cycles with deionized (DI) water and ethanol. Finally, the hollow CoSn(OH)$_6$ nanocubes were dried in oven at 70 $^{\rm o}$C for 8 h.

Synthesis of SnO$_2$/Co@C nanocubes

CoSn(OH)$_6$ powder and abundant **1, 4-benzenedicarboxylic acid** (H$_2$BDC) (1:5 w/w) were together ground in a mortar by hand for about 20 min. Then, the homogeneous mixture was successively annealed at 300 $^{\rm o}$C for 1 h and 320 $^{\rm o}$C for 0.5 h in a Muffle furnace, the residual H$_2$BDC was allowed to volatilize away at 320 $^{\rm o}$C. The resultant intermediate gray powder (CoSnO$_3$@MOF) was finally calcinated in argon gas at 550 $^{\rm o}$C for 3 h to obtain the final product, black SnO$_2$/Co@C powder.

Synthesis of ZnO@MOF and Zn$_3$V$_2$O$_8$@MOF

The precursor of ZnO microflowers were synthesized by a hydrothermal method. First, 15 mL of 0.5 M zinc acetate dehydrate aqueous solution and 30 mL of NaOH aqueous solution (5M) were mixed. Then, the mixed solution was added into 50 mL Teflon-lined autoclave and allowed to stay at 80 °C for 12 h. After cooling to room temperature, white precipitate was washed by centrifugal separation for several times with DI water and finally dried at 70 $^{\rm o}$C.

In a typical synthesis of precursor Zn$_3$V$_2$O$_7$(OH)$_2$·2H$_2$O nanoplates, 184 mg of V$_2$O$_5$, 1.5 g of cetyltrimethylammonium bromide (CTAB), 240 mg of NaOH were dissolved into 30 mL of DI water at 80 $^{\rm o}$C. Then 4 mL of aqueous solution containing 893 mg of Zn(NO$_3$)$_2$·6H$_2$O was added into the transparent buff solution and stirred for 10 min. Then, a white slurry was obtained and transferred into a 50 mL Teflon-lined autoclave and maintained at 200 °C for 18 h. After the solution was cooled down to room

temperature, white precipitate was collected and washed several times with deionized water and ethanol, and dried at 70 °C for 8 h.

ZnO@MOF and $Zn_3V_2O_8$@MOF were obtained by the same treatments as $CoSnO_3$@MOF.

Characterizations

X-ray diffraction (XRD) characterization was performed to investigate the crystallographic information of samples using a D8 Advance X-ray diffractometer with non-monochromated Cu Kα X-ray source (λ=1.054056 Å). Scanning electron microscopy (SEM) images were collected by a JEOL JSM-7100F at an acceleration voltage of 15 kV. Transmission electron microscopy (TEM) and high resolution TEM (HRTEM) images were recorded with a JEM-2100F/Titan G2 60-300 microscope. Brunauer-Emmett-Teller (BET) surface areas and pore size distribution were measured using Tristar II 3020 instrument by nitrogen adsorption at 77 K. Thermogravimetric analysis (TGA) was performed using a Netzsch STA 449C simultaneous analyzer. Raman spectra were obtained using a Renishaw INVIA micro-Raman spectroscopy system. X-ray photoelectron spectroscopy (XPS) measurements were conducted using a VG MultiLab 2000 instrument. Fourier transform-infrared (FT-IR) transmittance spectra were recorded using a Nicolet 60-SXB IR spectrometer.

Electrochemical measurements

The electrochemical measurements were carried out using CR 2016 coin cells with lithium metal as the counter electrodes at room temperature. The working electrode consisted of active material (SnO_2/Co@C nanocubes), carbon black, and polymer binder (carboxymethyl cellulose, CMC, Aldrich) in a weight ratio of 7:2:1. The slurry was equably deposited on Cu foil and dried overnight at 70 °C to obtain the working electrode. Then, the Cu foil with active material was punched into round slices with the diameter of about 1 cm. The loading mass of the active material on each electrode disc was about 1.5 mg cm^{-2}. The electrolyte was 1 M $LiPF_6$ in a 50:50 w/w mixture of ethylene carbonate and diethyl carbonate. Cell assembly was carried out in an Ar-filled glove box with the concentrations of moisture and oxygen below 0.1 ppm. All the specific capacities were calculated based on the mass of SnO_2/Co@C. Galvanostatic charge/discharge measurements were performed with a multichannel battery testing system (LAND CT2001A). Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed with a CHI 600e electrochemical workstation and Autolab PGSTAT 302N.
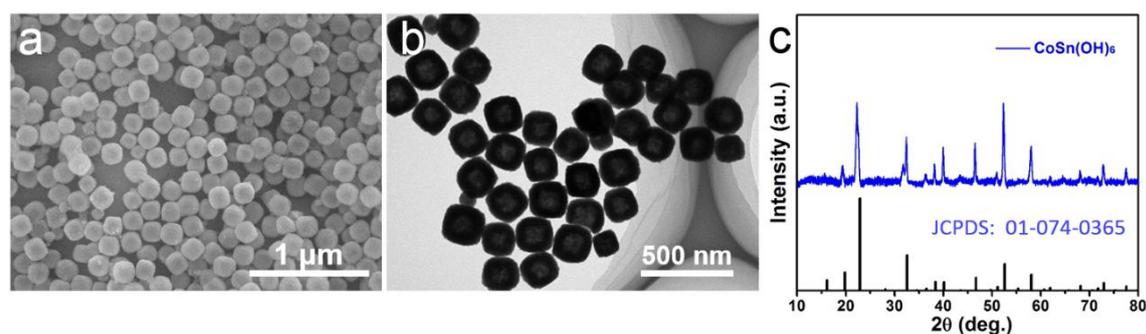
Figure S1. (a) SEM image, (b) TEM image, (c) XRD pattern of hollow $CoSn(OH)_6$ nanocubes.
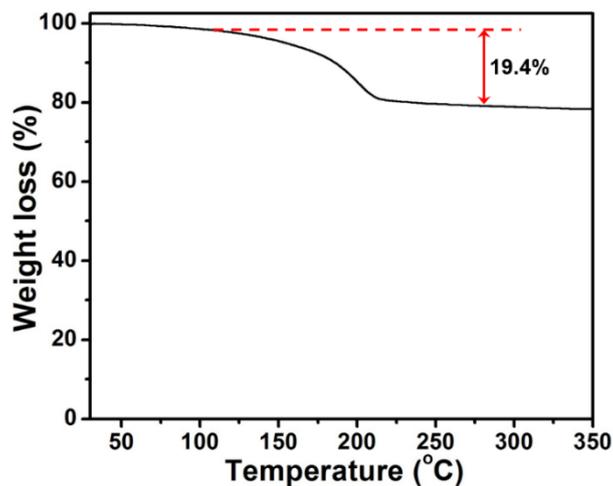
Figure S2. TGA curve of CoSn(OH)$_6$ which was tested in air from 30 $^{\circ}$C to 350 $^{\circ}$C with the temperature rising rate of 2 $^{\circ}$C min^{-1}.
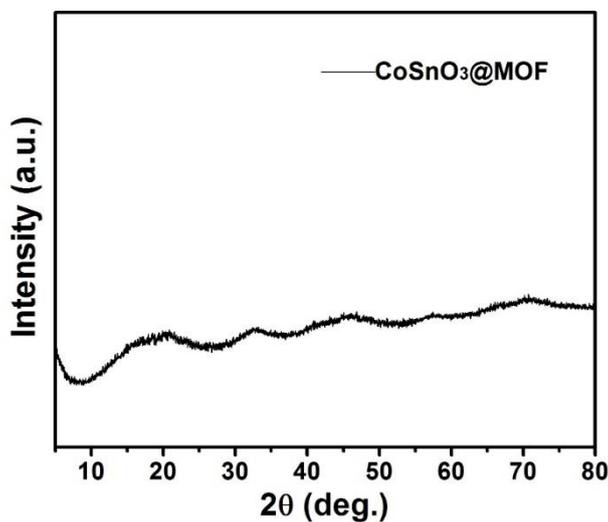
Figure S3. XRD pattern of the hollow CoSnO$_3$@MOF nanocubes.
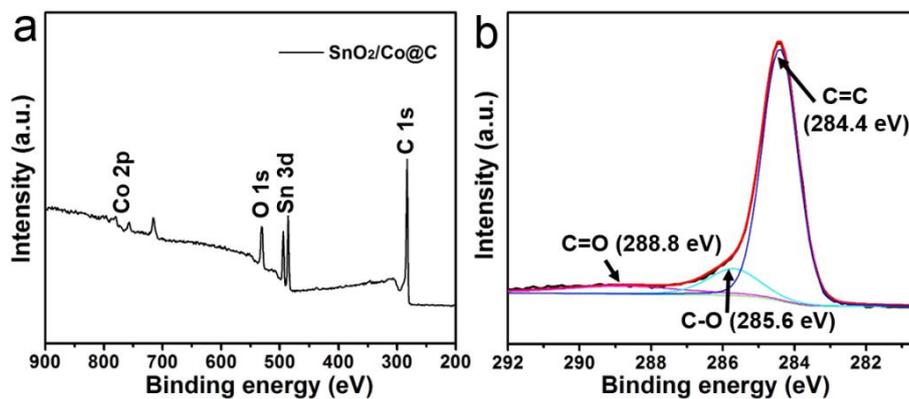
Figure S4. (a) XPS spectrum for survey scans of SnO$_2$/Co@C nanocubes and (b) corresponding C 1s core-level spectrum.
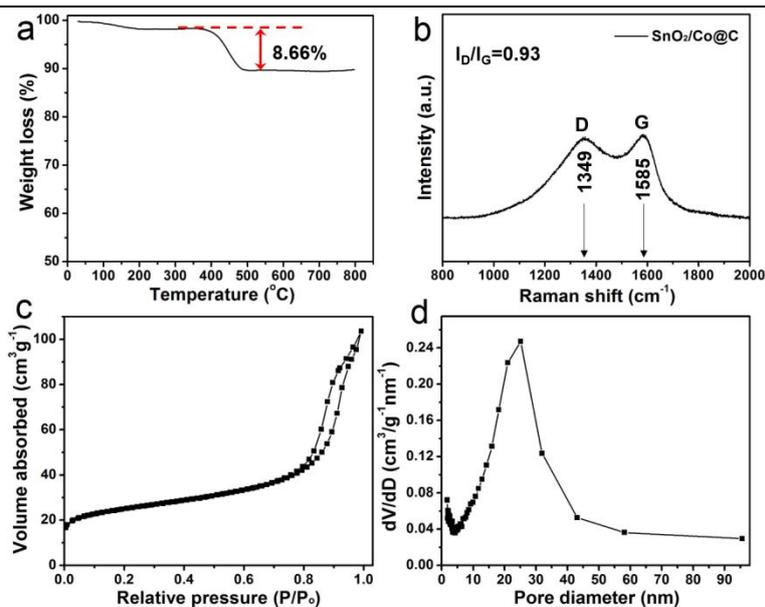
Figure S5. (a) TGA curve, (b) Raman spectrum, (c, d) N_2 adsorption/desorption isotherm and the corresponding pore size distribution of $SnO_2/Co@C$ nanocubes.
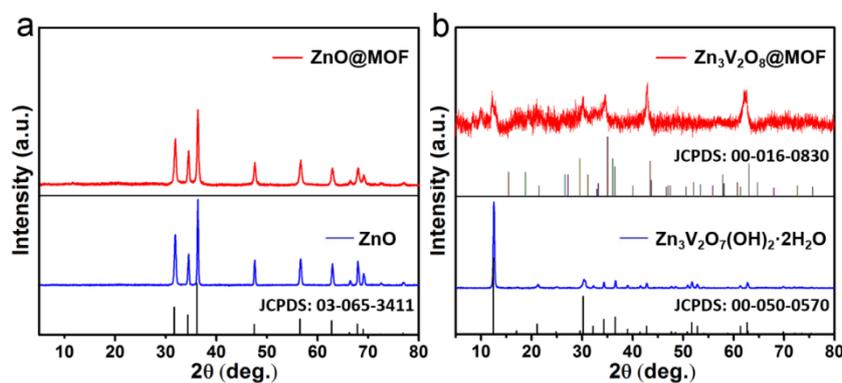
Figure S6. XRD patterns of (a) ZnO and ZnO@MOF microflowers, (b) $Zn_3V_2O_7(OH)_2 \cdot 2H_2O$ and $Zn_3V_2O_8@MOF$ nanoplates, respectively.
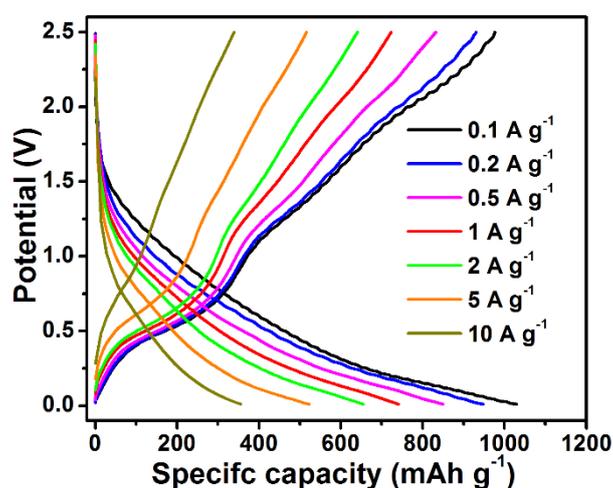
Figure S7. The charge-discharge voltage profiles of the SnO2/Co@C nanocubes at different current densities.
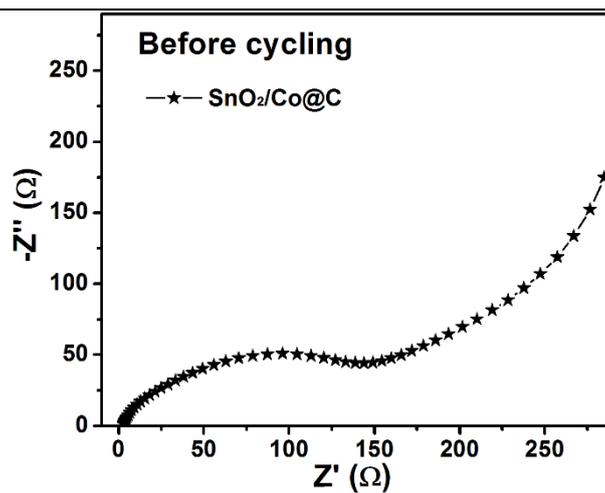
Figure S8. Nyquist plot of the $SnO_2/Co@C$ nanocubes electrode.
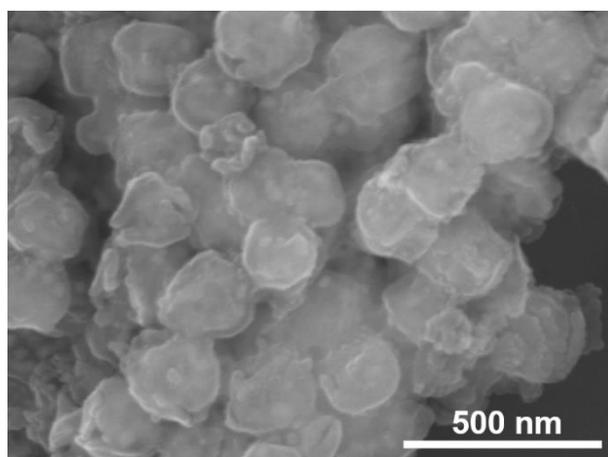
Figure S9. SEM image of $SnO_2/Co@C$ nanocubes after cycling for 100 cycles under the current density of 200 mA g^{-1} within the potential range of 0.01~2.5 V.

Table S1. Electrochemical performance comparison of various SnO_2-based anodes.

SnO_2-based anode materials	Voltage range (V)	Current density (mA g^{-1})	Discharge capacity (mAh g^{-1})	Reference
SnO_2 SMCs@C	0.01~3	50	870.9 (120 cycles)	[1]
		2500	431.1	
SnO_2 @C-NTs	0.01~2	500	602 (100 cycles)	[2]
		5000	361	
SnO_2 Hollow Spheres@C	0.01~2.5	50	900 (100 cycles)	[3]
		2000	669.9	
Chestnut-like SnO_2/C	0.005~2.5	78.2	930 (100 cycles)	[4]
		1564	410	
$SnO2$/NC	0.01~2	500	491 (100 cycles)	[5]
		5000	372	
SnO_2 QDs@GO	0.01~3	100	1121 (100 cycles)	[6]
		2000	553 (2000 cycles)	
SnO_2/Co @C	0.01~2.5	200	800 (100 cycles)	This work
		5000	400 (1800 cycles)	

*The numbers in brackets under the column of "Discharge capacity" refer to cycle numbers, the values in front of brackets are the discharge capacities after cycling for the corresponding cycles; the values without brackets are extracted from rate capacity curves.

References

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