Supporting Information

Stepwise Chelation-Etching Synthesis of Carbon-Confined Ultrafine SnO_2 Nanoparticles for Stable Sodium Storage

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Experimental

Preparation of $CoSn(OH)_6$ nanocubes

1.40 g tin chloride pentahydrate ($SnCl_4·5H_2O$) was dissolved in 20 mL H_2O to obtain a homogeneous light red solution (named as solution A). 0.9517 g cobalt chloride hexahydrate ($CoCl_2·6H_2O$) and 1.1864 g sodium citrate dihydrate ($Na_3C_6H_5O_7·2H_2O$) were dissolved in 120 mL H_2O to obtain a homogeneous solution (named as solution B). 1.60 g sodium hydroxide (NaOH) was dissolved in 20 mL H_2O to obtain a homogeneous solution (named as solution C). Solution A was added into solution B, forming a light pink turbid liquid; then solution C was added dropwise followed by stirring for 1 h. Finally, pink $CoSn(OH)_6$ powder was obtained after washing and drying in oven at 70 °C for 12 h.

Preparation of $CoSn(OH)_6$@polydopamine nanocubes

336 mg $CoSn(OH)_6$ powder and 406.5 mg tris(hydroxymethyl)aminomethane was dissolved in 330 mL H_2O to obtain a light pink turbid liquid, then diluted hydrochloric acid was added to the light pink $CoSn(OH)_6$ turbid liquid dropwse until the pH value reached 8.5. 100.8 mg dopamine hydrochloride powder was dissolved in 6 mL H_2O, forming colorless solution; then it was added to the light pink $CoSn(OH)_6$ turbid liquid followed by stirring for 24 h. Finally, the greyish-black $CoSn(OH)_6$@polydopamine powder was obtained after washing and drying in oven at 70 °C for 12 h.

Preparation of $CoSnO_3$@NC nanocubes

The as-prepared $CoSn(OH)_6$@polydopamine powder was annealed at 500 °C (3 °C min^{-1}) under the nitrogen atmosphere for 1 h. Then, the black $CoSnO_3$@NC powder was obtained.

Preparation of SnO_2@NC nanocubes

75 mg $CoSnO_3$@NC composite (0.3mmol, based on the molar of Co) and a certain amount of ethylenediaminetetraacetic acid (EDTA) were added to 70 mL H_2O and stirred under sonication for 10 min. Then the black turbid liquid was transferred into 100 mL Teflon-lined sealed autoclave and maintained at 120 °C for 12 h. Afterward, the autoclave was cooled down to room temperature naturally and the samples were washed with distilled water 6 times. The final products were dried at 70 °C for 12 h in an oven. SnO_2@NC-1, SnO_2@NC-1.2, SnO_2@NC-1.5, SnO_2@NC-2 respectively correspond to the product obtained when the additive amount of EDTA is 87.67 mg (0.3 mmol, M_{CoSnO3}:M_{EDTA}=1:1), 105.2 mg (0.36 mmol, M_{CoSnO3}:M_{EDTA}=1:1.2), 131.5 mg (0.45 mmol, M_{CoSnO3}:M_{EDTA}=1:1.5), 175.34 mg (0.6 mmol, M_{CoSnO3}:M_{EDTA}=1:2).

Characterization

The crystallographic information of the final products were measured using a Bruker D8 Discover X-ray diffractometer (XRD) equipped with a Cu-Kα radiation source; the samples were scanned over a 2θ range from 20° to 80° at room temperature. Scanning electron microscope (SEM) images were collected using a JEOL-7100F SEM. Transmission electron microscope (TEM) and high-resolution TEM (HRTEM) images were collected using a JEM-2100F TEM. The Brunauer-Emmett-Teller (BET) specific surface area was calculated from nitrogen adsorption isotherms measured at 77 K using a Tristar-3020 instrument. Energy-dispersive X-ray spectra (EDS) was recorded using an Oxford IE250 system. X-ray photoelectron spectroscopy (XPS) measurements were performed using a VG MultiLab 2000 instrument. Thermogravimetric analysis (TGA) was performed using a Netzsch STA 449 C simultaneous analyzer under an air flow with a temperature ramp of 10 °C min^{-1}. Raman spectra was obtained using a Renishaw INVIA micro-Raman spectroscopy system. Fourier transform infrared spectroscopy (FTIR) was recorded using a Thermo

Nicolet Nexus instrument. Inductively coupled plasma atomic emission spectrometry (ICP-AES) was performed using an Optima 4300DV instrument.

Electrochemical measurements

Typical 2016 coin cells were assembled in an argon-filled glovebox with moisture and oxygen concentrations below 1.0 ppm. Sodium foil was used as the counter electrode and a solution of $NaClO_4$ (1 M) in EC: DMC = 1:1 (Vol %) with 5 wt.% FEC was used as the electrolyte. The anode was composed of a grinded mixture of 70 wt.% active material, 20 wt.% acetylene black and 10 wt.% carboxymethylcellulose. Copper foil was used as the current collectorq. Galvanostatic charge/discharge measurements were performed using a multichannel battery testing system (LAND CT2001A). Cyclic voltammograms (CV, 0.01-3 V) and electrochemical impedance spectra (EIS) were collected using an Autolab potentiostat/galvanostat. Specific capacities were calculated based on the mass of active material. The mass loading of each electrode was 1-1.5 mg cm^{-2}.

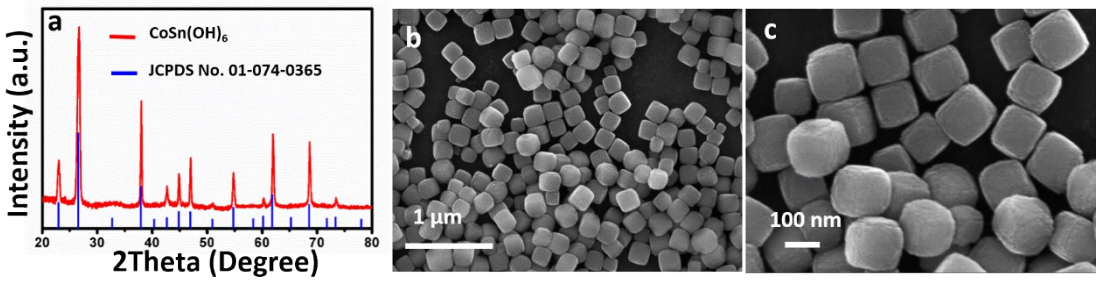

Fig. S1 (a) XRD pattern, (b, c) SEM images of the initial product $CoSn(OH)_6$.

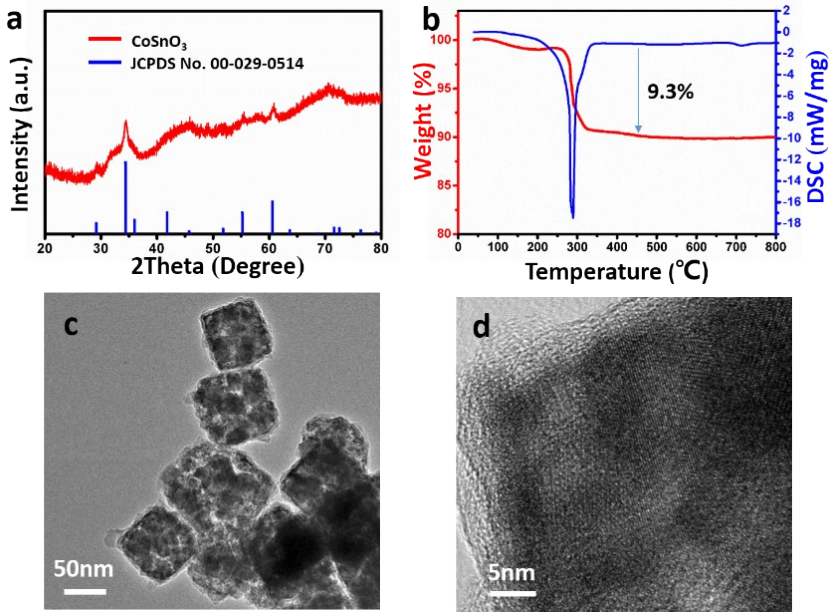

Fig. S2 (a) XRD pattern (b) TG curves and (c, d) TEM images of $CoSnO_3$@NC.

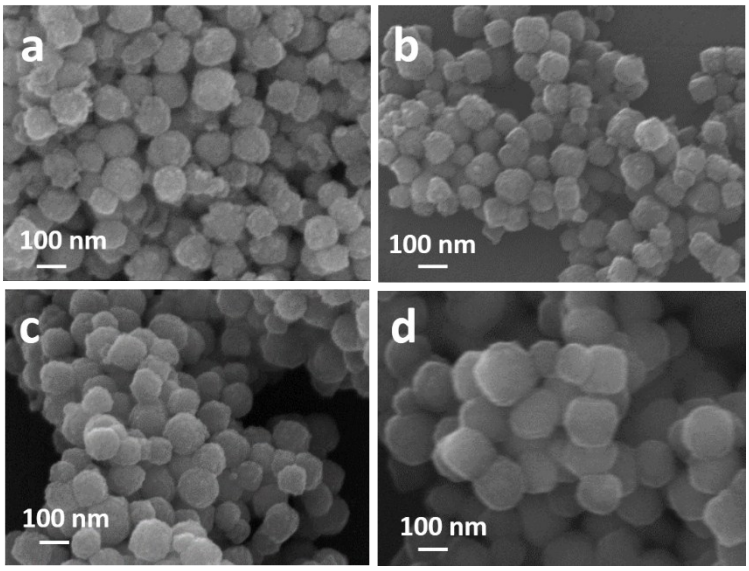

Fig.S3 SEM images of SnO_2@NC-1 (a), SnO_2@NC-1.2 (b), SnO_2@NC-1.5 (c), SnO_2@NC-2 (d).

Tab. S1 ICP results of SnO_2@NC-1.

	Gauged molar concentration (mmol g^{-1})	Ratio (Sn/Co)
Co	0.143	10.3
Sn	1.478	

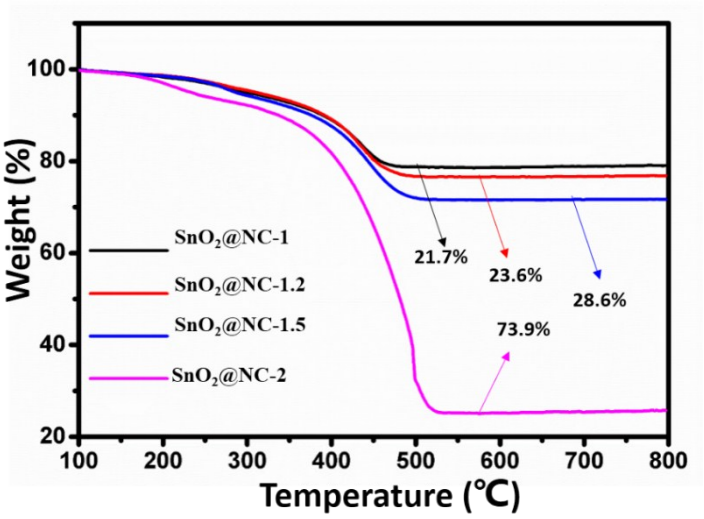

Fig. S4 TG curves of SnO_2@NC.

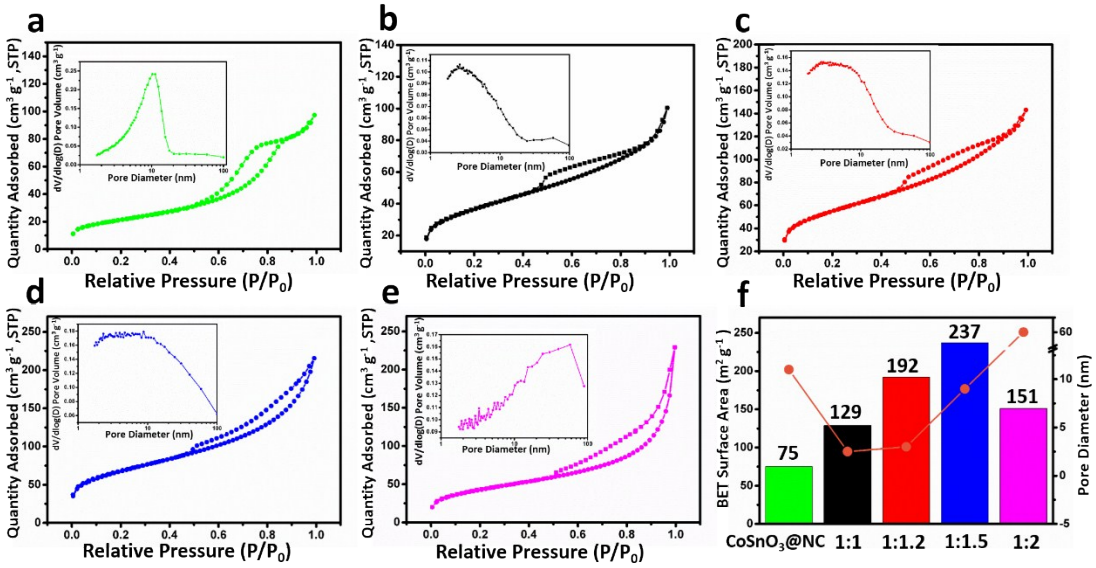

Fig.S5 N_2 adsorption-desorption isotherms of $CoSnO_3$@NC (a), SnO_2@NC-1 (b), SnO_2@NC-1.2 (c), SnO_2@NC-1.5 (d) and SnO_2@NC-2 (e), respectively. The inserted pictures are the corresponding BJH pore size distribution plots; (f) BET specific surface area of $CoSnO_3$@NC and SnO_2@NC and corresponding most probable distribution of pore diameter.

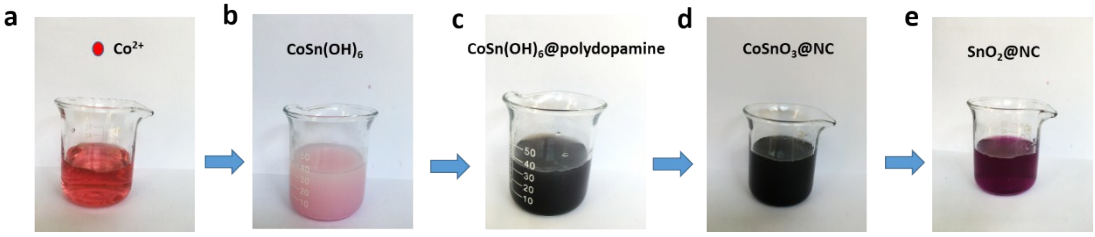

Fig. S6 Digital photo of colour change during the process: (a) aqueous solution after adding all the agents except NaOH; (b) aqueous turbid liquid of as-prepared $CoSn(OH)_6$; (c) aqueous turbid liquid of $CoSn(OH)_6$@polydopamine; (d) aqueous turbid liquid of $CoSnO_3$@NC; (e) supernatant after EDTA chelating $CoSnO_3$@NC.

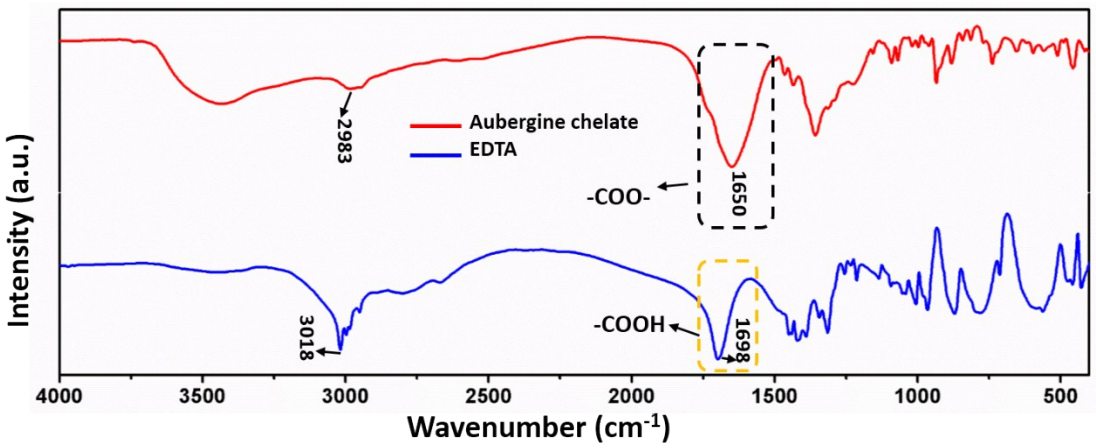

Fig. S7 Fourier transform infrared spectroscopy of EDTA and the aubergine chelate of SnO_2@NC-1.2 after chelation.

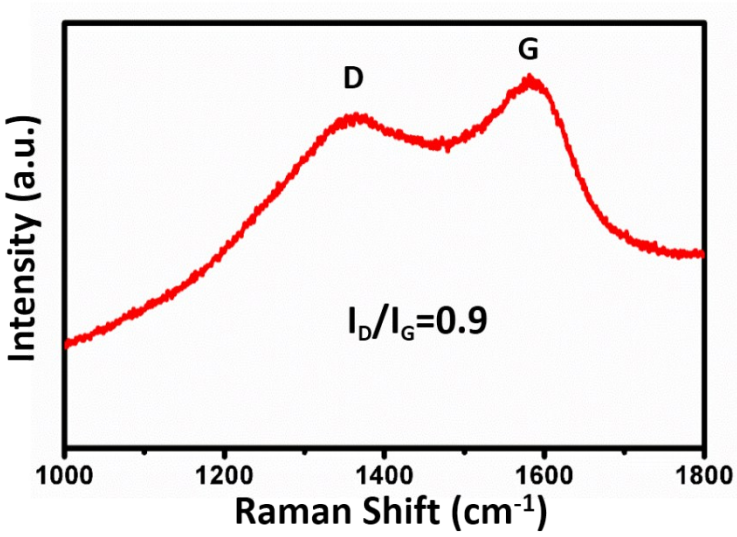

Fig. S8 Raman spectrum of SnO_2@NC-1.2.

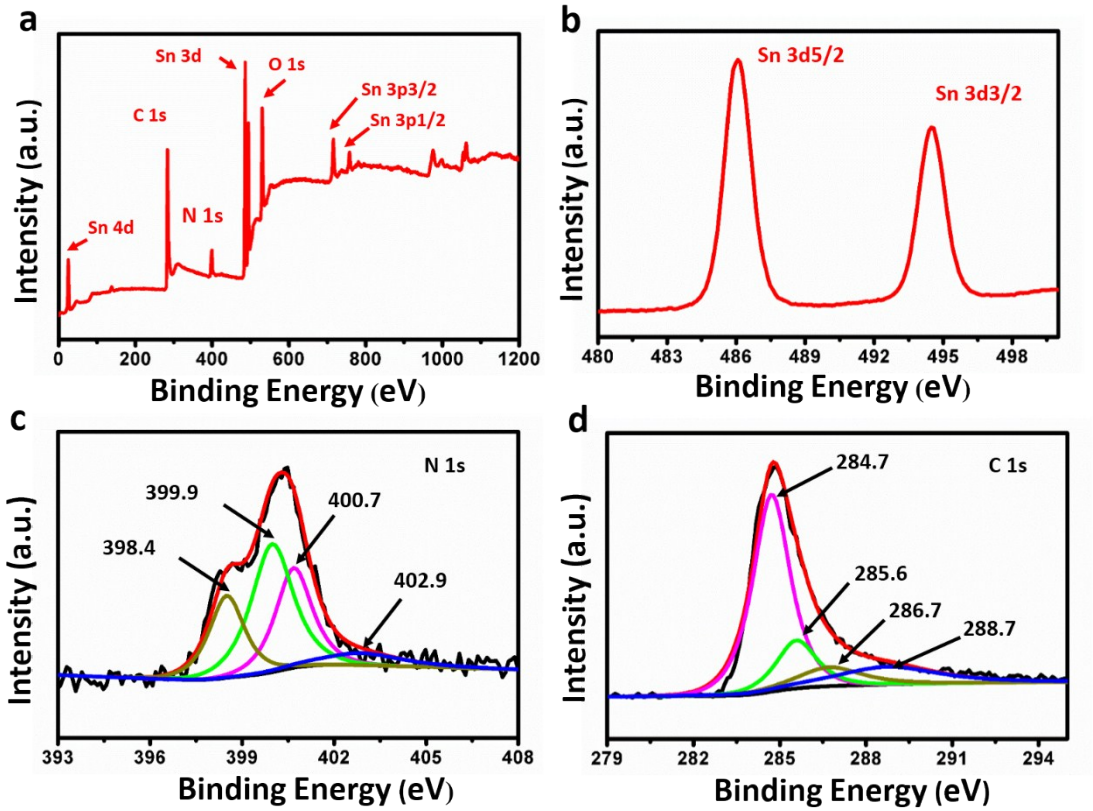

Fig. S9 XPS analysis of SnO_2@NC-1.2 : (a) the survey spectrum, (b) XPS Sn 3d spectra, (c) high-resolution spectrum of N 1s, (d) C 1s spectrum.

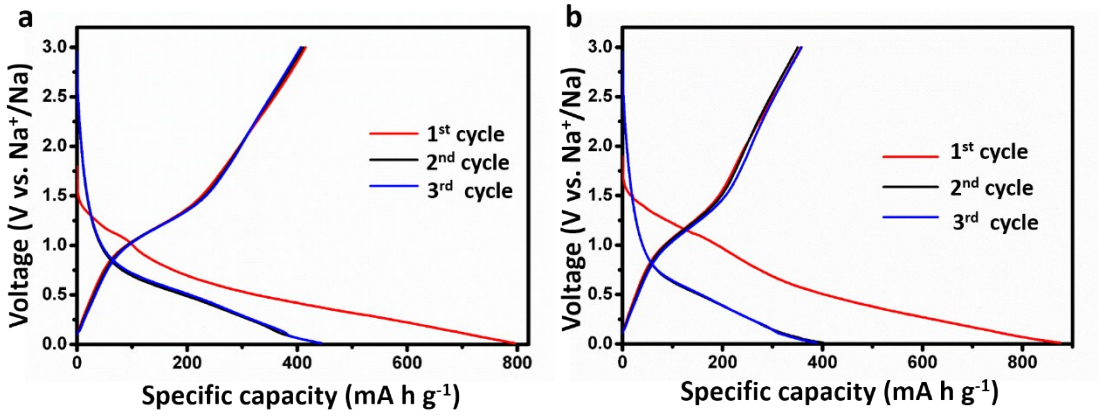

Fig. S10 Charge–discharge profiles of (a) SnO_2@NC-1 and (b) SnO_2@NC-1.5 at a current density of 50 mA g^{-1} respectively.

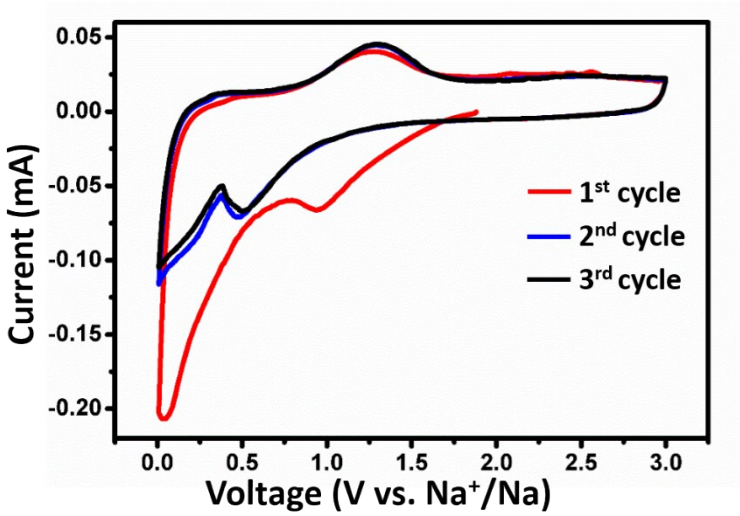

Fig. S11 Cyclic voltammetry curves at 0.1 mV s^{-1} sweep rate of SnO_2@NC-1.2 electrode for the first three cycles.

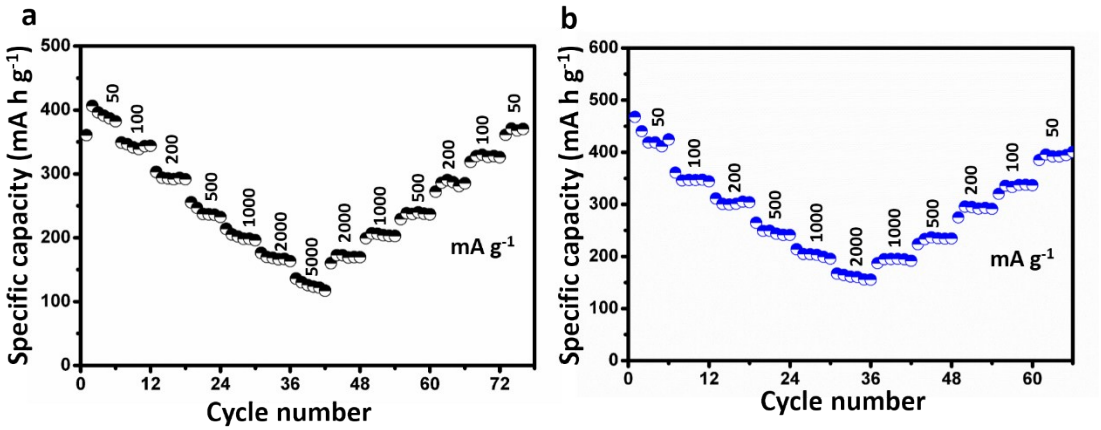

Fig. S12 Rate performance of (a) SnO_2@NC-1 and (b) SnO_2@NC-1.5 at various current densities, respectively.

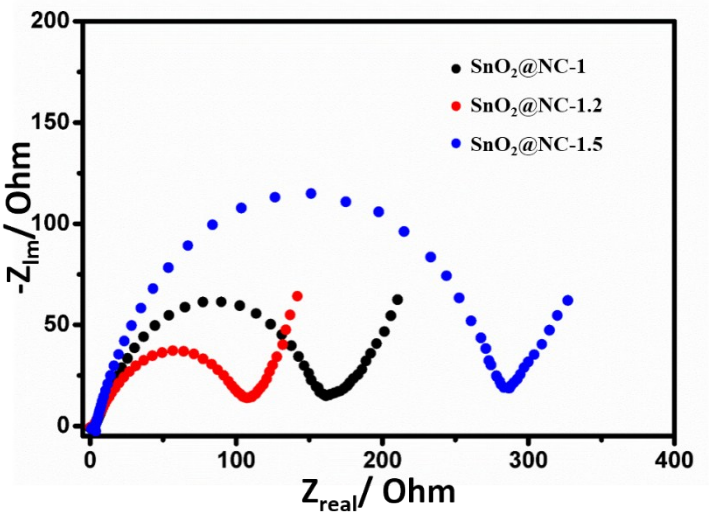

Fig. S13 Nyquist plots of SnO_2@NC electrode after 80 cycles at a current density of 1000 mA g^{-1}.

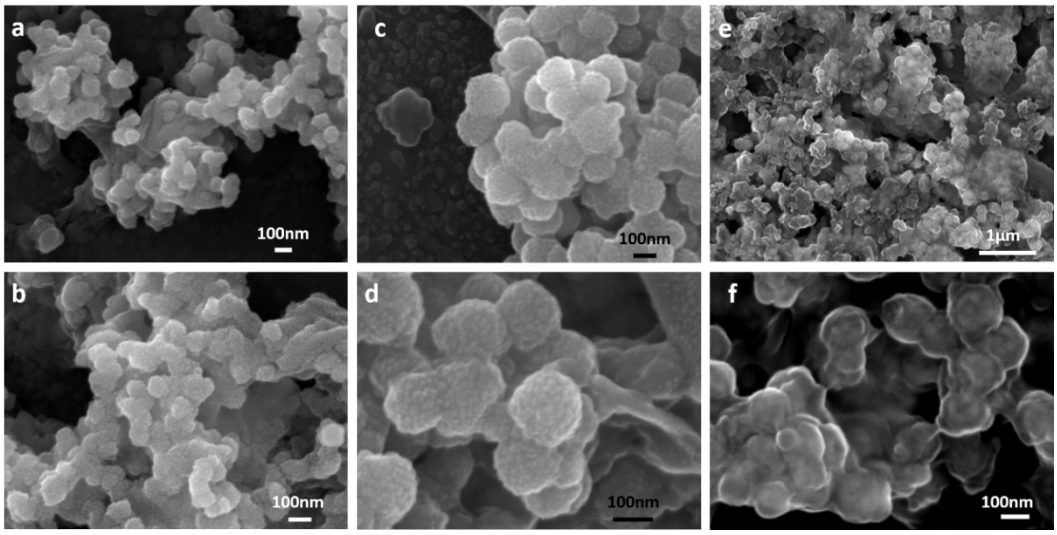

Fig. S14 SEM images of (a, b) SnO_2@NC-1, (c, d) SnO_2@NC-1.2 and (e, f) SnO_2@NC-2 electrode after 80 cycles at a current density of 1000 mA g^{-1}.

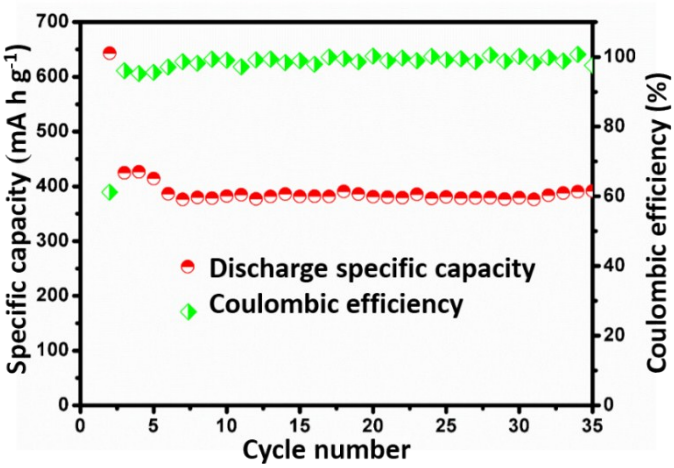

Fig. S15 Cycling performance and coulombic efficiency of SnO_2@NC-1.2 at a current density of 200 mA g^{-1}.

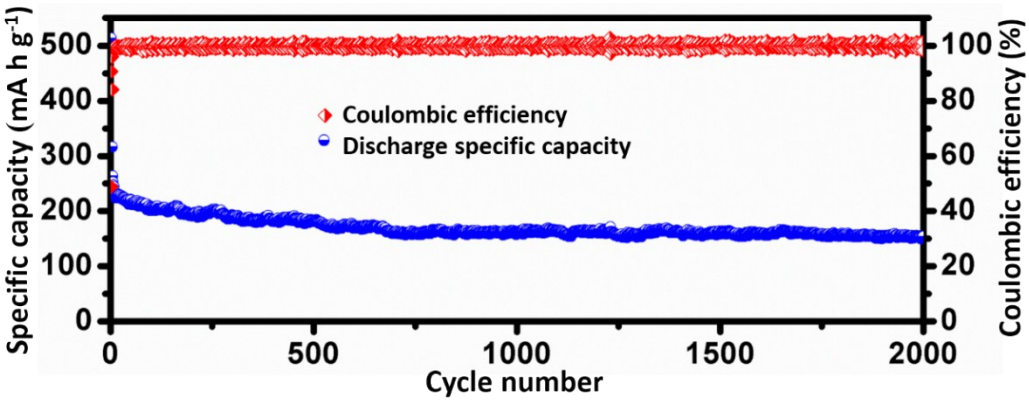

Fig. S16 Cycling performance and coulombic efficiency of SnO_2@NC-1.2 at a current density of 2000 mA g^{-1}. (The electrode was activated at a current density of 50 mA g^{-1} for the first three cycles.)

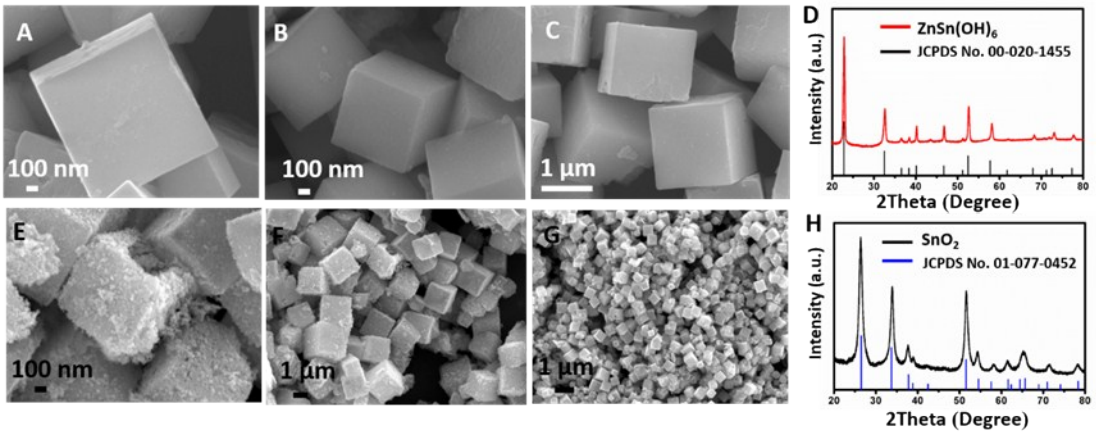

Fig. S17 (A, B, C) SEM images and (D) XRD pattern of $ZnSn(OH)_6$, (E, F, G) SEM images and (H) XRD pattern of the obtained SnO_2.

Table S2. Summary of the representative SnO_2-based anode materials for SIBs.

Materials	SnO_2 content wt.%	R_{low} [a] mA h g^{-1}/A g^{-1}	R_{high} [b] mA h g^{-1}/A g^{-1}	C [c] mA h g^{-1}/A g^{-1}/cycle	Ref
SnO_2/nitrogen-doped graphene	47	339/0.02	170/0.64	246/0.08/100	1
Amorphous SnO_2 /graphene aerogel	50.7	576.2/0.05	84.4/0.8	380.2/0.05/100	2
SnO_2/CNT	72	630.4/0.1	324.1/1.6	223.2/1.6/300	3
SnO_2/graphene	80	512/0.05	34/0.5	220/0.1/100	4
SnO_2–Graphene DualAerogel	70	448/0.05	184/1	221/0.2/200	5
SnO_2@3D graphene	71.5	551/0.05	210/0.8	432/0.1/200	6
Mesoporous NiO/SnO_2@rGO	74.6	No data	No data	254.8/0.05/40	7
Triple-walled SnO_2@N-doped carbon@SnO_2 nanotubes	70.4	586/0.025	320/0.4	492/0.025/50	8
SnO_2–carbon	60	459/0.08	133/5.12	371/0.08/200	9
Ultrafine SnO_2–RGO	76.4	480/0.05	125/1	330/0.1/150	10
Carbon/SnO_2/carbon cloth	No data	501/0.134	394/6.7	314/0.134/100	11
Al_2O_3/SnO_2/carbon cloth	No data	455/0.134	245/6.7	377/0.134/100	11
Mesoporous Sn/SnO_2	No data	500/0.05	209.8/1	372.3/0.05/50	12
Hollow SnO_2/SnS_2	No data	497.8/0.3	245.4/2.5	485.6/0.3/100	13
$Sn_2Nb_2O_7$/SnO_2@3D carbon nanocomposites	60.38	302/0.1	135/5	210/1/500 300/0.1/100	14
SnO_2/3D graphene	75	321/0.08	266/1.2	223/0.08/350	15
Mesoporous ultrafine SnO_2@N-dopped carbon	**76.4**	**560/0.05**	**236/2 180/5**	**255.4/1/1000 385/0.2/35**	**This work**

a) Rate performance at low current density; b) rate performance at high current density; c) cycling performance.

References

1. X. Xie, D. Su, J. Zhang, S. Chen, A. K. Mondal and G. Wang, *Nanoscale*, 2015, **7**, 3164-3172.
2. L. Fan, X. Li, B. Yan, J. Feng, D. Xiong, D. Li, L. Gu, Y. Wen, S. Lawes and X. Sun, *Adv. Energy Mater.*, 2016, **6**, 1502057.
3. J. Cui, Z. Xu, S. Yao, J. Huang, J. Huang, S. Abouali, M. A. Garakani, X. Ning and J. Kim, *J. Mater. Chem. A*, 2016, **4**, 10964-10973.
4. H. Lai, B. Feng, Y. Jiang, N. Shi, C. Liang, S. Chang, S. Guo, B. Cui and H. Cao, *Mater. Lett.*, 2016, **166**, 292-295.
5. Z. Li, J. Ding, H. Wang, K. Cui, T. Stephenson, D. Karpuzov and D. Mitlin, *Nano Energy*, 2015, **15**, 369-378.
6. L. Pei, Q. Jin, Z. Zhu, Q. Zhao, J. Liang and J. Chen, *Nano Res.*, 2014, **8**, 184-192.
7. Y. He, A. Li, C. Dong, C. Li and L. Xu, *Chem. Eur. J.*, 2017, **23**, 13724–13733.
8. J. Yue, W. Wang, N. Wang, X. Yang, J. Feng, J. Yang and Y. Qian, *J. Mater. Chem. A*, 2015, **3**, 23194-23200.
9. J. Ding, Z. Li, H. Wang, K. Cui, A. Kohandehghan, X. Tan, D. Karpuzov and D. Mitlin, *J. Mater. Chem. A*, 2015, **3**, 7100-7111.
10. Y. Wang, Y. Lim, M. Park, S. Chou, J. Kim, H. Liu, S. Dou and Y. Kim, *J. Mater. Chem. A*, 2014, **2**, 529-534.
11. Y. Liu, X. Fang, M. Ge, J. Rong, C. Shen, A. Zhang, H. A. Enaya and C. Zhou, *Nano Energy*, 2015, **16**, 399-407.
12. D. Tang, Q. Huang, R. Yi, F. Dai, M. L. Gordin, S. Hu, S. Chen, Z. Yu, H. Sohn, J. Song and D. Wang, *Eur. J. Inorg. Chem.*, 2016, **13-14**, 1950-1954.
13. K. Wang, Y. Huang, X. Qin, M. Wang, X. Sun and M. Yu, *ChemElectroChem*, 2017, **4**, 1-7.
14. P. Zhai, J. Qin, L. Guo, N. Zhao, C. Shi, E. Liu, F. He, L. Ma, J. Li and C. He, *J. Mater. Chem. A*, 2017, **5**, 13052-13061.
15. J. Lee, J. Song, Y. Cha, S. Fu, C. Zhu, X. Li, Y. Lin and M. Song, *Nano Res.*, 2017, 1-17.