Electronic Supplementary Information

Heterogeneous NiS/NiO multi-shelled hollow microspheres with enhanced electrochemical performances for hybrid-type asymmetric supercapacitors

**Fig. S1.** The EDX spectra of the annealing products obtained from different ratio of NiO and S.
Fig. S2. TG curves of the nickel oxide/sulfide compounds. NiO can be oxidized to Ni$_2$O$_3$ at around 400 °C while Ni$_3$O$_4$ will decompose to NiO at higher temperatures. The final residues are all NiO for the tests.
Fig. S3. The XRD analysis of two obtained samples when the mole ratio of 2:1, 1:2 (NiO:S) are applied.
**Fig. S4** XPS spectrum of Ni 2p of (NiO)0.1(NiS)0.9 multi-shelled hollow microspheres.

**Fig. S5.** SEM (a) and TEM (b) images of the multi-shelled (NiO)_{0.85}(NiS)_{0.15} hollow microspheres.
Fig. S6. SEM (a) and TEM (b) images of the multi-shelled (NiO)$_{0.65}$(NiS)$_{0.35}$ hollow microspheres.

Fig. S7. SEM (a) and TEM (b) images of the multi-shelled (NiO)$_{0.4}$(NiS)$_{0.6}$ hollow microspheres.
Fig. S8. SEM image (a), TEM image (b), HRTEM image (c), SAED patterns (d) and elemental mapping images (e-g) of the multi-shelled NiS hollow microspheres.
Fig. S9. Nitrogen adsorption-desorption isotherms and corresponding pore size distribution curves (the inset) of the NiO and (NiO)$_{0.1}$(NiS)$_{0.9}$ multi-shelled hollow microspheres.

Fig. S10. Elemental mapping images (a-d) of (NiO)$_{0.1}$(NiS)$_{0.9}$ hollow microspheres.
Fig. S11. CV curves of multi-shelled nickel-based hollow microspheres within a non-Faradaic potential window (vs. SCE) at different scan rates. (a) NiO, (b) (NiO)$_{0.85}$(NiS)$_{0.15}$, (c) (NiO)$_{0.65}$(NiS)$_{0.35}$, (d) (NiO)$_{0.4}$(NiS)$_{0.6}$, (e) (NiO)$_{0.1}$(NiS)$_{0.9}$ and (f) NiS.
Fig. S12. CV curves performed at different scan rates of four samples. (a) NiO, (b) (NiO)$_{0.85}$(NiS)$_{0.15}$, (c) (NiO)$_{0.65}$(NiS)$_{0.35}$, (d) (NiO)$_{0.4}$(NiS)$_{0.6}$, (e) (NiO)$_{0.1}$(NiS)$_{0.9}$ and (f) NiS.
Fig. S13. The charge-discharge curves at different current densities of four samples. (a) NiO, (b) (NiO)_{0.85}(NiS)_{0.15}, (c) (NiO)_{0.65}(NiS)_{0.35}, (d) (NiO)_{0.4}(NiS)_{0.6}, (e) (NiO)_{0.1}(NiS)_{0.9} and (f) NiS.
Fig. S14. CV curve at 10 mV s\(^{-1}\) (a) and the galvanostatic charge–discharge curve at current density of 2 A g\(^{-1}\) (b) of the AC electrode.