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Electronic Supplementary Information

Cobalt sulfides/dodecahedral porous carbon as anode materials for Na-ion batteries

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Experiment details

Preparation of ZIF-67 nanocrystals.

The ZIF-67 nanocrystals were prepared according to the previously reported methods with a little modification. [1] Typically, 5 mmol cobalt nitrate hexahydrate $Co(NO_3)_2 \cdot 6H_2O$ and 20 mmol 2-methylimidazole were dissolved in 100 mL methanol, respectively. The latter clear organic solution was poured into the former pink Co^{2+} solution under strong magnetically stirring for 1 h to completely mix the component solutions. The homogeneous mixed solution aged at room temperature for 24 h, and then the pink precipitates were obtained. The pink ZIF-67 nanocrystals were collected by centrifugation, washed with ethanol several times, and finally dried at 60 °C overnight.

Synthesis of cs-CoS/DPC core-shell dodecahedron

Typically, ZIF-67 and pure sulfur powder was mixed with a weight ratio of 2:1 by ground in agate mortar, and then transferred into a combustion boat. The boat was heated in Ar atmosphere from room temperature to 155 °C at the heating rate of 5 °C min^{-1} and maintained for 5 h, and then the temperature was elevated to 600 °C with a heating rate of 5 $^oC\ min^{-1}$ and maintained for another 5 h.

Materials Characterization

X-ray diffraction patterns (XRD) were collected by a Rigaku3014 using graphite-monochromated Cu Karadiation. Field-emission scanning electron microscopy (SEM) images taken on a Nova NanoSEM 230 and transmission electron microscopy (TEM) images obtained by using a Tecnai G2 20ST were employed to

observe the morphology of the as-prepared samples. Raman spectra (Raman) were recorded on a Jobin-Yvon LabRAM HR-800 Raman spectrometer.

Electrochemical tests

Electrochemical experiments were carried out by using CR-2032 type coin cells. To prepare the working electrode, the cs-CoS/DPC material was ground with pure Super P as conductive additive and carboxymethyl cellulose (CMC) as binder with a weight ratio of 7:2:1 in distilled water by using mortar. The resulting homogeneous slurry was casted onto pure Cu foil and then dried in a vacuum oven at 80 ^{o}C for 12 h. The dried electrodes were punched into round discs with a diameter of 1.0 cm and the mass loading of active materials cs-CoS/DPC on the electrode was 1.0-1.5 mg cm^{-2}. The electrolyte employed in this work was 1 M $NaClO_4$ in a solvent mixture of ethylene carbonate/diethyl carbonate/fluoroethylene carbonate (EC/DEC/FEC, 1:1:0.1, v/v/v). The sodium metal and whatman glass fiber member (GF/D) were used as counter electrode and separator, respectively. The coin cells were assembled in an argon-filled glovebox (Universal 2440/750) in which oxygen and water contents were less than 1 ppm. Galvanostatic charge/discharge test were conducted with a battery test system. Electrochemical tests were carried out at room temperature. Cyclic voltammetry (CV) was tested at a scan rate of 0.1 mV s^{-1} in the fixed voltage range of 0.01 V-3 V at room temperature.

1. R. Wu, D. P. Wang, X. Rui, B. Liu, K. Zhou, A. W. Law, Q. Yan, J. Wei and Z. Chen, *Advanced materials*, 2015, 27, 3038-3044.

Figure S1

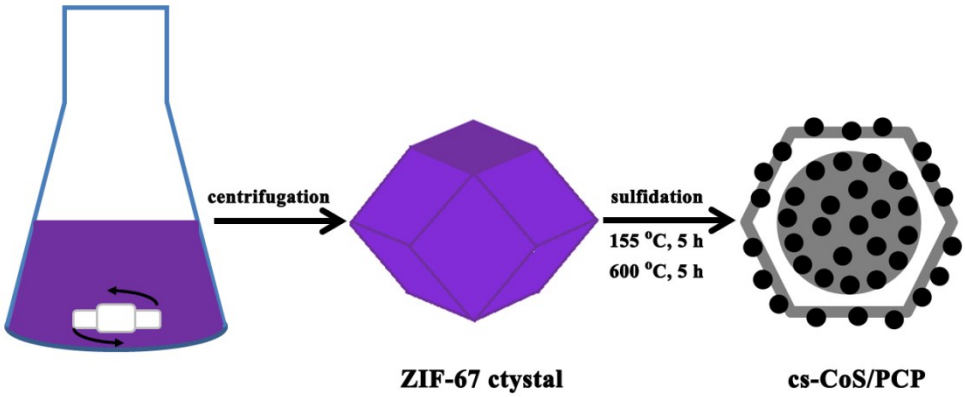

Fig S1. Schematic illustration for the synthesis of the 3D cs-CoS/DPC composite (the black dots represent the CoS particles, the grey part express the carbon core and shell matrix).

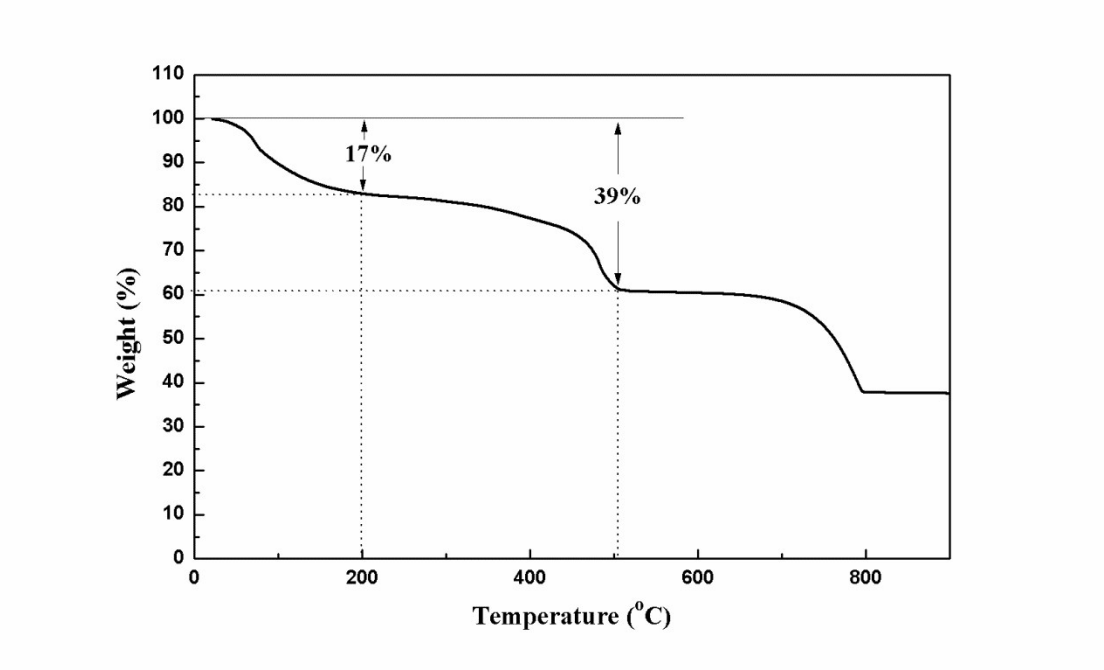

Fig. S2 TGA curve of CoS/DPC composite under air atmosphere with a heating rate of 10 ^{o}C min^{-1}

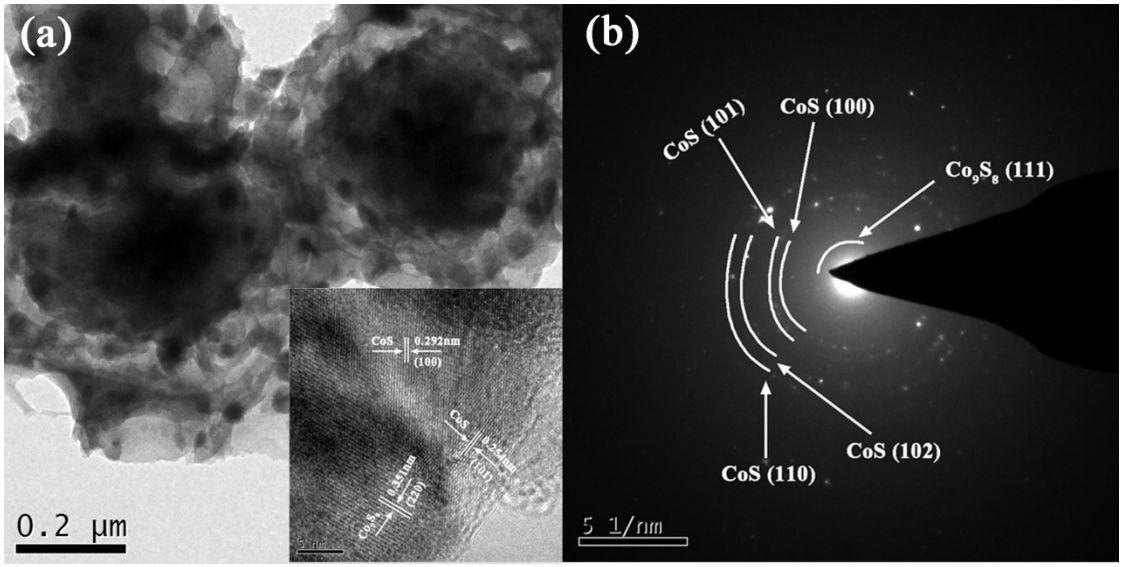

Fig. S3 TEM image and corresponding SAED patterns of cs-Co_xS_y/DPC (inset: HRTEM image)

Table S1 Sodium storage properties of Co_xS_y/C reported recently

Materials	Discharge plateau voltage(V)	Initial discharge capacity (mAh g^{-1})	Electrochemical Performance (mAh g^{-1})	Reaction mechanism	Reference
Co_xS_y/C	0.8	600	380 (50^{th}) at 0.5 A g^{-1}	Conversion	This Work
Co_3S_4-PNS/GS	0.9	890	329 (50^{th}) at 0.5 A g^{-1}	Insertion	1
CoS_2	1.4	790	194 (100^{th}) at 0.1A g^{-1}	Conversion	2
CoS_2-MWCNT	1.4	800	568 (100^{th}) at 0.1A g^{-1}	Conversion	2
bare $Co_{1-x}S$	0.7	673	~10 (50^{th}) at 0.5 A g^{-1}	Conversion	3
Co_9S_8/C	0.5	689	404 (50^{th}) at 0.5 A g^{-1}	Conversion	3
∗PNS: porous nanosheets; GS: graphene sheets; MWCNT: multi walled carbon nanotubes					

References

1. Y. Du, X. Zhu, X. Zhou, L. Hu, Z. Dai and J. Bao, Co_3S_4 porous nanosheets embedded in graphene sheets as high-performance anode materials for lithium and sodium storage, *J. Mater. Chem. A*, 2015, **3**, 6787-6791.
2. Z. Shadike, M. H. Cao, F. Ding, L. Sang and Z. W. Fu, Improved electrochemical performance of CoS_2-MWCNT nanocomposites for sodium-ion batteries, *Chem. commun.*, 2015, **51**, 10486-10489.
3. Y. N. Ko and Y. C. Kang, Co_9S_8-carbon composite as anode materials with improved Na-storage performance, *Carbon*, 2015, **94**, 85-90.