Electronic Supplementary Information (ESI)

Formation of multi-shelled nickel-based sulfides hollow spheres for rechargeable alkaline batteries†

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Experimental section

Synthesis multi-shelled NiO hollow spheres: All reagents were analytical grade and purchased from Beijing Chemical Co. Ltd., and used without further purification. Nickel acetatetetrahydrate ($Ni(Ac)_2{\cdot}4H_2O$) was used as the metal precursor. Taking NiO quadruple-shelled hollow spheres as an example, a typical synthesis process is described as follows: Carbonaceous microspheres (CMSs) were synthesized through the emulsion polymerization reaction of source under hydrothermal conditions as described elsewhere. Freshly-prepared CMSs (0.8 g) were dispersed in 0.1M nickel acetate solution (water/ethanol = 2:3, v/v, 100 mL) with the aid of ultrasonication. After ultrasonic dispersion for 30 min, the resulting suspension was aged for 6 h at 40 °C in a water bath, vacuum filtered, washed with deionized water at least three times, and then dried at 60 °C in an oven for 12 h. The resultant composite microspheres were heated in air at 1 °C min^{-1} up to 500 °C, kept at this temperature for 2 h, and cooled naturally to room temperature. The quadruple-shelled NiO hollow spheres were formed as a gray-powder product. Detailed experimental parameters are listed in Table S1 in the ESI.

Synthesis of multi-shelled NiS_2 hollow spheres: multi-shelled NiS_2 hollow spheres are prepared via an atom-exchange process. The as-prepared multi-shelled NiO hollow spheres are sulfurated by thermal vaporization of sulfur powder under argon flow. 20 mg of multi-shelled NiO hollow spheres and 250 mg of sulfur powder are put two separate positions in a porcelain boat with sulfur power at the upstream side of the tube furnace. Then, the samples are annealed at 350 °C for 0.5 h with a heating rate of 5 °C min^{-1} under argon atmosphere with a flow rate of 50 sccm. Multi-shelled NiS_2 hollow spheres are obtained after cooling to room temperature under argon.

Synthesis of multi-shelled Ni_3S_2 and NiS hollow spheres: multi-shelled Ni_3S_2 hollow spheres are prepared via a low-temperature sulfuration process. The as-prepared multi-shelled NiO hollow spheres are sulfurated by thermal decomposition of CH_4N_2S under Ar-H_2 flow. 10 mg of multi-shelled NiO hollow spheres and 30 mg of CH_4N_2S are put two separate positions in a porcelain boat with CH_4N_2S at the upstream side of the tube furnace. Then, the samples are annealed at 300 °C for 4 h with a heating rate of 2 °C min^{-1} under Ar-H_2 atmosphere with a flow rate of 70 sccm. Multi-shelled Ni_3S_2 hollow spheres are obtained after cooling to room temperature under Ar-H_2. The synthesis procedures of multi-shelled NiS hollow spheres are similar to multi-shelled NiS_2 hollow spheres except for the amount of sulfur powder.

Materials characterization

Powder X-ray diffraction (XRD) patterns were recorded on a Panalytical X'Pert PRO MPD [Cu Ka radiation (λ, 1.5405 Å)], operating at 40 kV and 30 mA. Field emission scanning electron microscopy (FESEM) images were obtained using a JSM-6700 microscope operating at 5.0 kV. Transmission electron microscopy (TEM) images were taken on a FEI Tecnai F20 instrument using an accelerating voltage of 200 kV. The nitrogen adsorption-desorption isotherms under liquid nitrogen (-196 °C) were measured on a Quantochrome Autosorb-1MP sorption analyzer with prior degassing under vacuum at 200 °C overnight. XPS data was collected with an ESCALab220i-XL electron spectrometer, and corrected by the reference of C1s (284.8 eV).

Electrochemical measurements

The working electrode consists of 70 wt. % of active material, 20 wt. % of conductive carbon black (Super-P-Li), and 10 wt. % of polymer binder (polyvinylidene fluoride, PVDF). The mixture is then pressed onto a Ni foam as the working electrode and dried at 120 °C for 12 h under vacuum. Electrochemical measurements on the capacitive performance are conducted with a CHI 660D electrochemical workstation in an aqueous KOH electrolyte (6.0 M) using a three-electrode cell, where a Pt foil serves as the counter electrode and a Ag/AgCl (KCl saturated) electrode as the reference electrode. The specific capacity of the electrodes is calculated from the chronopotentiometry curves based on the following equation: $C = I\Delta t/m\Delta V$, where I is the discharge current, Δt is the discharge time, ΔV is the voltage range, and m is the mass of the electroactive material.

Fabrication and evaluation of alkaline battery

Alkaline battery are fabricated by assembling multi-shelled NiS_2 hollow spheres cathode and activated carbon (AC) anode in 6.0 M KOH solution. The mass ratio of positive electrode to negative electrode is determined according to the well-known charge balance equation ($q^+= q^-$). In the relation, the charge stored by each electrode usually depends on the specific capacity (C), the potential range (ΔV) and the mass of the electrode (m) following equation: $q = mC\Delta V$. To obtain $q^+= q^-$, the mass balance will be expressed as following equation: $m^+/m^- = C^-\Delta V^- /C^+\Delta V^+$, C^+ and C^- are the specific capacity of NiS_2 and AC electrodes, respectively. ΔV^+ and ΔV^- are the voltage range of one scanning segment of NiS_2 and AC electrodes, respectively. The specific capacity (C) of the alkaline battery is calculated from the chronopotentiometry curves according to the following equation: $C = I\Delta t/m\Delta V$, where I is the discharge current, Δt is the discharge time, ΔV is the voltage range, and m is the total mass of active materials on both electrodes.

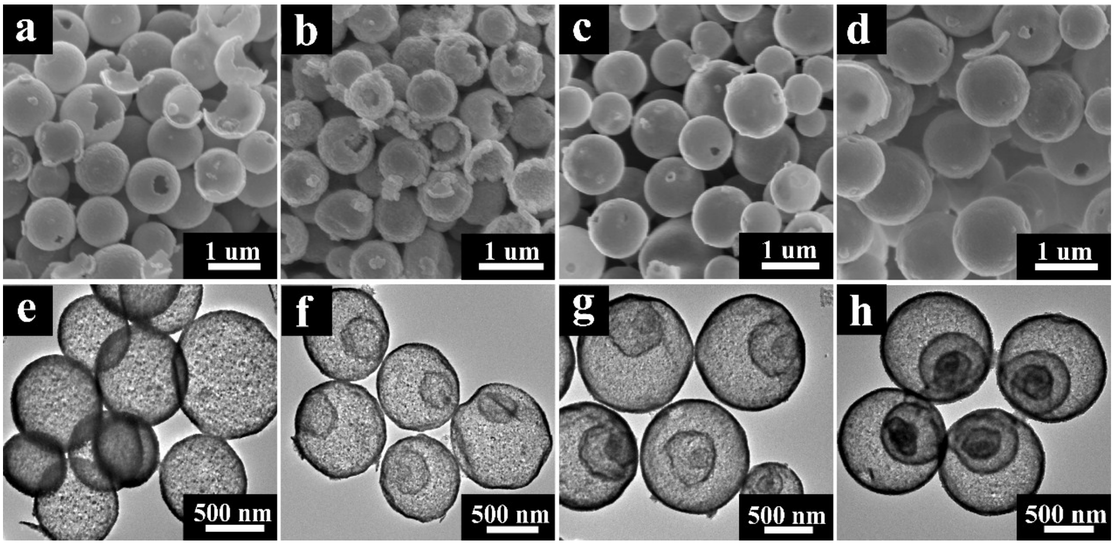

Fig. S1 FESEM (a-d) and TEM (e-h) images of single-, double-, triple-, quadruple-shelled NiO hollow spheres.

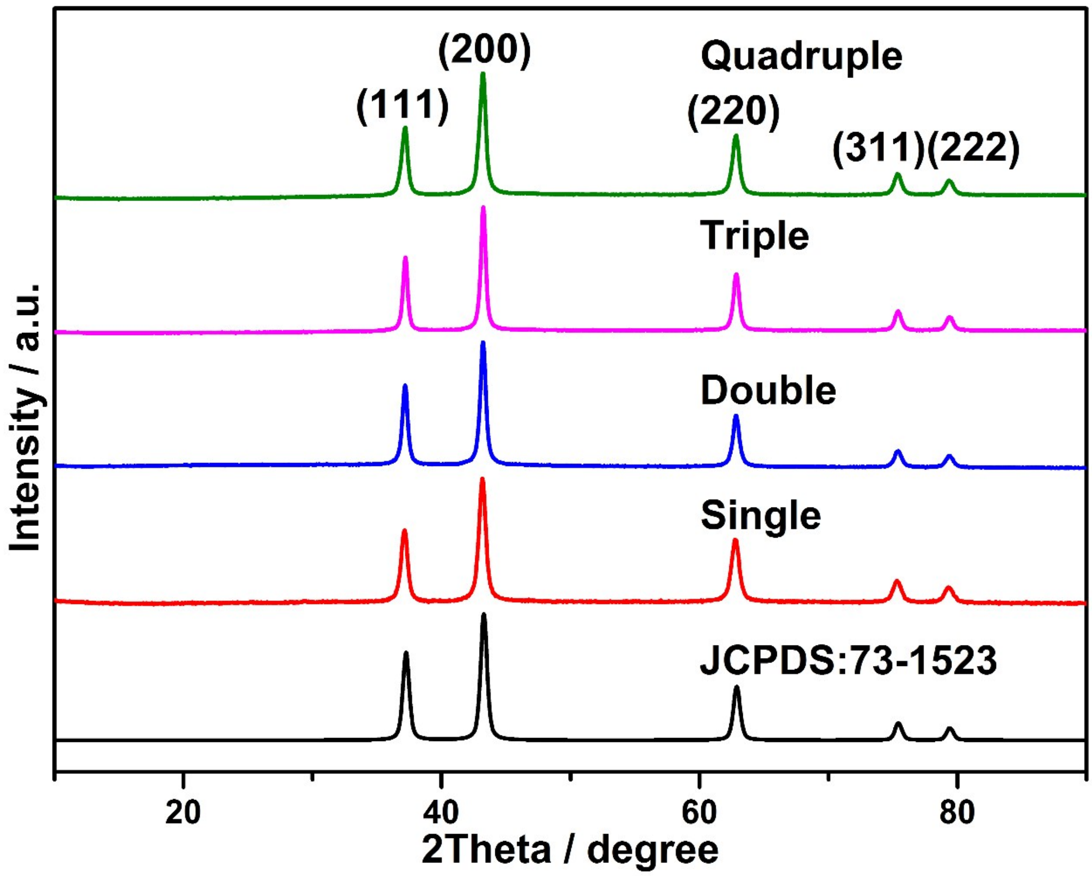

Fig. S2 XRD patterns of single-, double-, triple-, quadruple-shelled NiO hollow spheres.

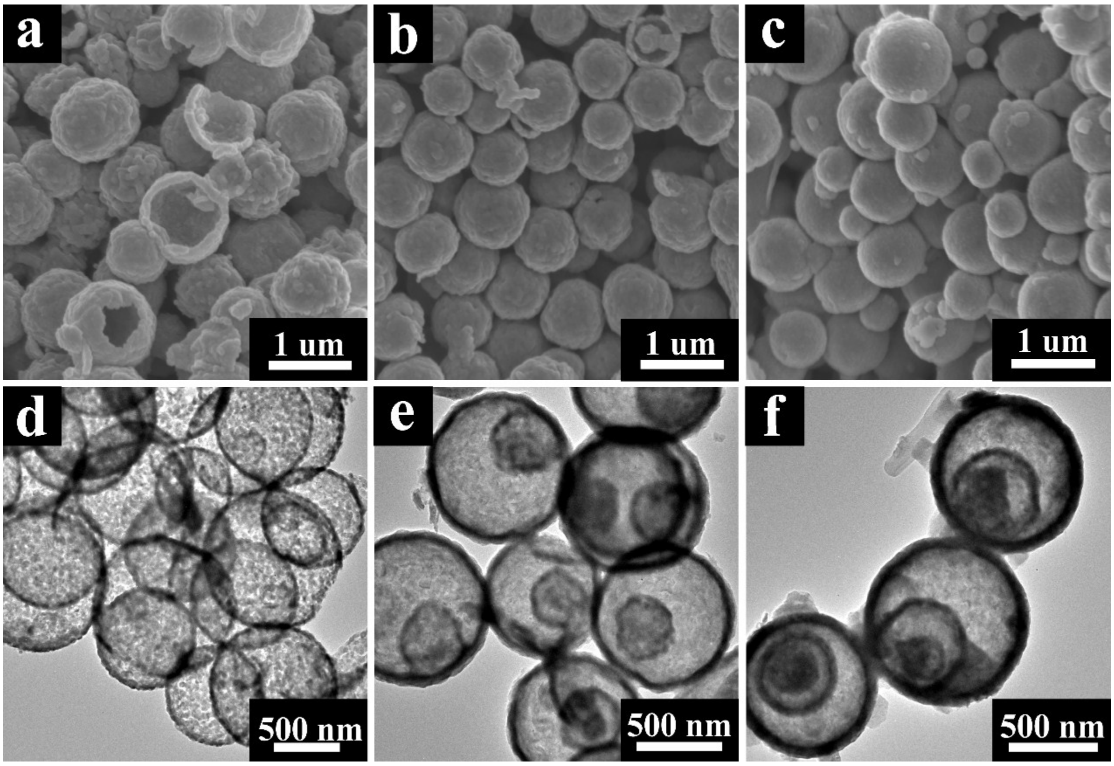

Fig. S3 FESEM and TEM images of (a, d) single-, (b, e) double-, (c, f) triple-shelled NiS_2 hollow spheres.

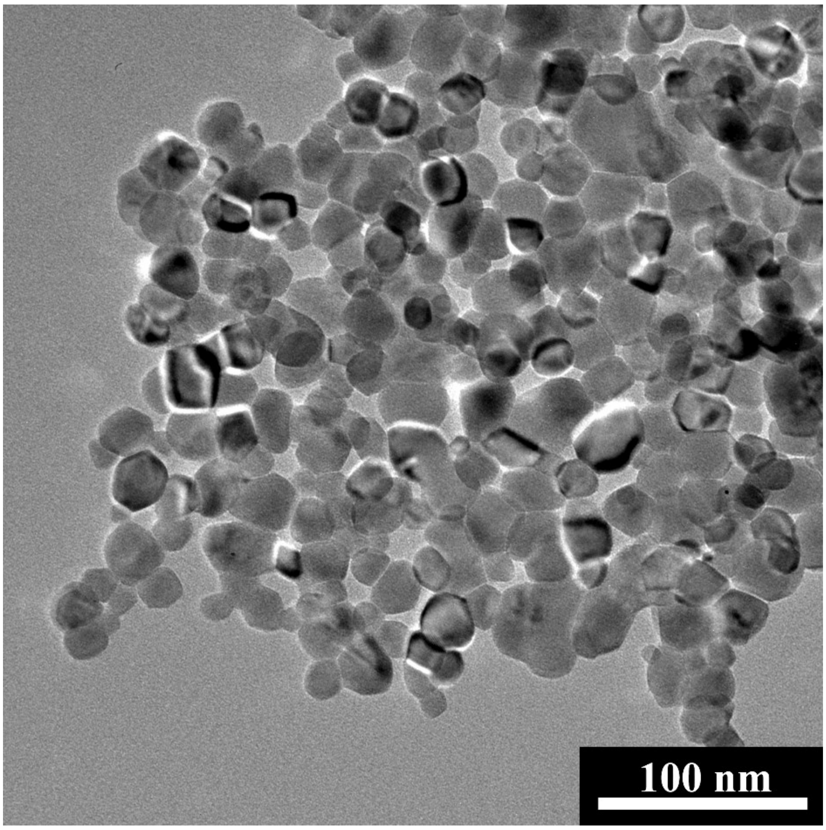

Fig. S4 TEM image of NiS_2 nanoparticles.

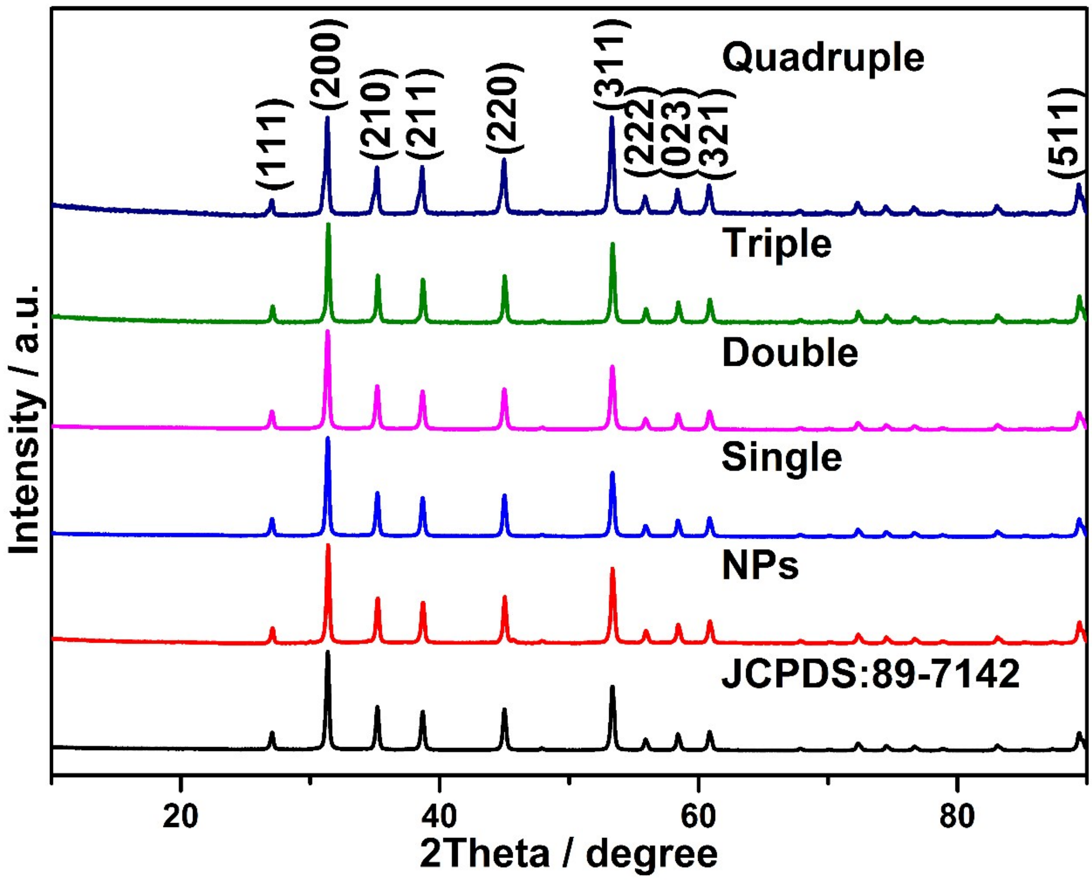

Fig. S5 XRD patterns of single-, double-, triple-, quadruple-shelled NiS_2 hollow spheres and NiS_2 nanoparticles.

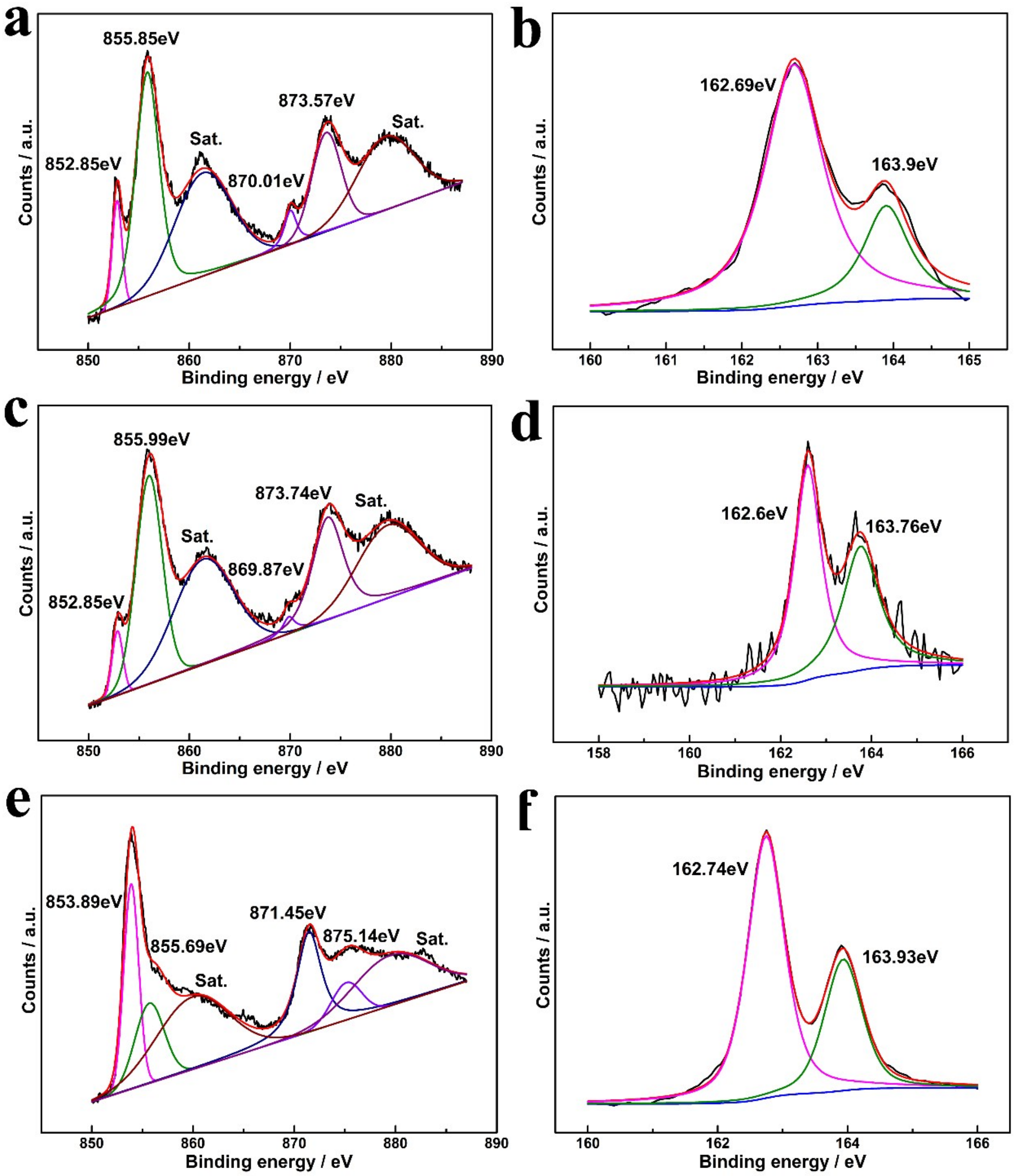

Fig. S6 High-resolution XPS spectras of (a, b) Ni_3S_2, (c, d) NiS, (e, f) NiS_2.

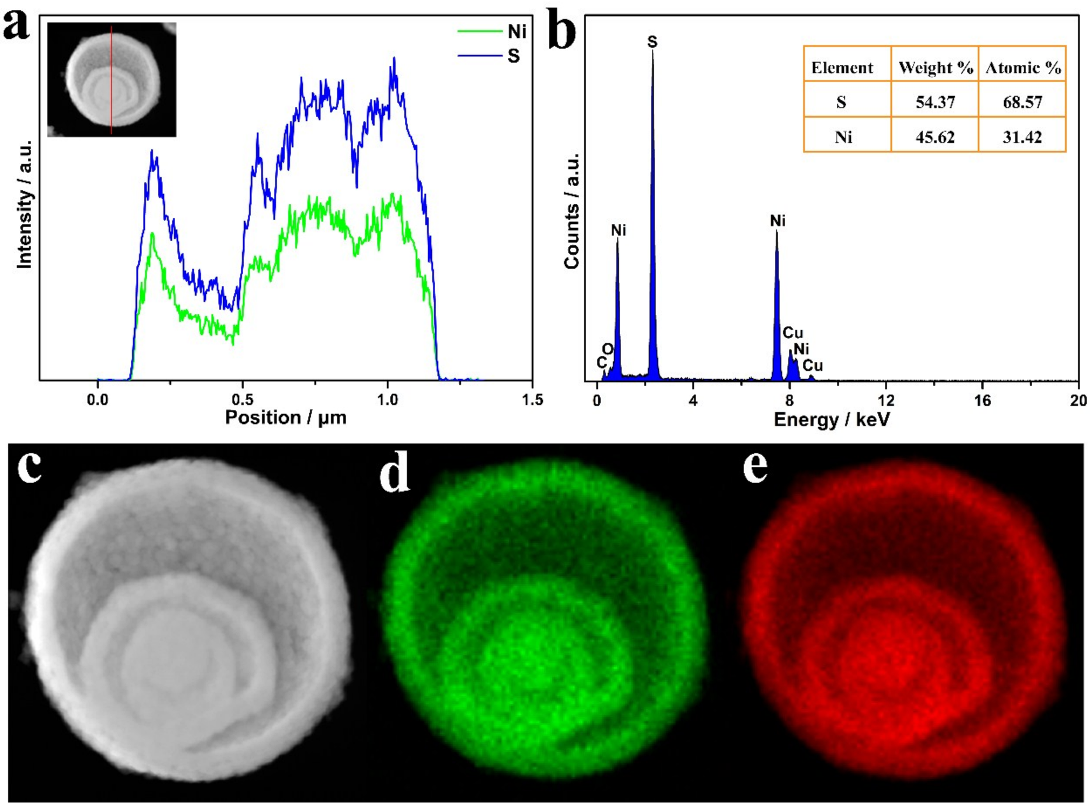

Fig. S7 (a) line-scanning of nickel and sulfur elements across a selected area (red line ink in the insert image) of a quadruple-shelled NiS_2 hollow sphere, (b) EDX curve and (c-e) HAADF-STEM element mapping images of corresponding quadruple-shelled NiS_2 hollow sphere: (d) Ni, (e) S.

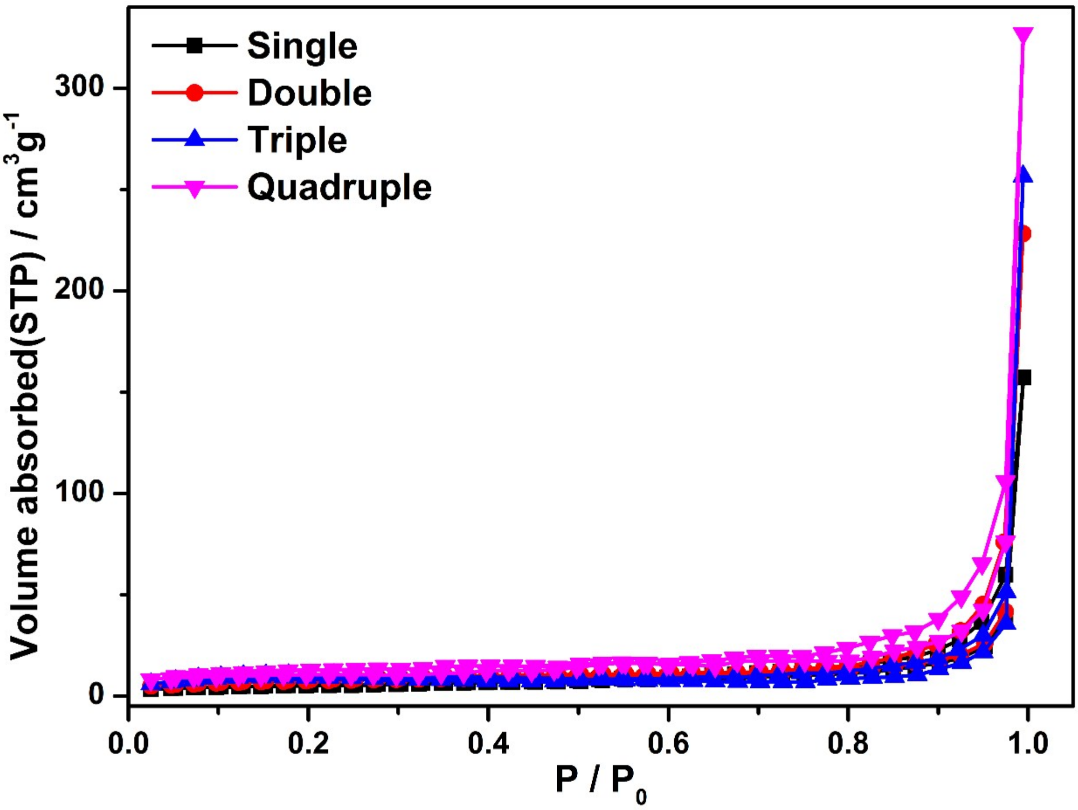

Fig. S8 N_2 absorption-desorption isotherms of single-, double-, triple-, quadruple-shelled NiS_2 hollow spheres.

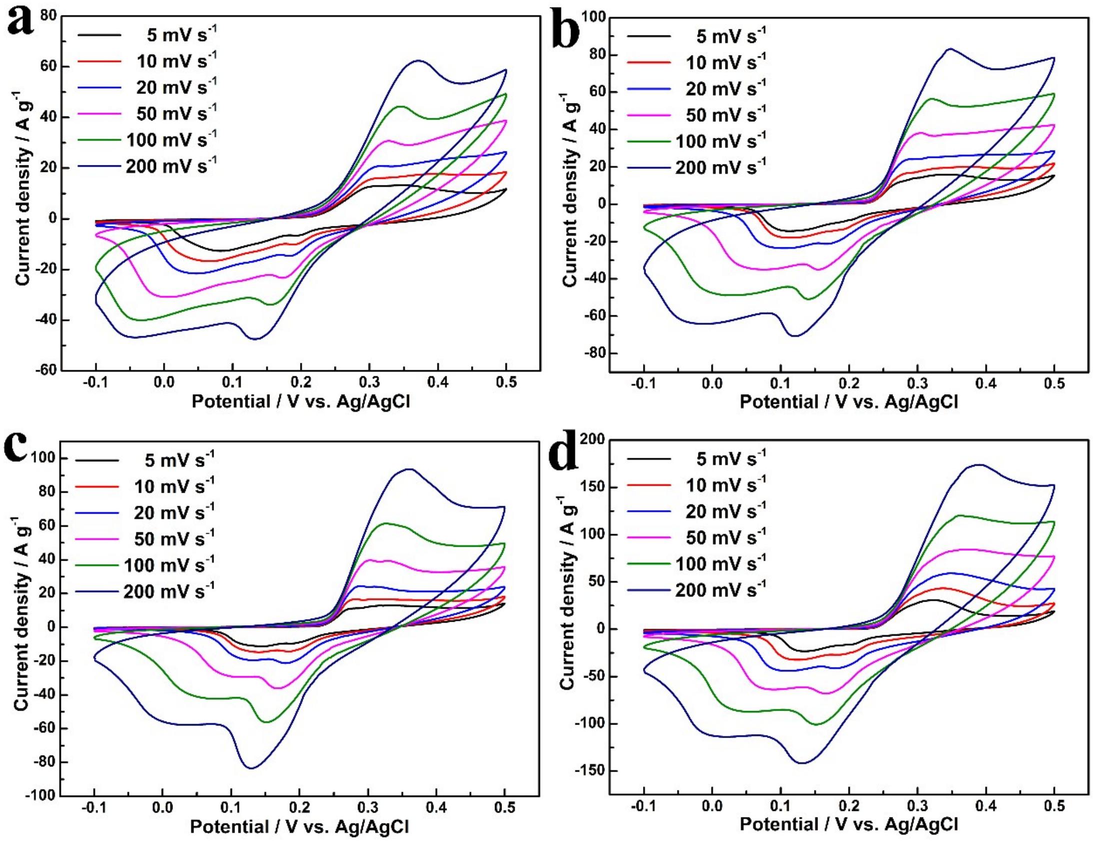

Fig. S9 CV curves of NiS_2 nanoparticles, single-, double-, triple-shelled hollow spheres at different scan rates.

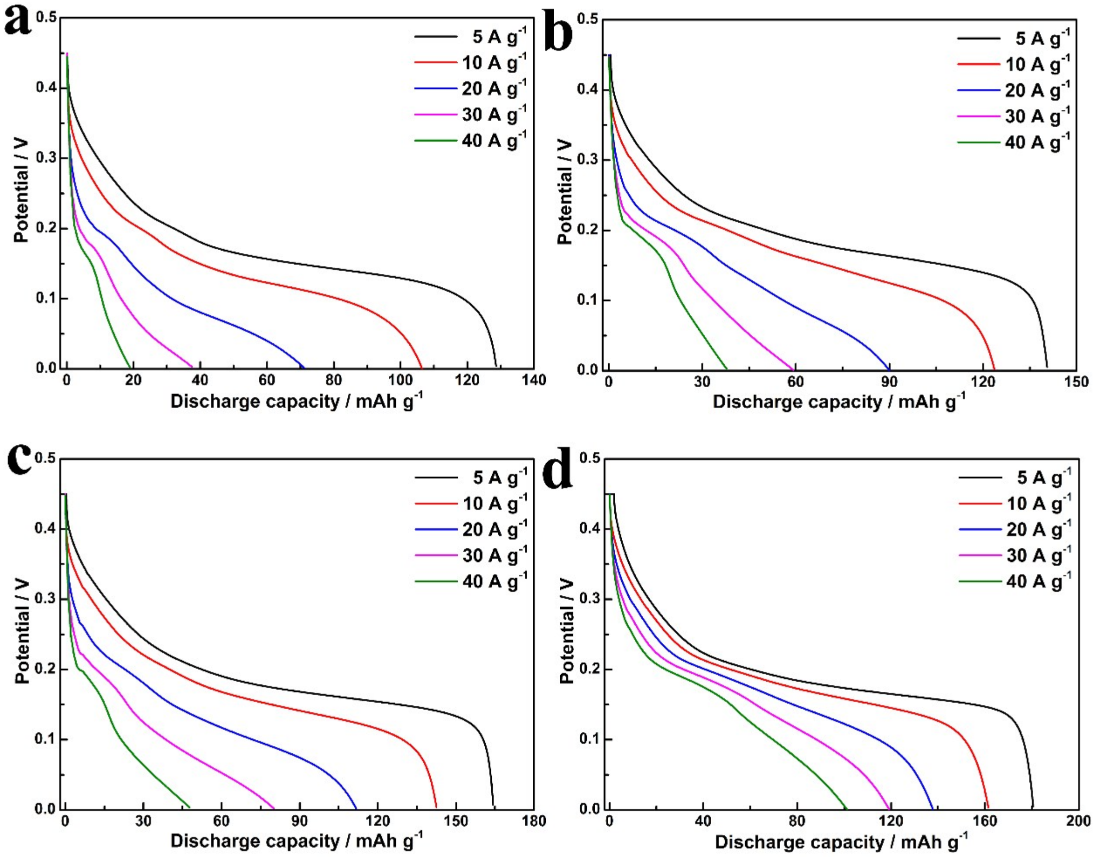

Fig. S10 Galvanostatic charge/discharge curves of NiS_2 nanoparticles, single-, double-, triple-shelled hollow spheres at various current densities.

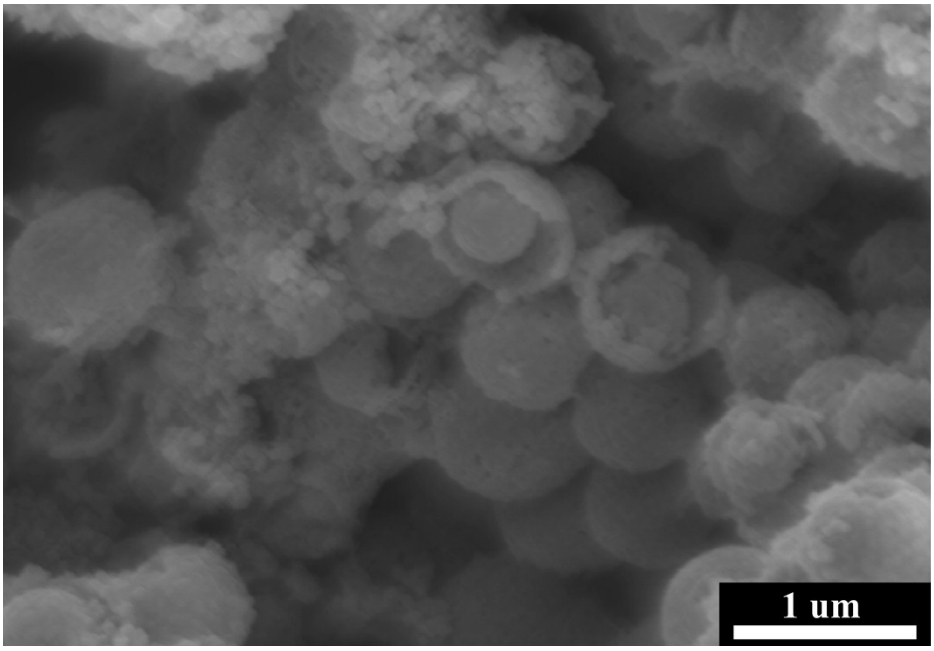

Fig. S11 The SEM image of quadruple-shelled NiS_2 hollow spheres after 5000 cycles.

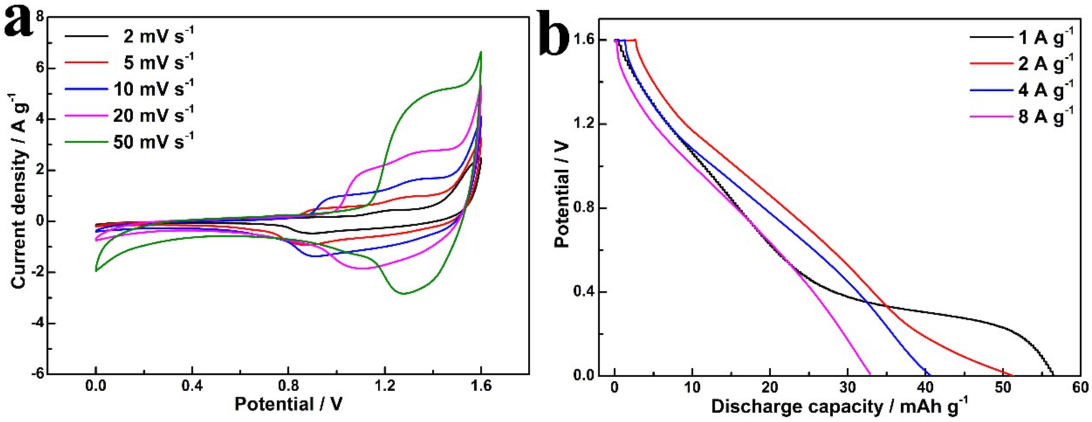

Fig. S12 Electrochemical evolution of the NiS_2//AC rechargeable alkaline battery: (a) CV curves at different scan rates, (b) Galvanostatic charge/discharge curves at various current densities.

Table S1. Summary of synthesis conditions of various multi-shelled NiO hollow spheres.

Structures	Concentration (M)	Water : ethanol	Absorbtion temperature (°C)	Absorbtion time (h)	Heating rate (°C/min)	Calcination teparature (°C)
Single-shelled	0.1	∞	20	6	5	500
Double-shelled	0.1	1:6	30	6	1	500
Triple-shelled	0.1	3:7	40	6	1	500
Quadruple-shelled	0.1	2:3	40	6	1	500

Table S2. The specific area and pore volume of NiS_2 multi-shelled hollow spheres

	NPs	Single	Double	Triple	Quadruple
Specific area (m^2/g)	64.9	18.41	27.31	32.61	36.31
Pore volume (m^3/g)	0.445	0.2438	0.3539	0.3938	0.4271

Table S3. Comparison of the electrochemical performance of alkaline rechargeable battery in literatures

Electrode materials	Specific capacity (mAh g^{-1})	Electrolyte	Voltage window (V)	Current density (A g^{-1})	reference
Flaky Ni_3S_2	99.58	1 M KOH	0-0.5 (Ag/AgCl)	2	1
RGO-Ni_3S_2	197.77	2 M KOH	0.1-0.6 (Hg/HgO)	0.75	2
flower-like NiS	119.1	2 M KOH	0-0.5 (Hg/HgO)	2	3
NiS_2 nanocube	77.2	3 M KOH	0-0.4 (SCE)	1.25	4
Hollow Ni_3S_2/RGO	126.95	2 M KOH	0.1-0.55 (Hg/HgO)	1	5
NiS hollow sphere	180.25	2 M KOH	-0.15-0.55 (SCE)	4.08	6
NiS box-in-box	91.5	3 M KOH	0-0.5 (SCE)	1	7
NiS_2 hollow spheres	153.5	2 M KOH	0-0.4 (SCE)	1	8
$NiCo_2S_4$ nanotube	102.5	6 M KOH	-0.1-0.4 (SCE)	4	9
Onion-like $NiCo_2S_4$	141.11	6 M KOH	0-0.5 (SCE)	2	10
Ni-Co-S/G	207.2	6 M KOH	0-0.5 (Hg/HgO)	1	11
Quadruple-shelled NiS_2 hollow sphere	215.97	6 M KOH	0-0.45 (Ag/AgCl)	5	This work

Notes and references

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