## **Electronic Supplementary Information**

## Rational design of multi-shelled CoO/Co<sub>9</sub>S<sub>8</sub> hollow microspheres for high-performance hybrid supercapacitors

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**Fig. S1.** SEM images(a-e) and TEM (b-f) images of the carbon spheres (a and b), the core-shelled  $CS@Co_2CO_3(OH)_2$  (c and d) and the multi-shelled  $Co_3O_4$  hollow spheres (e and f), respectively.



Fig. S2. The XRD patterns of the CS@Co<sub>2</sub>CO<sub>3</sub>(OH)<sub>2</sub> precursor.



Fig. S3. TG and DSC curves of the mixture of  $Co_3O_4$  and S powder.



**Fig. S4.** XRD patterns of the multi-shelled cobalt oxides/sulfides composite hollow spheres.



Fig. S5. SEM images of the multi-shelled CoO/CoS (a) and the CoS/Co $_9$ S<sub>8</sub> (b) hollow spheres.



**Fig. S6.** Nitrogen adsorption-desorption isotherms (a) and pore size distribution (b) of the multi-shelled CoO  $/Co_9S_8$  composite hollow spheres.



Fig. S7. The elemental mapping results from SEM of CoO /  $Co_9S_8$  microspheres.



Fig. S8. TG curves of the CoO/  $Co_9S_8$  powders measured in air with a ramp rate of 10  $^{\circ}C$  min<sup>-1</sup>.



**Fig. S9.** XRD pattern (a), SEM images (b and c) and TEM image (d) of the core-shelled CS@CoO microspheres.



Fig. S10. SEM image (a) and TEM image (b) of the multi-shelled CoO hollow spheres.



**Fig. S11.** CV curves of multi-shelled cobalt oxides/sulfides hollow microspheres within a non-Faradaic potential window (vs. SCE) at different scan rates. (a)  $CoO/Co_9S_8$ , (b)  $CoS/Co_9S_8$ , (c) CoO/CoS, (d) CoO.



**Fig. S12.** CV curves performed at different scan rates (a) and GCCD curves at different current densities (b) of the CS@CoO microspheres.



**Fig. S13.** CV curves performed at different scan rates of the multi-shelled cobalt oxides/sulfides composite hollow microspheres. (a)  $Co_9S_8/CoO$ , (b)  $CoS/Co_9S_8$ , (c) CoO/CoS, (d) CoO.



Fig. S14. GCCD curves performed at different current densities of the multi-shelled cobalt oxides/sulfides composite hollow microspheres. (a) CoO, (b) CoO/CoS, (c)  $CoS/Co_9S_8$ , (d) CoO/  $Co_9S_8$ .



**Fig. S15.** The capacity retention at different current densities of the four multishelled cobalt oxides/sulfides composite hollow microspheres and CS@CoO microspheres.



**Fig. S16.** Nyquist plots of theelectrochemical impedance spectroscopy (EIS) spectra for four multi-shelled cobalt oxides/sulfides composite hollow microspheres and CS@CoO microspheres.



Fig. S17. Long-term cycling performance of multi-shelled CoO/Co $_9$ S $_8$  at 50 A g<sup>-1</sup>.



**Fig. S18.**The CV curve of the AC electrode at 10 mV s<sup>-1</sup> (a) and the galvanostatic charge–discharge curve of the AC electrode at a current of  $1 \text{ A g}^{-1}$  (b).