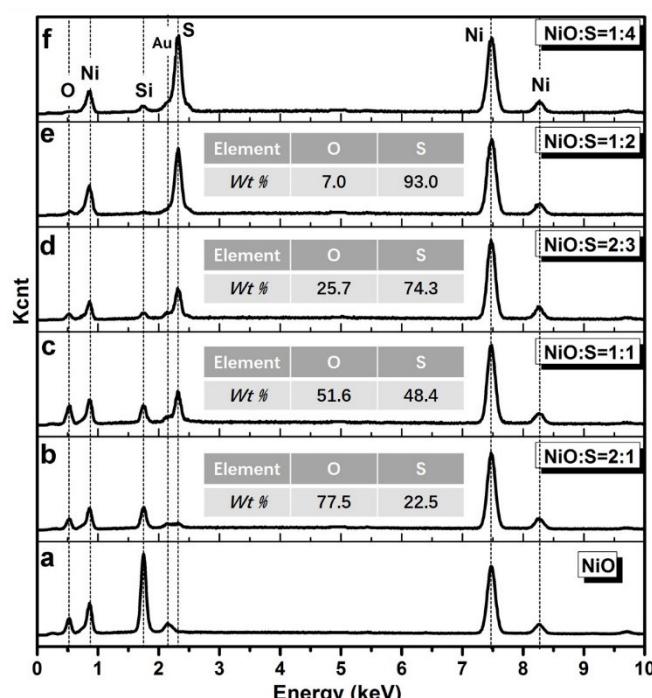
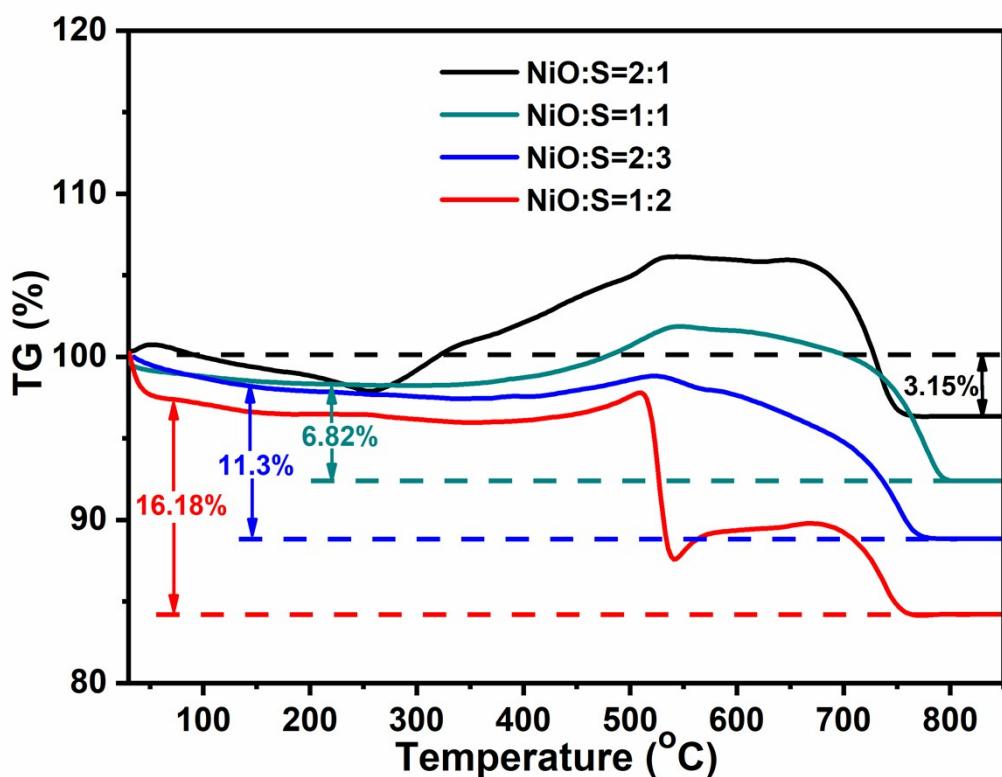


Electronic Supplementary Information

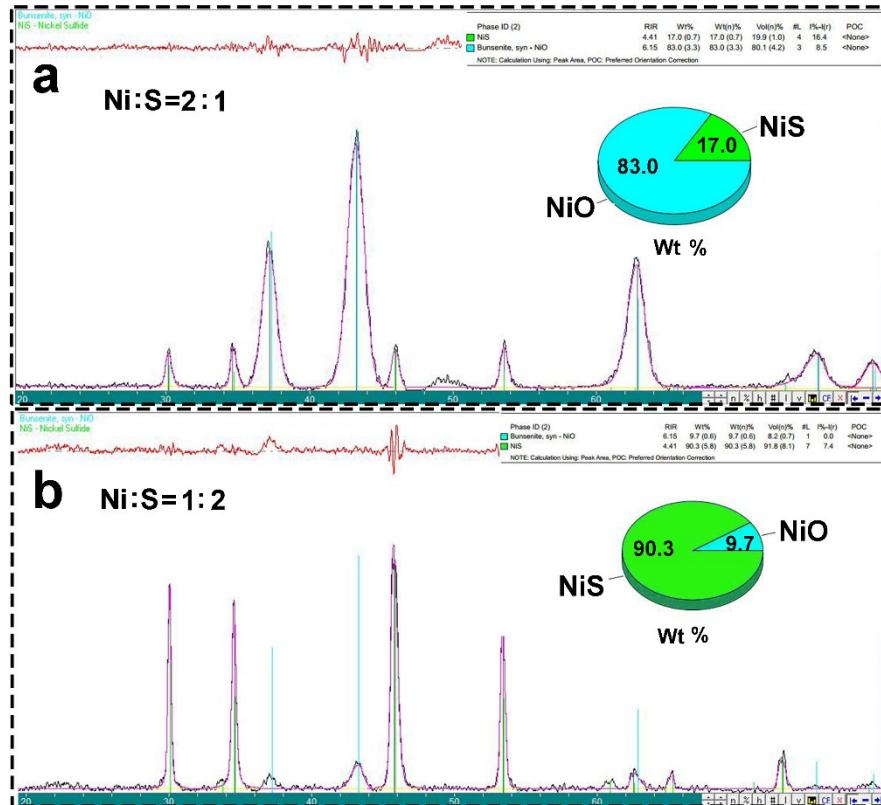
**Heterogeneous NiS/NiO multi-shelled hollow microspheres  
with enhanced electrochemical performances for hybrid-type  
asymmetric supercapacitors**



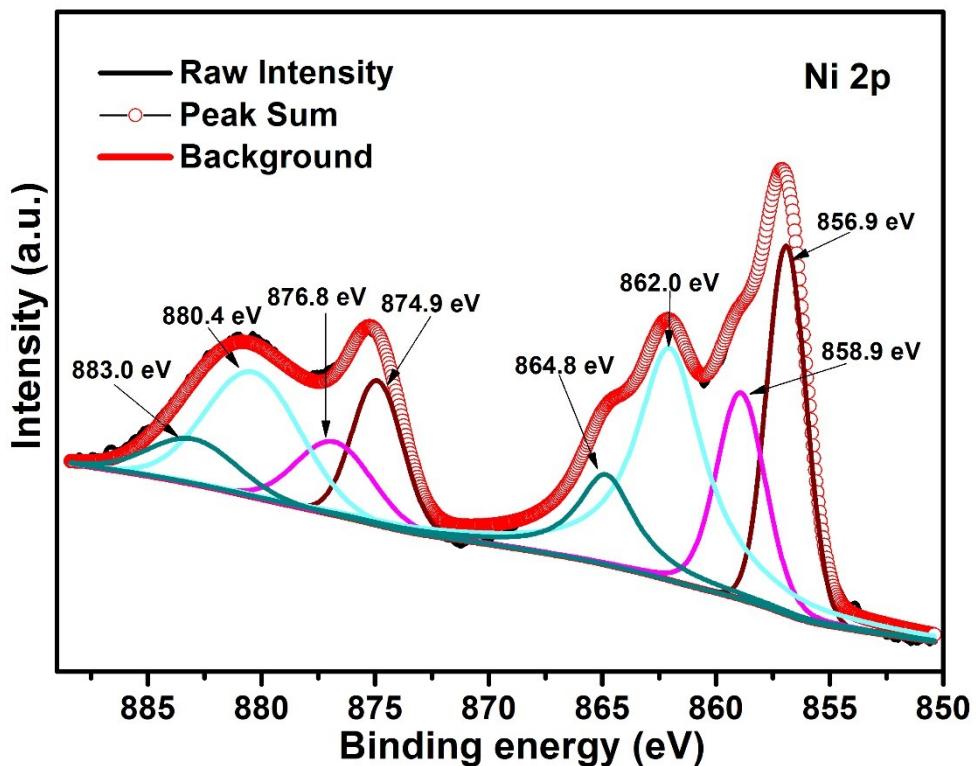
**Fig. S1.** The EDX spectra of the annealing products obtained from different ratio of NiO and S.



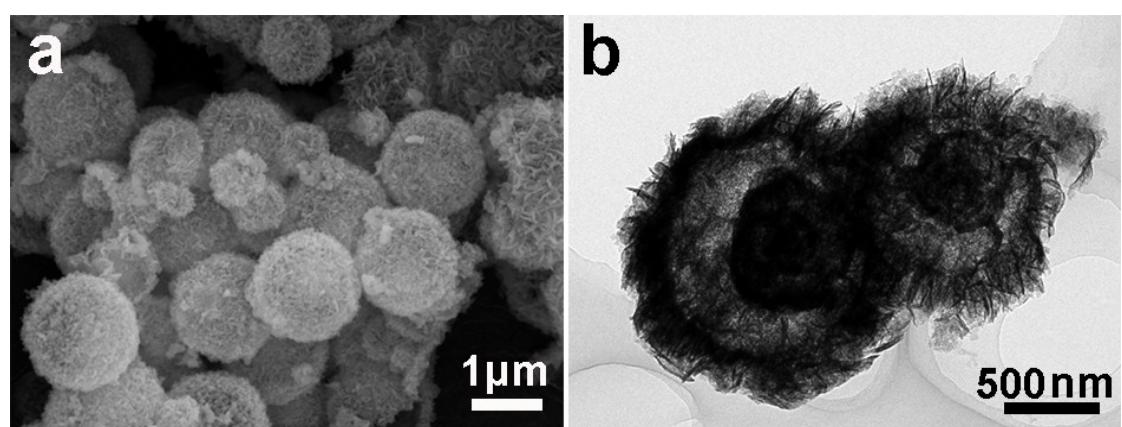
**Fig. S2.** TG curves of the nickel oxide/sulfide compounds. NiO can be oxidized to  $\text{Ni}_2\text{O}_3$  at around 400 °C while  $\text{Ni}_2\text{O}_3$  will decompose to NiO at higher temperatures. The final residues are all NiO for the tests.



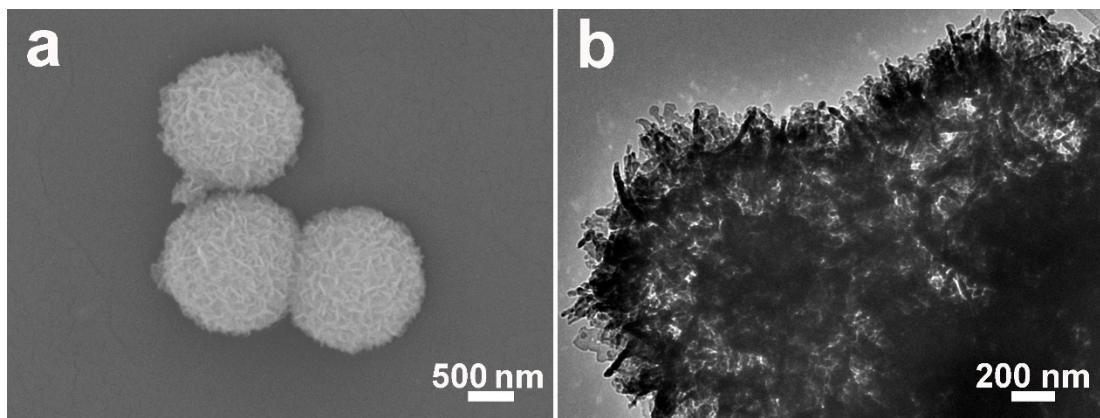
**Fig. S3.** The XRD analysis of two obtained samples when the mole ratio of 2:1, 1:2 (NiO:S) are applied.



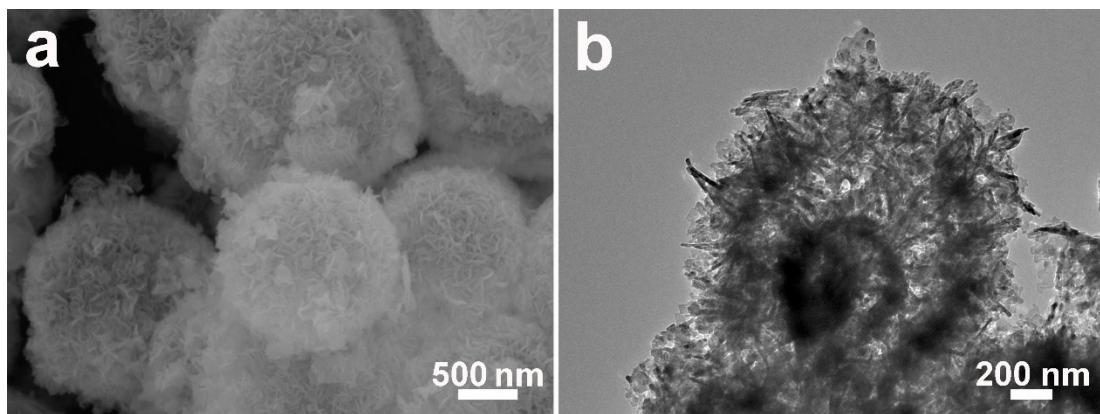
**Fig. S4** XPS spectrum of Ni 2p of  $(\text{NiO})_{0.1}(\text{NiS})_{0.9}$  multi-shelled hollow microspheres.



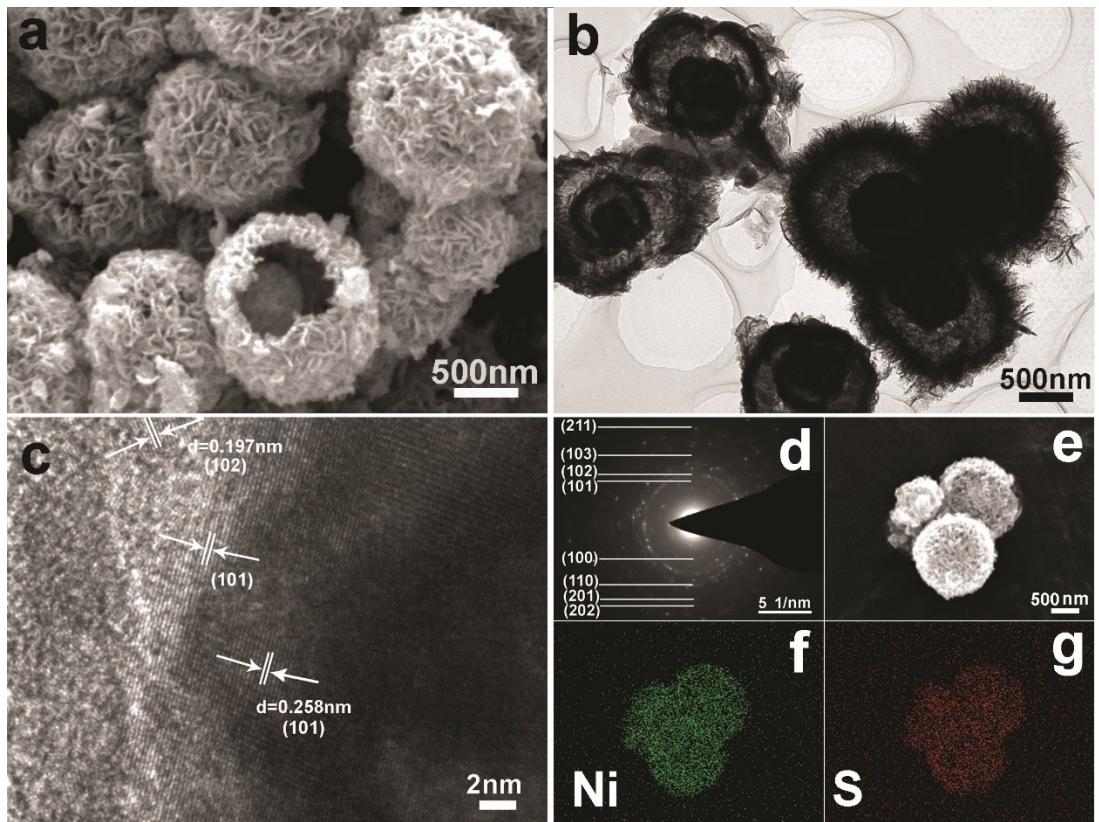
**Fig. S5.** SEM (a) and TEM (b) images of the multi-shelled  $(\text{NiO})_{0.85}(\text{NiS})_{0.15}$  hollow microspheres.



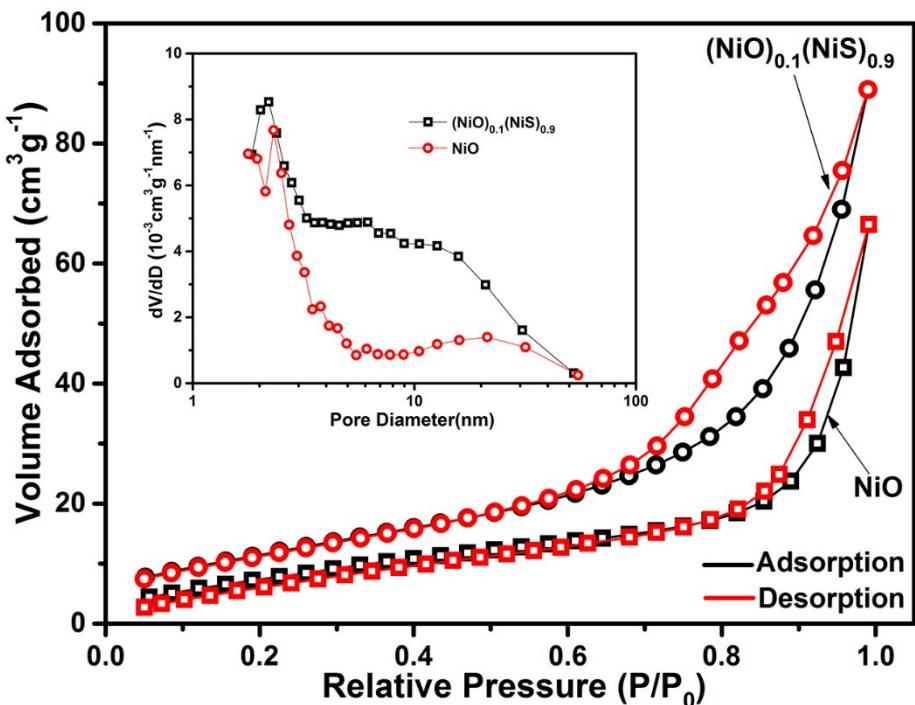
**Fig. S6.** SEM (a) and TEM (b) images of the multi-shelled  $(\text{NiO})_{0.65}(\text{NiS})_{0.35}$  hollow microspheres.



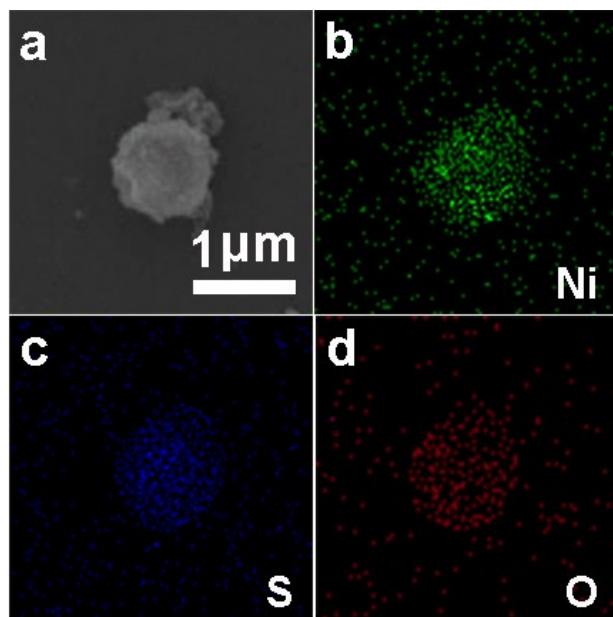
**Fig. S7.** SEM (a) and TEM (b) images of the multi-shelled  $(\text{NiO})_{0.4}(\text{NiS})_{0.6}$  hollow microspheres.



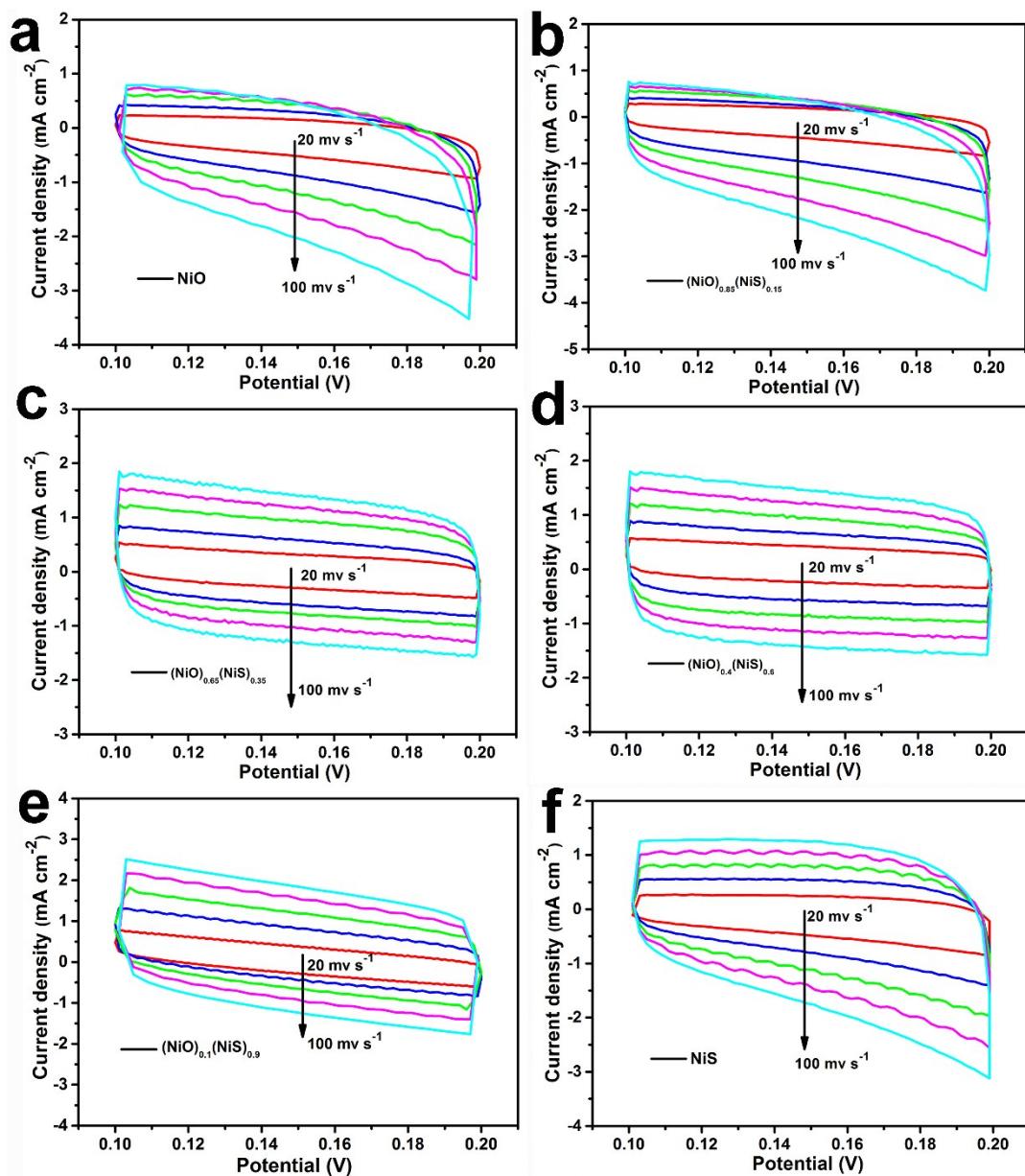
**Fig. S8.** SEM image (a), TEM image (b), HRTEM image (c), SAED patterns (d) and elemental mapping images (e-g) of the multi-shelled NiS hollow microspheres.



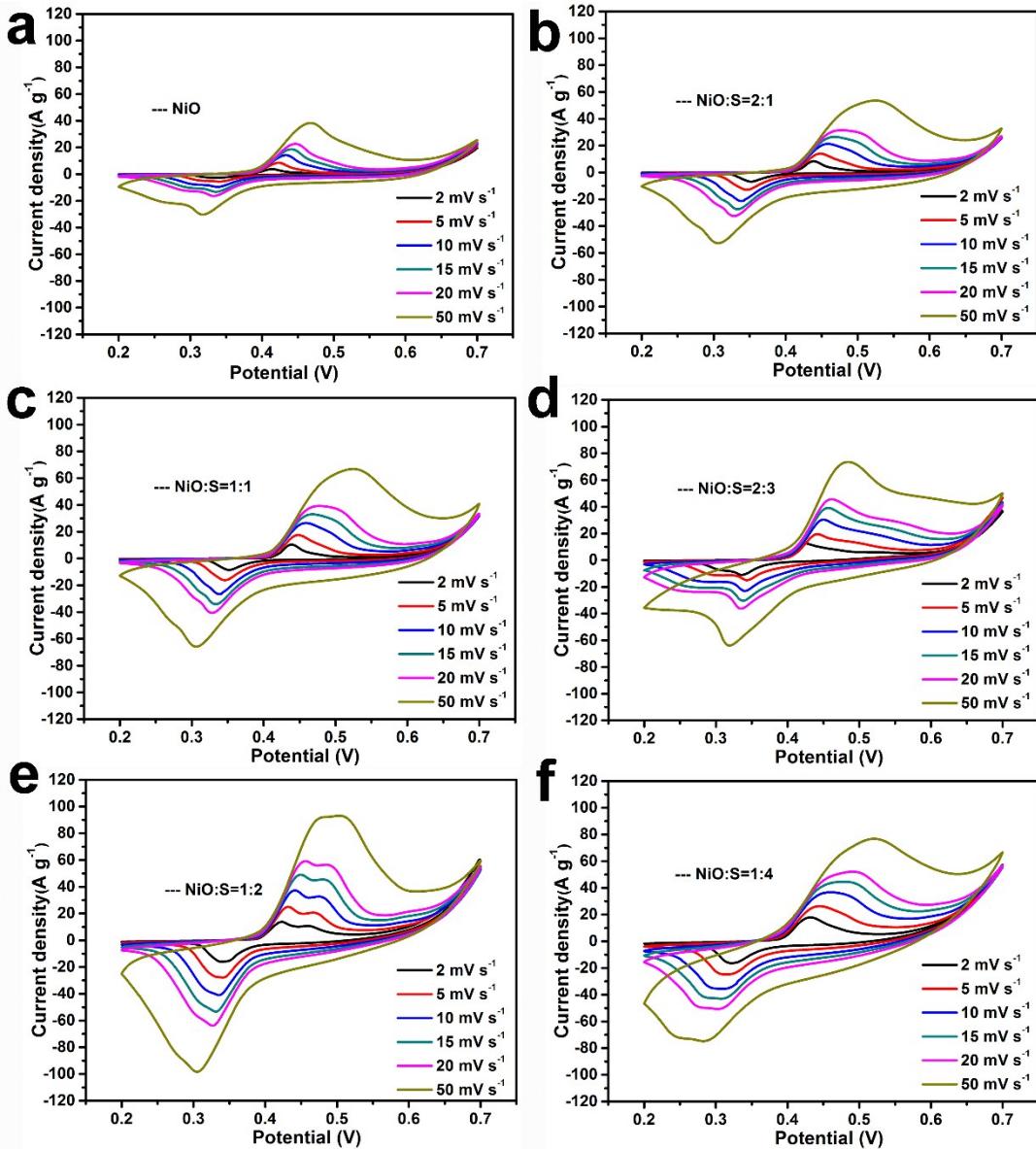
**Fig. S9.** Nitrogen adsorption-desorption isotherms and corresponding pore size distribution curves (the inset) of the NiO and  $(\text{NiO})_{0.1}(\text{NiS})_{0.9}$  multi-shelled hollow microspheres.



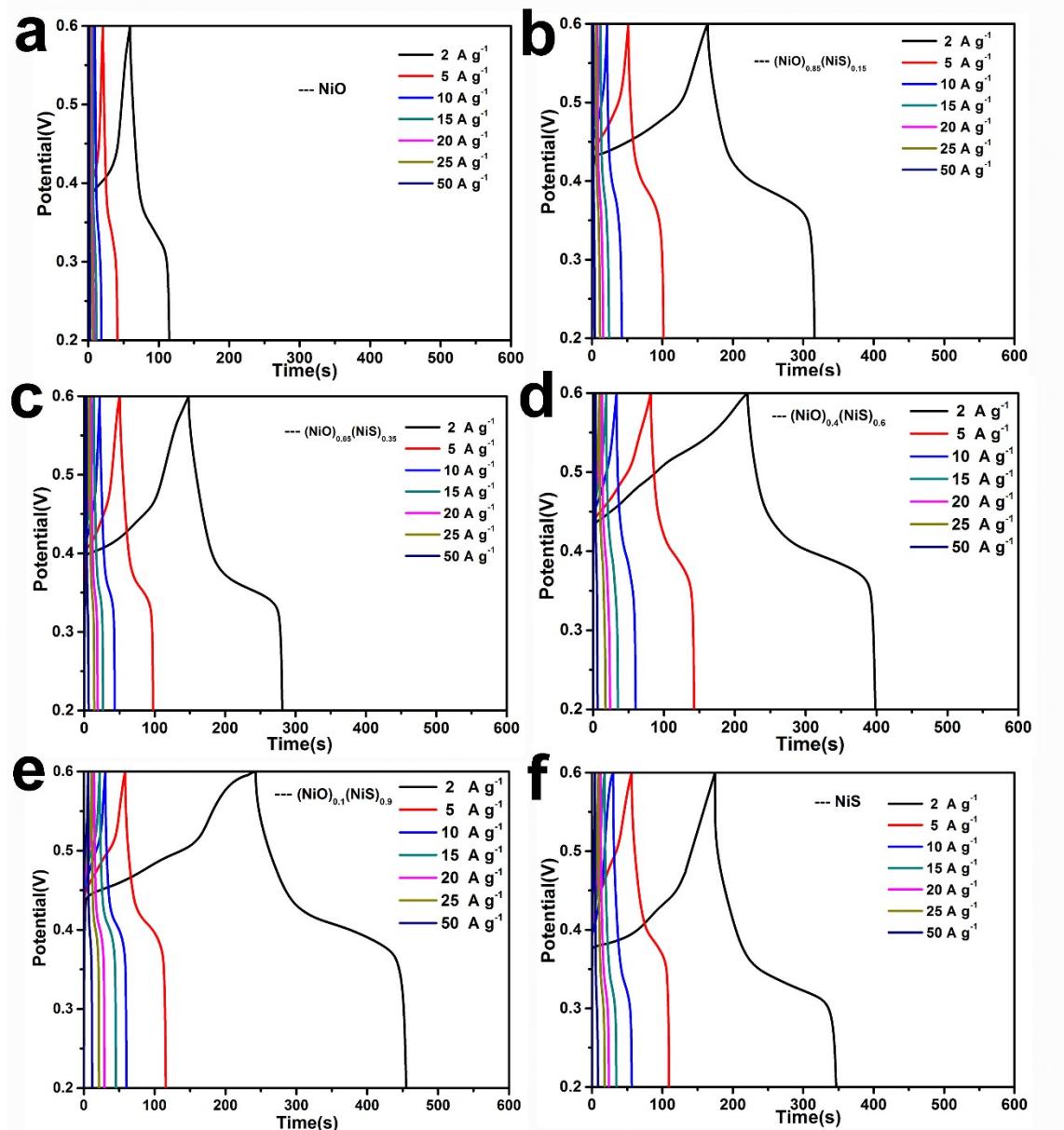
**Fig. S10.** Elemental mapping images (a-d) of  $(\text{NiO})_{0.1}(\text{NiS})_{0.9}$  hollow microspheres.



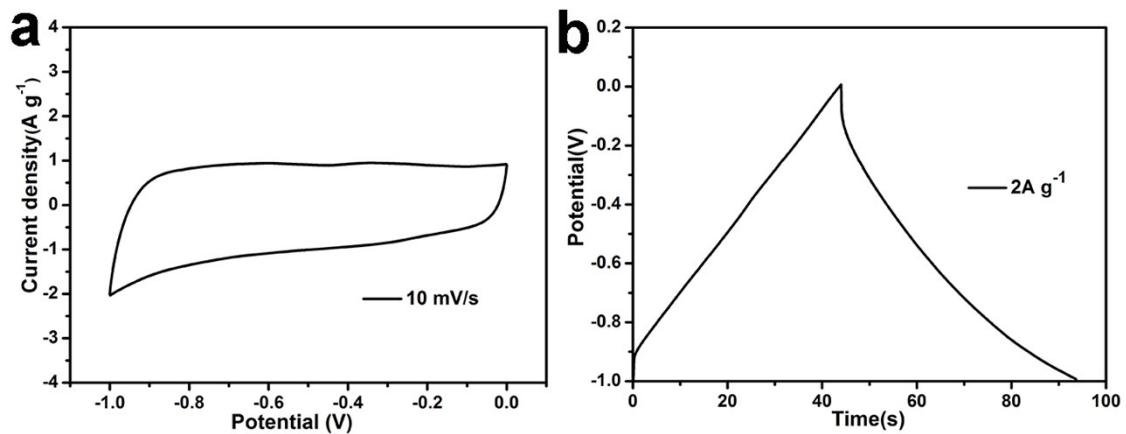
**Fig. S11.** CV curves of multi-shelled nickel-based hollow microspheres within a non-Faradaic potential window (vs. SCE) at different scan rates. (a) NiO, (b)  $(\text{NiO})_{0.85}(\text{NiS})_{0.15}$ , (c)  $(\text{NiO})_{0.65}(\text{NiS})_{0.35}$ , (d)  $(\text{NiO})_{0.4}(\text{NiS})_{0.6}$ , (e)  $(\text{NiO})_{0.1}(\text{NiS})_{0.9}$  and (f) NiS.



**Fig. S12.** CV curves performed at different scan rates of four samples. (a) NiO, (b)  $(\text{NiO})_{0.85}(\text{NiS})_{0.15}$ , (c)  $(\text{NiO})_{0.65}(\text{NiS})_{0.35}$ , (d)  $(\text{NiO})_{0.4}(\text{NiS})_{0.6}$ , (e)  $(\text{NiO})_{0.1}(\text{NiS})_{0.9}$  and (f) NiS.



**Fig. S13.** The charge-discharge curves at different current densities of four samples. (a) NiO, (b)  $(\text{NiO})_{0.85}(\text{NiS})_{0.15}$ , (c)  $(\text{NiO})_{0.65}(\text{NiS})_{0.35}$ , (d)  $(\text{NiO})_{0.4}(\text{NiS})_{0.6}$ , (e)  $(\text{NiO})_{0.1}(\text{NiS})_{0.9}$  and (f) NiS.



**Fig. S14.** CV curve at  $10 \text{ mV s}^{-1}$  (a) and the galvanostatic charge–discharge curve at current density of  $2 \text{ A g}^{-1}$  (b) of the AC electrode.