Electronic Supplementary Information

Rational design of multi-shelled CoO/Co₉S₈ 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$_2$CO$_3$(OH)$_2$ (c and d) and the multi-shelled Co$_3$O$_4$ hollow spheres (e and f), respectively.

**Fig. S2.** The XRD patterns of the CS@Co$_2$CO$_3$(OH)$_2$ precursor.
Fig. S3. TG and DSC curves of the mixture of Co₃O₄ 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/Co₉S₈ (b) hollow spheres.
Fig. S6. Nitrogen adsorption-desorption isotherms (a) and pore size distribution (b) of the multi-shelled CoO/Co$_9$S$_8$ composite hollow spheres.

Fig. S7. The elemental mapping results from SEM of CoO/Co$_9$S$_8$ microspheres.
Fig. S8. TG curves of the CoO/Co$_9$S$_8$ powders measured in air with a ramp rate of 10 $^\circ$C min$^{-1}$.

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$_9$S$_8$, (b) CoS/Co$_9$S$_8$, (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$_9$S$_8$/CoO, (b) CoS/Co$_9$S$_8$, (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/CoS$_8$, (d) CoO/Co$_9$S$_8$. 
Fig. S15. The capacity retention at different current densities of the four multi-shelled cobalt oxides/sulfides composite hollow microspheres and CS@CoO microspheres.

Fig. S16. Nyquist plots of the electrochemical 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$^{-1}$.

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