Supporting information

Fabrication of N, S co-doped Carbon Nanotube Hollow Architecture Confining with CoS_2 Anode: Towards Li and Na Storage

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1. Experimental

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1.1 Synthesis of ZIF8. For the synthesis of ZIF8 polyhedron, $Zn(NO_3)_2 \cdot 6H_2O$ (7.44 g, 0.025 mol) and 2-methylimidazole (defined as 2-MeIm; 7.72 g, 0.094mol) were dissolved into 100 mL methanol (defined as MeOH) to obtain two clear solutions, separately. Subsequently, the solution of 2-MeIm was slowly added to the solution of $Zn(NO_3)_2 \cdot 6H_2O$. The hybrid solution was stirred at room temperature for 24 h, and the white precipitates were obtained by centrifugation. After that, the ZIF8 products were dried at 70 °C for 8 h.

1.2 Synthesis of core-shell ZIF8@ZIF67. The as-prepared ZIF8 (1.0 g) was well-dispersed in 100 mL MeOH by ultrasonication. $Co(NO_3)_2 \cdot 6H_2O$ (7.275 g, 0.025 mol) and 2-MeIm (7.72 g, 0.094mol) were dissolved in 150 mL of MeOH to form two transparent solutions, respectively. Subsequently, the solution of $Co(NO_3)_2 \cdot 6H_2O$ was poured into the ZIF8 suspension, and the solution of 2-MeIm was further incorporated into the compounded solution. After stirring at room temperature for overnight, the purple sediments were collected by centrifugation. After that, the ZIF8@ZIF67 products was dried at 70 °C for 8 h.

1.3 Synthesis of Co/NCNHF. The obtained ZIF-8@ZIF-67 was annealed at 900 °C for 4 h with the flow of Ar and cooled down naturally to room temperature. The black powder of N-doped carbon framework with embedded Co nanoparticles and rooted carbon nanotubes (defined as Co/NCNHF) was obtained.

1.4 Preparation of CoS_2/NSCNHF. The obtained Co/NCNHF was used as the template for the formation of N, S co-doped carbon framework with embedded CoS_2 nanoparticles as well as rooted carbon nanotubes (defined as CoS_2/NSCNHF). Typically, two porcelain boats placed separately with 0.4 g of S powder (the front area, close to Ar inlet) and 0.1 g of Co/NCNHF (the back area, close to Ar outlet)

were put into a tube furnace with Ar flow, at a distance of 10 cm. The front area was kept at 200 °C for 2 h. The back area was heated to 400 °C and maintained for 2 h. The product of CoS_2/NSCNHF was obtained after the natural cooling of furnace. Bare CoS_2 powders were provided by Shanghai Macklin Biochemical Co., Ltd.

1.5 Materials characterization. The crystal structure of the samples was investigated by X-ray diffraction (XRD) (TTR-III, Japan) using Cu Kα radiation, and the chemical composition of samples was analyzed by X-ray photoelectron spectroscopy (XPS) (ESCALAB 250, USA). Scanning electron microscopy (SEM) (JSM-6700F, Japan) and transmission electron microscopy (TEM) (JEM-2100F, Japan) were employed to observe the morphology of samples. N_2 adsorption/desorption experiments were performed on the surface area and porosity analyzer (ASAP 2020).

1.6 Electrochemical Measurements. The electrochemical cycling tests were conducted in CR2032 coin-type cells, which were assembled in an Ar filled glove box. The viscous slurry containing active materials, carbon black (Super-P), and polyvinylidene fluoride (PVDF) with the mass ratio of 7:2:1 was prepared and coated on a Cu foil via doctor-blade method, which was further dried in the vacuum oven at 80 °C for 12 h. For LIBs, Li foil was used as both reference and counter electrodes. Electrolyte and separator were 1.0 M LiPF6 in ethyl carbonate/diethyl carbonate (1:1 v/v ratio) and commercial Celgard 2325, respectively. For SIBs, Na foil was used as both reference and counter electrodes. Electrolyte and separator were 1.0 M $NaCF_3SO_3$ in diethylene glycol dimethyl ether (DEGDME) and glass fibers. The electrolytes of 1.0 M $NaClO_4$ in ethylene carbonate/diethyl carbonate (EC/DEC, 1:1 v/v ratio) and propylene carbonate (PC) were also used. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) characterizations were performed on CHI660E electrochemical workstation. Galvanostatic discharge/charge tests were

conducted on a Land battery tester (Land CT 2001A, Wuhan, China) in the voltage range of 0.01-3 V (vs Li/Li^+ and Na/Na^+) and 0.1-3 V (vs Na/Na^+).

2. Results and discussion

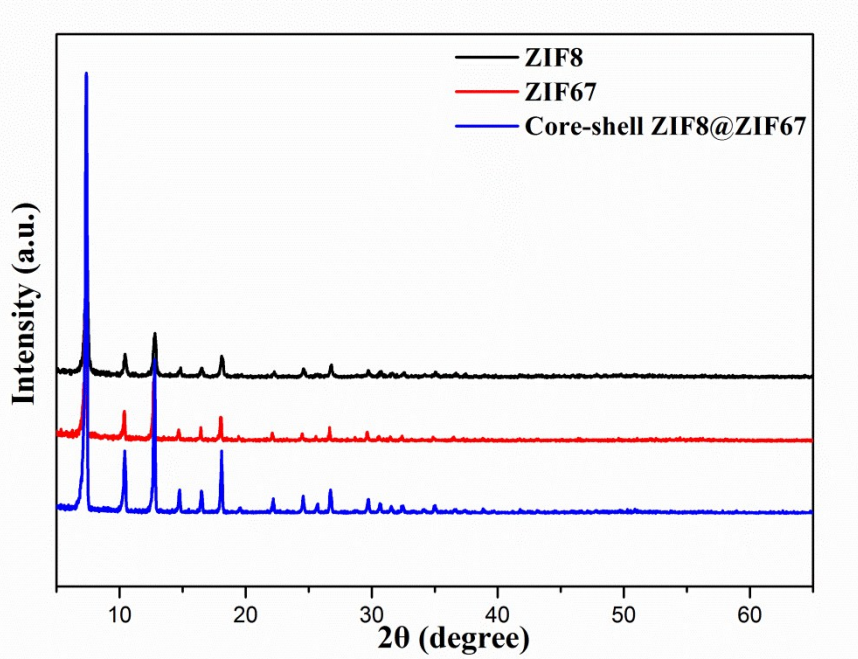

Fig. S1. XRD results of ZIF8, ZIF67 and core-shell ZIF8@ZIF67.

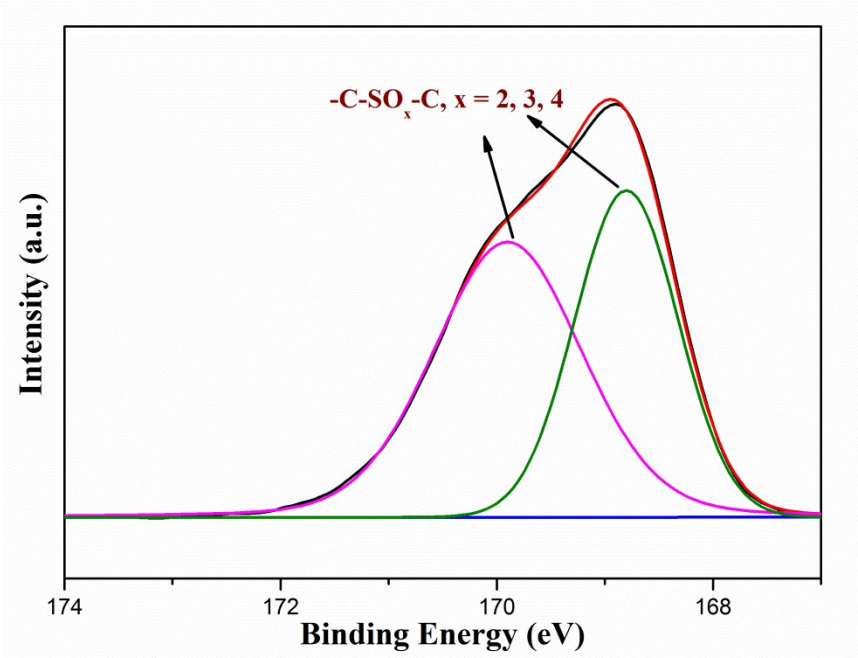

Fig. S2. S 2p spectrum of CoS_2/NSCNHF.

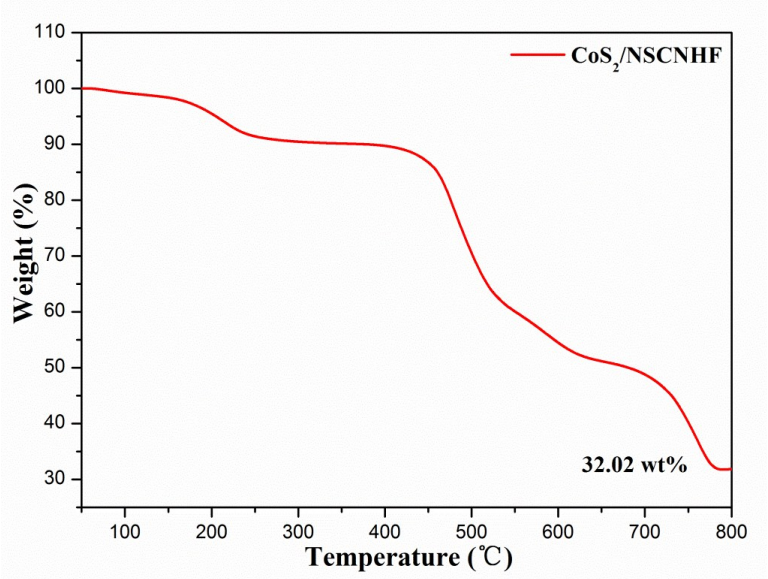

Fig. S3. TGA curve under air atmosphere.

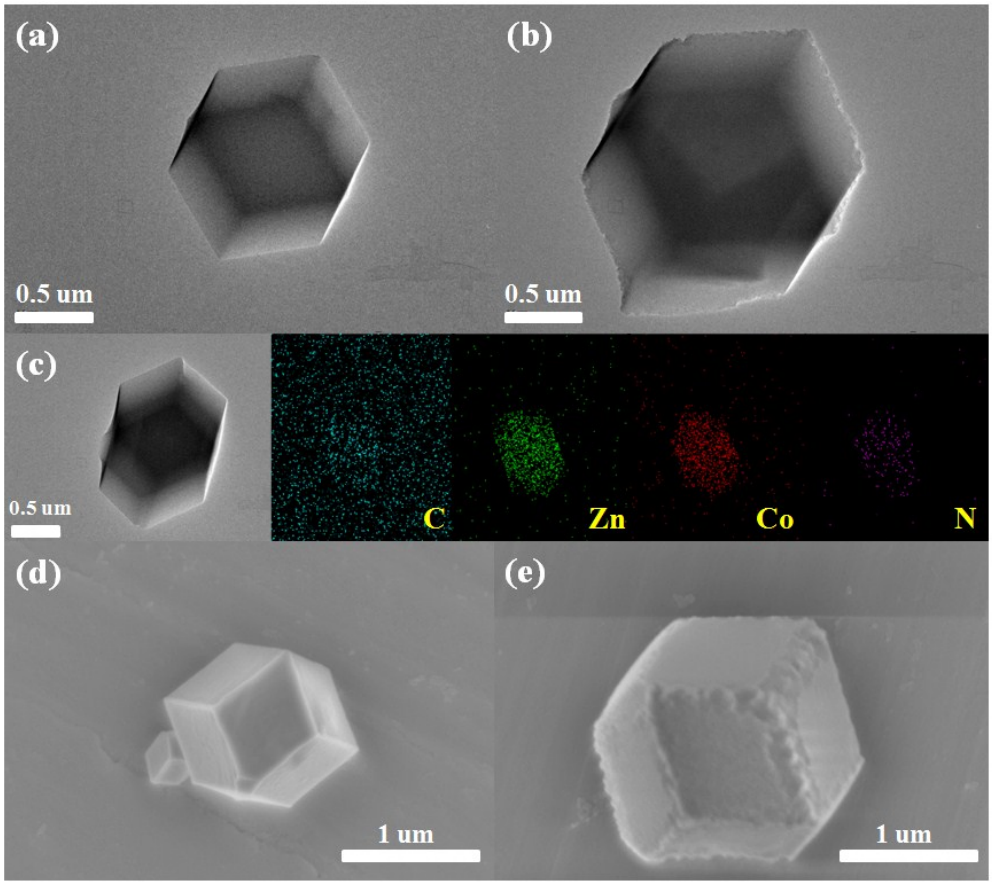

Fig. S4. (a and b) TEM images of ZIF8 and ZIF8@ZIF67; (c) TEM elemental mapping of ZIF8@ZIF67; (d and e)SEM images of ZIF8 and ZIF8@ZIF67.

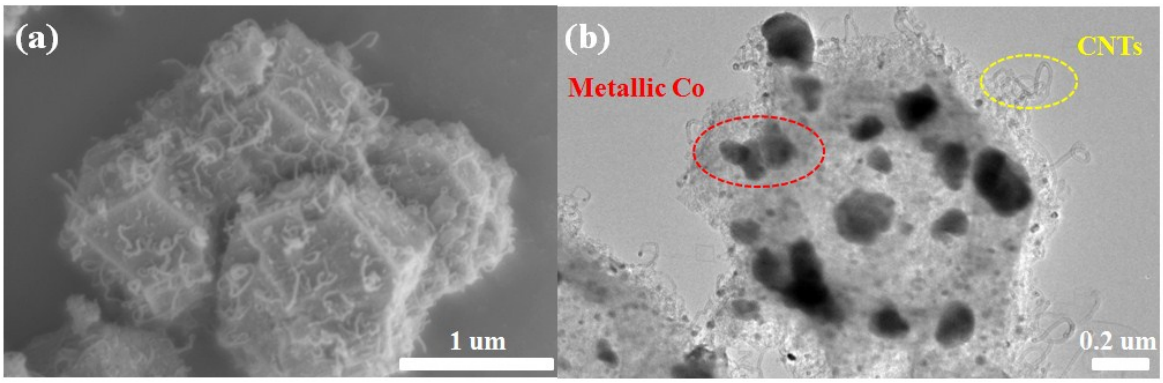

Fig. S5. (a) SEM and (b) TEM images of Co/NCNHF.

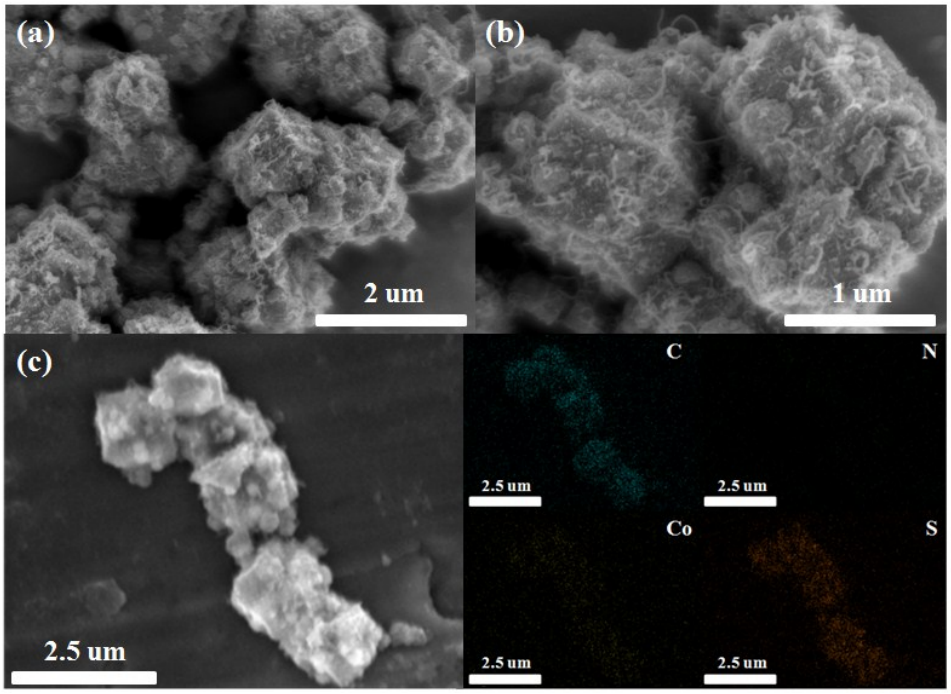

Fig. S6. (a and b) SEM images under different magnification and (c) elemental mapping results of CoS_2/NSCNHF.

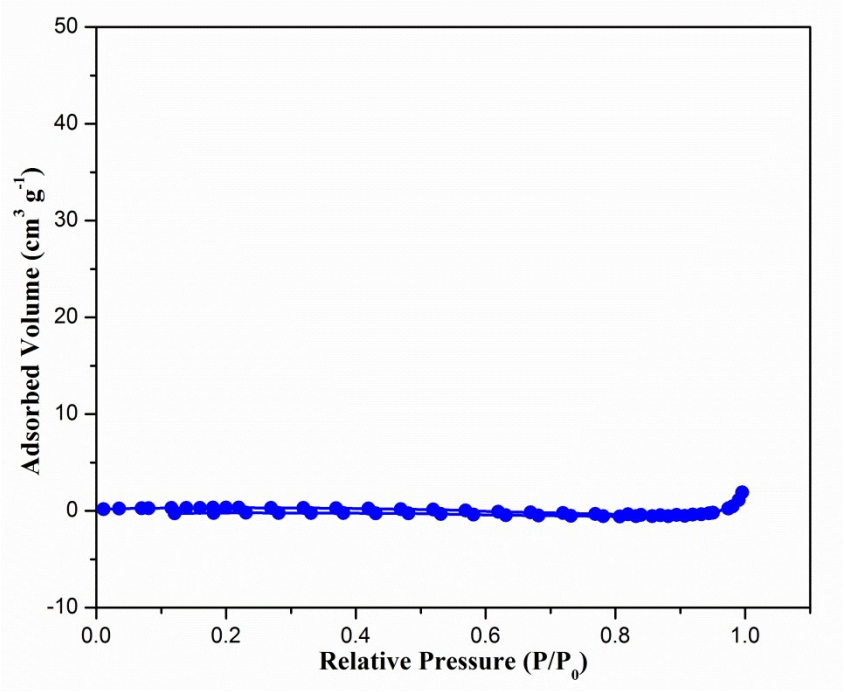

Fig. S7. N_2 adsorption/desorption curve of bare CoS_2.

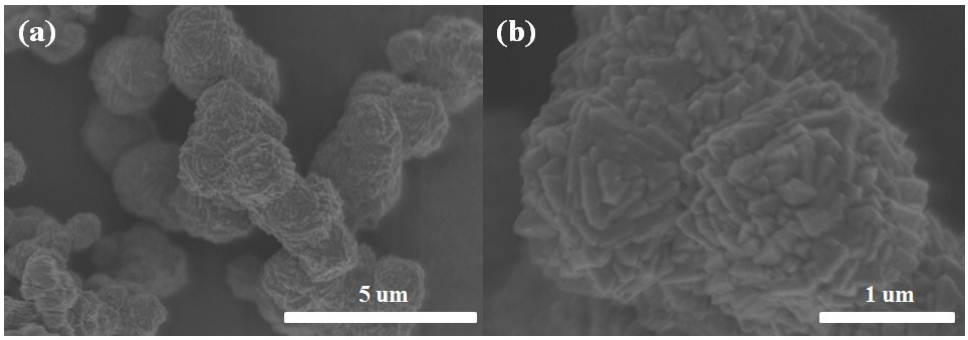

Fig. S8. SEM images of bare CoS_2.

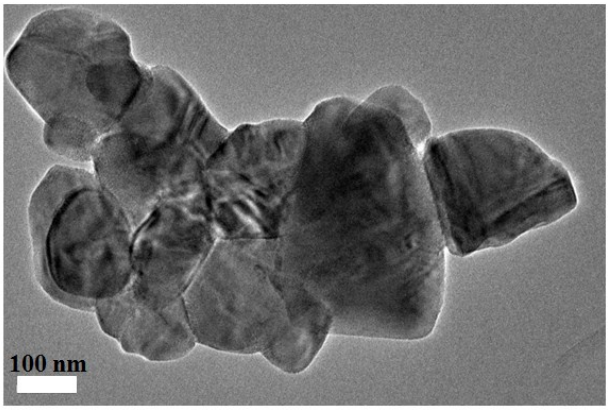

Fig. S9. TEM images of bare CoS_2.

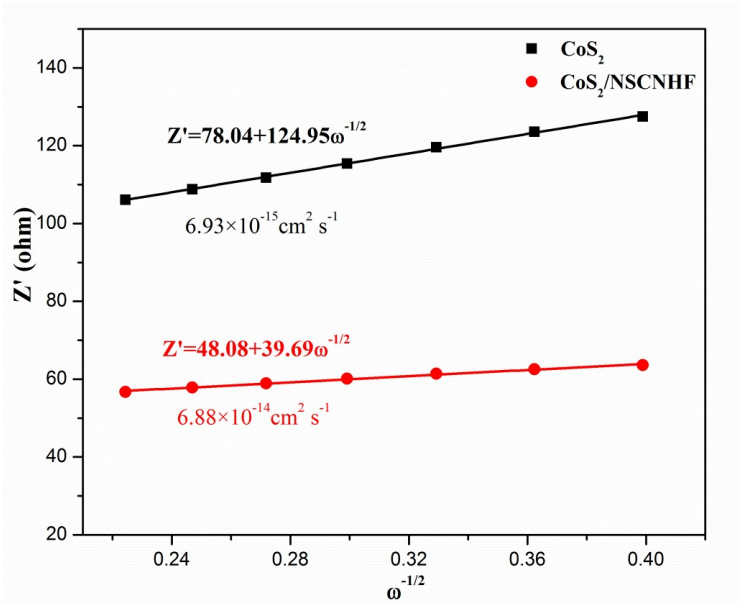

Fig. S10. The linear fitting plots between Z' and $\omega^{-1/2}$.

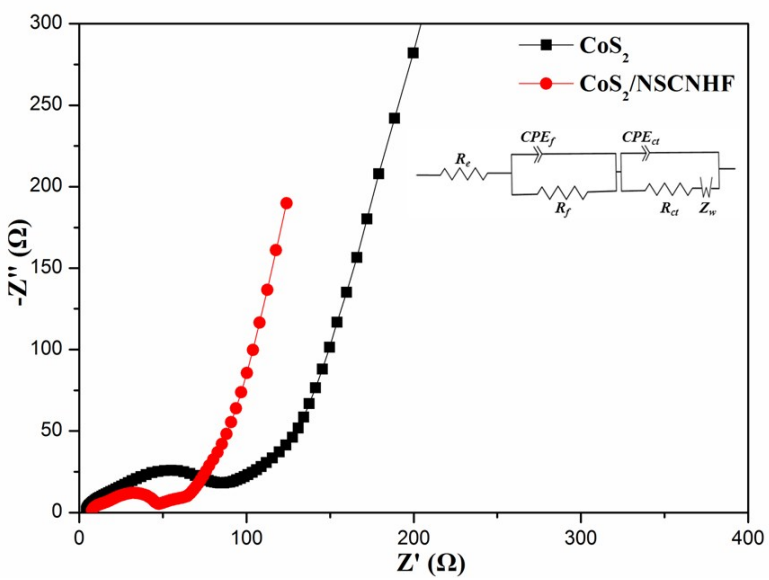

Fig. S11. Electrochemical impedance spectra (EIS) of bare CoS_2 and CoS_2/NSCNHF electrode after 21 cycles.

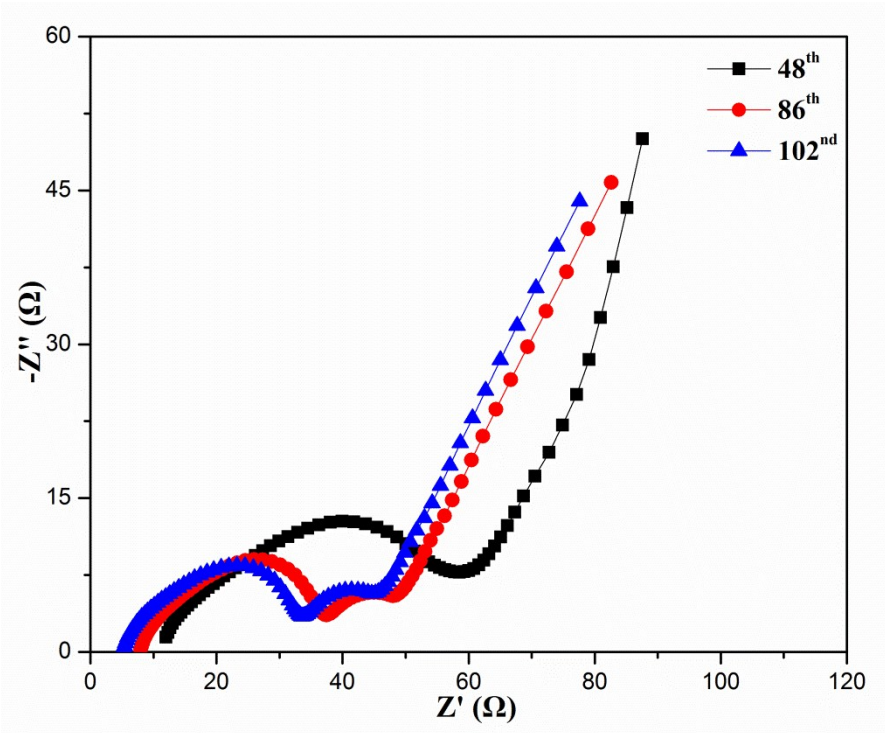

Fig. S12. Electrochemical impedance spectra (EIS) of CoS_2/NSCNHF electrode at different cycle.

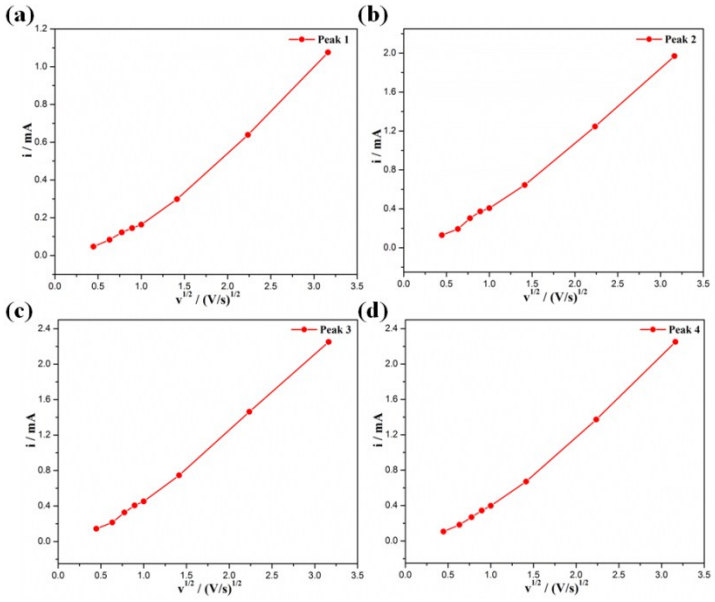

Fig. S13. i vs. $v^{1/2}$ plots at each redox peak of CV curves for Li storage (peak current: i, scan rate: v).

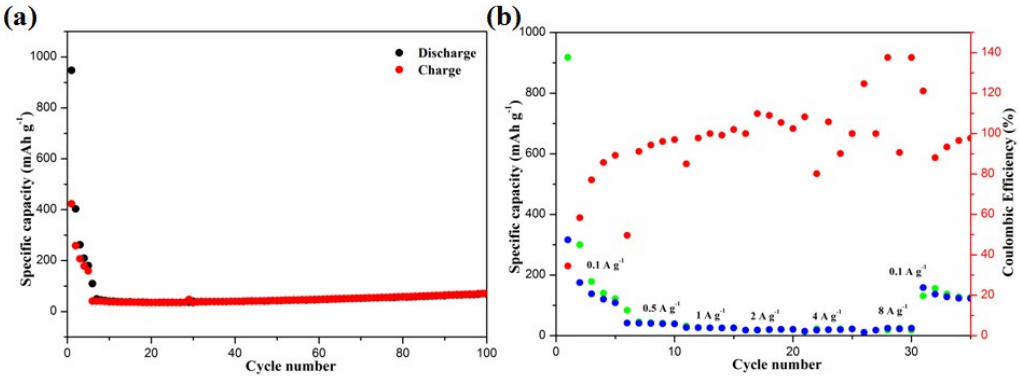

Fig. S14. Sodium storage performance of CoS_2.

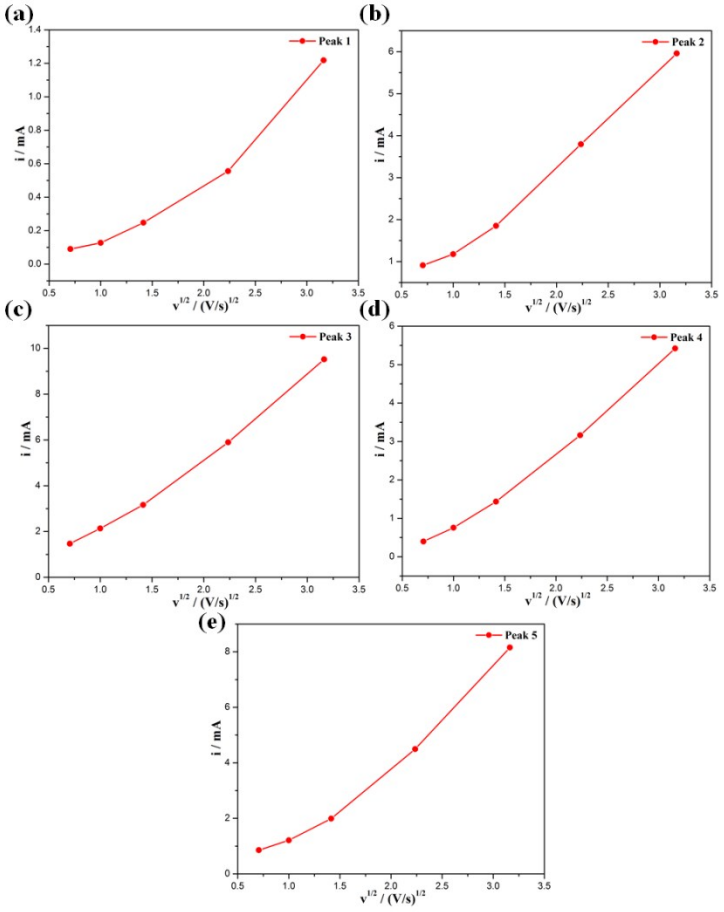

Fig. S15. i vs. $v^{1/2}$ plots at each redox peak of CV curves for Na storage (peak current: i, scan rate: v).