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Graphene quantum dots-modified $Co_3O_4/NiCo_2O_4$ yolk-shell polyhedrons as polysulfides-adsorptive sulfur host for lithium-sulfur batteries

Jing Xu[a], Kehao Tao[b], Yajun Zhu[a,c], Ting Zhou[a], Xiaofei Huang[a], Jinjin Li[b,*], Jinyun Liu[a,*]

Experimental

Materials

In this work, $Co(NO_3)_2 \cdot 6H_2O$, 2-methylimidazole and sulfur powders were purchased from Aladdin Reagent (Shanghai) Co., Ltd. Methanol and $Ni(NO_3)_2 \cdot 6H_2O$ were purchased from Sinopharm Chemical Reagent Co., Ltd. Graphene quantum dots (GQDs) aqueous solution (1 mg mL^{-1}) was purchased from Suzhou Hengqiu Technology Co., Ltd. All reagents were analytical-grade pure and were used as received without further purification.

Synthesis of ZIF-67

First, 1 mmol $Co(NO_3)_2 \cdot 6H_2O$ and 4 mmol 2-methylimidazole were dissolved in 25 mL methanol to form two solutions. The methanol solution containing 2-methylimidazole was poured into a methanol solution containing $Co(NO_3)_2 \cdot 6H_2O$ under stirring. After aging at room temperature for 24 h, the purple precipitate was collected by centrifugation, washed with deionized water and ethanol two times, and dried at 70 °C for 6 h.

Synthesis of $Co_3O_4/NiCo_2O_4$

The 40 mg ZIF-67 was ultrasonically dispersed in 25 mL ethanol solution containing 80 mg $Ni(NO_3)_2 \cdot 6H_2O$. After stirring for 30 min, ZIF-67/Ni-Co layered double hydroxide (ZIF-67/Ni-Co LDH) formed, which was collected by centrifugation and washed with deionized water and ethanol, dried at 70 °C overnight, and then the resulting yolk-shell

samples were annealed at 350 °C for 2 h in air at a heating rate of 1 °C min^{-1}. For control experiment, pure Co_3O_4 was also prepared by directly-heating ZIF-67 in air through the same approach.

Synthesis of Co_3O_4/$NiCo_2O_4$/GQDs@S

The Co_3O_4/$NiCo_2O_4$ polyhedrons (0.1 g) were mixed with 20 mL of GQDs solution and ultrasonicated for 5 min, then the mixture was collected and heated in an oven at 160 °C for 2 h. At last, Co_3O_4/$NiCo_2O_4$/GQDs was mixed with sulfur powders at a typical mass ratio of 3:7, sealed in argon gas, and placed in a reactor at 155 °C for 20 h. For comparison, Co_3O_4/$NiCo_2O_4$@S without GQDs, and Co_3O_4@S were also prepared by the similar method.

Characterization

The samples were characterized on transmission electron microscopy (TEM, Hitachi HT-7700), scanning electron microscopy (SEM, Hitachi S4800), high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2010), X-ray diffraction (XRD, Rigaku SmartLab) through a Cu Kα radiation source, X-ray photoelectron spectroscopy (XPS, Thermo Scientific), and UV-visible spectroscopy (HITACHI, U-2910). Inductively coupled plasma optical emission spectrometer (ICP-OES, Thermo Scientific iCAP PRO) was used to measure the metal content of the sample.

Electrochemical measurements

The active materials, carbon black and polyvinylidene fluoride binder were uniformly mixed in N-methylpyrrolidone at a ratio of 7:2:1 to prepare a mixed slurry, then the slurry was coated on aluminum foil. The cathode had a typical sulfur loading of about 1.0 mg cm^{-2}. The lithium metal was used as the anode with the electrolyte of 1.0 M LiTFSI in a 1:1 (v/v) 1,3-dioxolane/dimethyl ether mixture with 1.0 wt% $LiNO_3$. The electrolyte to sulfur ratio used in each battery was about 20 μL mg^{-1}. Celgard-2400 film was used as separator. Type-2032 coin cells were assembled in a glove box (Mikrona Super 1220/750/900) filled with argon gas. The charge and discharge tests were carried out on a NEWARE battery testing system. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed on an electrochemical working station (ChenHua CHI660e).

Adsorption towards polysulfides

In order to study the adsorption of $Co_3O_4/NiCo_2O_4$/GQDs towards polysulfides, A Li_2S_6 solution was prepared by using S and Li_2S (molar ratio=5:1) in 1, 2-dimethoxy-ethane (50 mL) under stirring for 72 h. $Co_3O_4/NiCo_2O_4$/GQDs or Co_3O_4 was put into 3 mL Li_2S_6 solution for adsorption. After overnight, the adsorbed solution was measured by using UV-vis spectroscopy (LAMBDA 850). All adsorption processes were carried out in glove box. In addition, initial Li_2S_6 solution was measured on UV-vis spectroscopy for comparison.

Theoretical calculations

First-principle calculations were performed in a Materials Studio software, setting 500 eV as the cutoff energy. The adsorption energies towards the polysulfide (Li_2S_4, Li_2S_6, Li_2S_8) on hosts were obtained by the following relation: $E_{ads} = E_{sub+S} - E_S - E_{sub}$, where the E_{sub+S}, where E_S and E_{sub} were the calculated energies of polysulfide–host, polysulfide, and host, respectively.

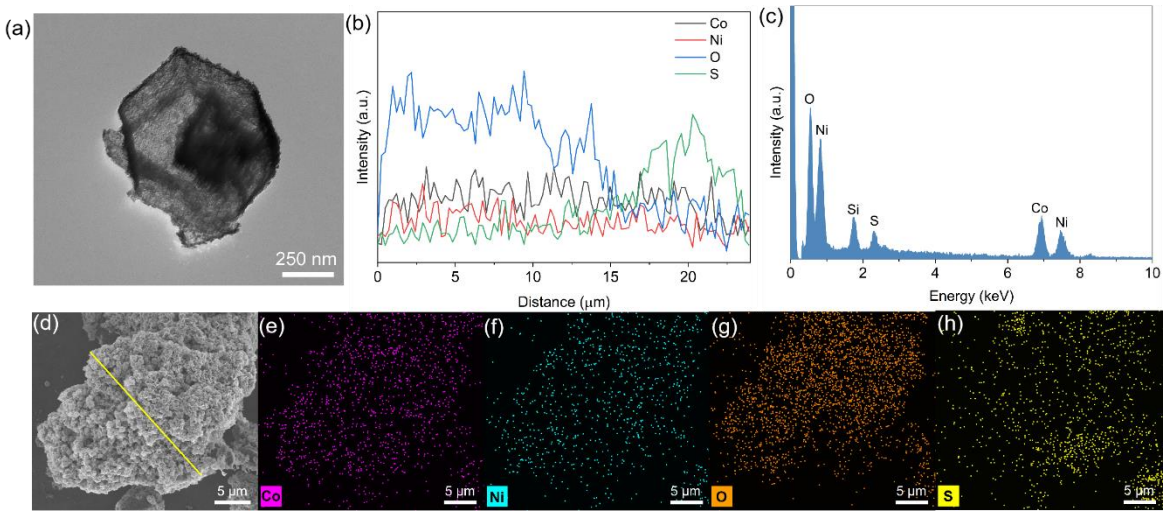

Fig. S1 (a) TEM image of $Co_3O_4/NiCo_2O_4$/GQDs. (b) Line-scanning curves and (c) EDS spectrum of $Co_3O_4/NiCo_2O_4$/GQDs@S. (d) SEM and (e-h) elemental mapping images of $Co_3O_4/NiCo_2O_4$/GQDs@S.

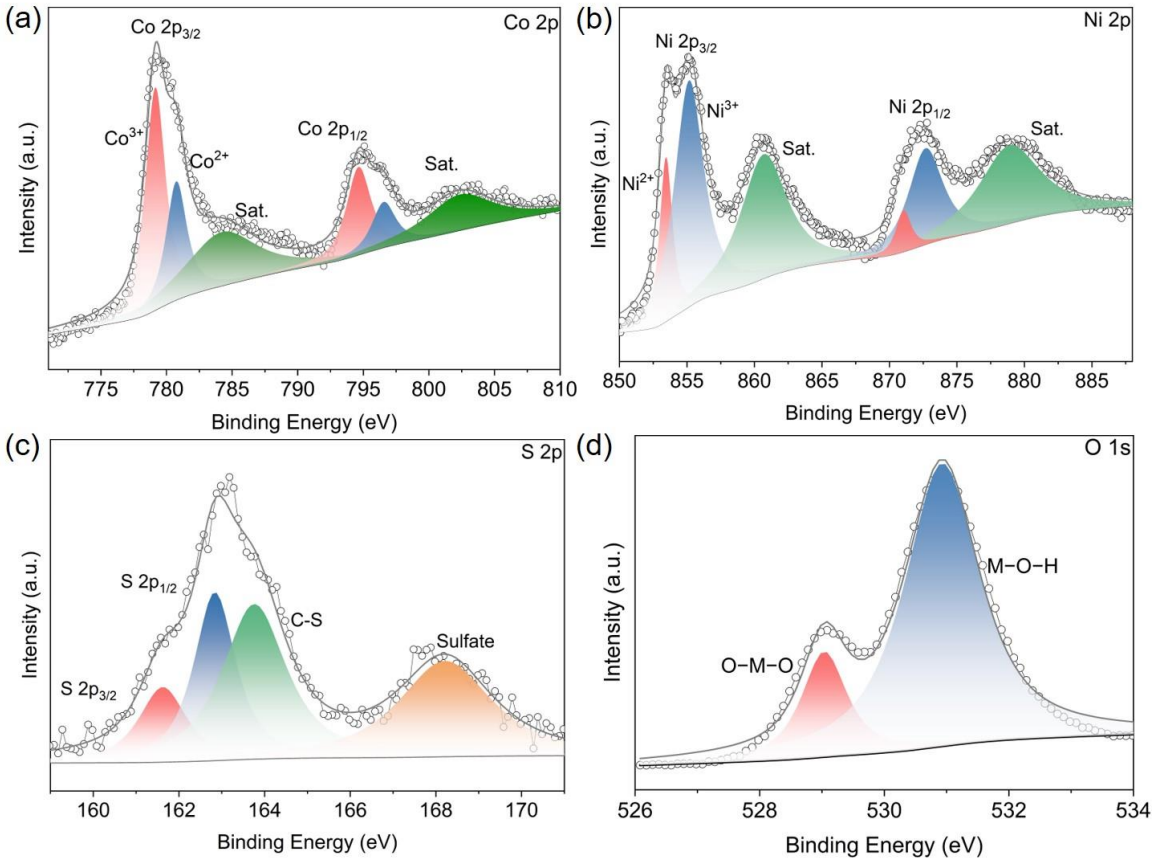

Fig. S2 XPS spectra of $Co_3O_4/NiCo_2O_4$/GQDs@S: (a) Co 2p, (b) Ni 2p, (c) S 2p, (d) O 1s.

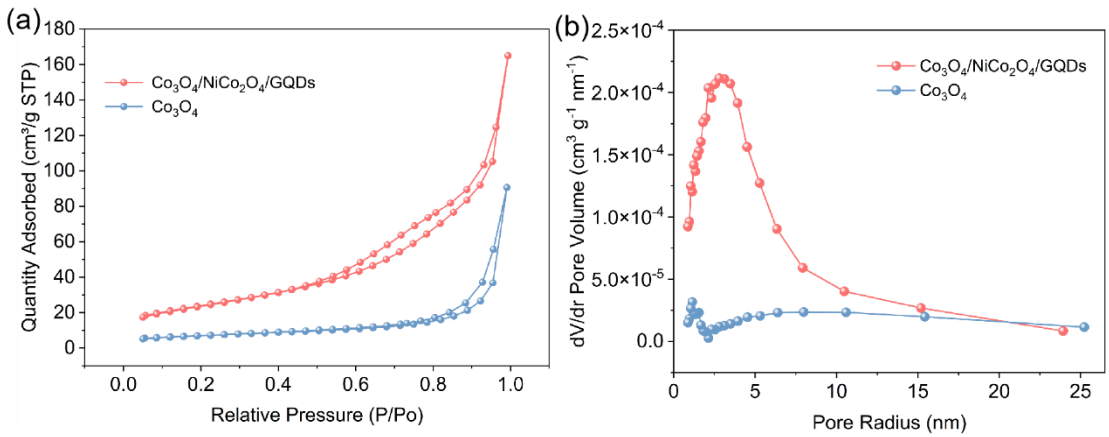

Fig. S3 (a) N_2 adsorption–desorption isotherms. (b) Pore-size distribution.

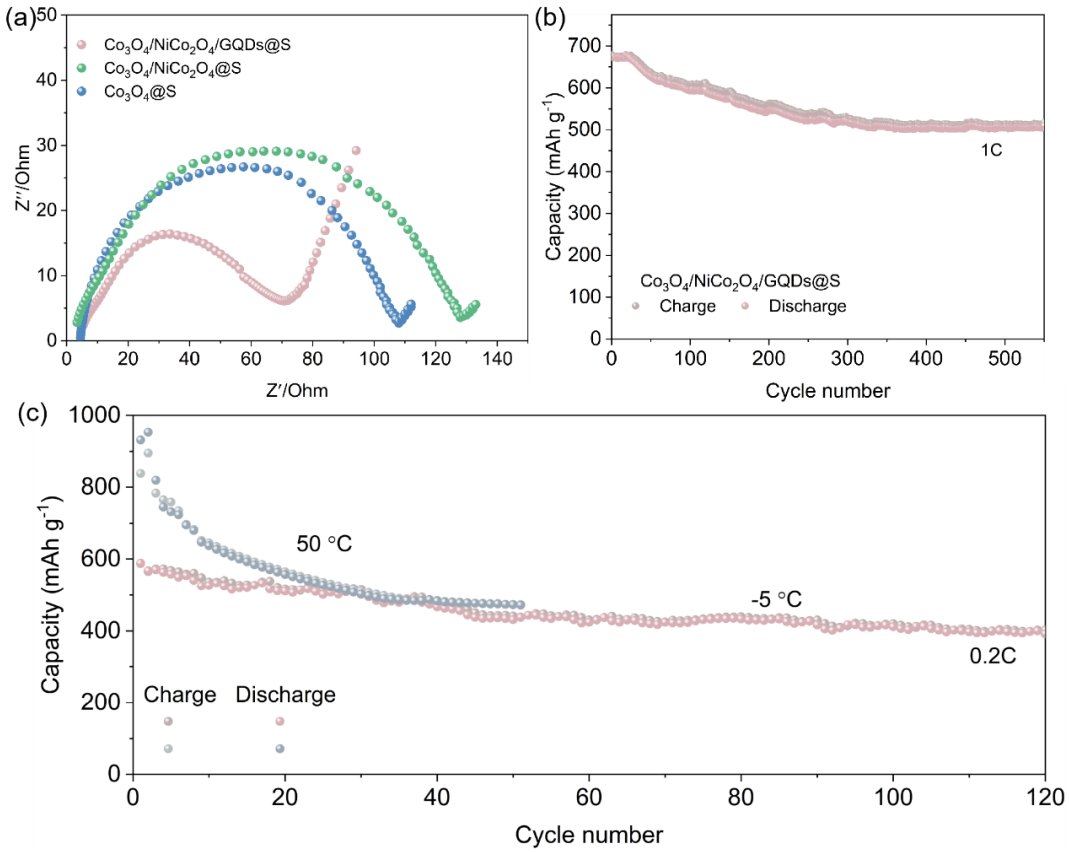

Fig. S4 (a) EIS spectra of $Co_3O_4/NiCo_2O_4$/GQDs@S, $Co_3O_4/NiCo_2O_4$@S and Co_3O_4@S after 100 cycles at 0.2 C. (b) Long-term cycle performance of $Co_3O_4/NiCo_2O_4$/GQDs@S at 1C. (c) Cycling properties under –5 °C and 50 °C.

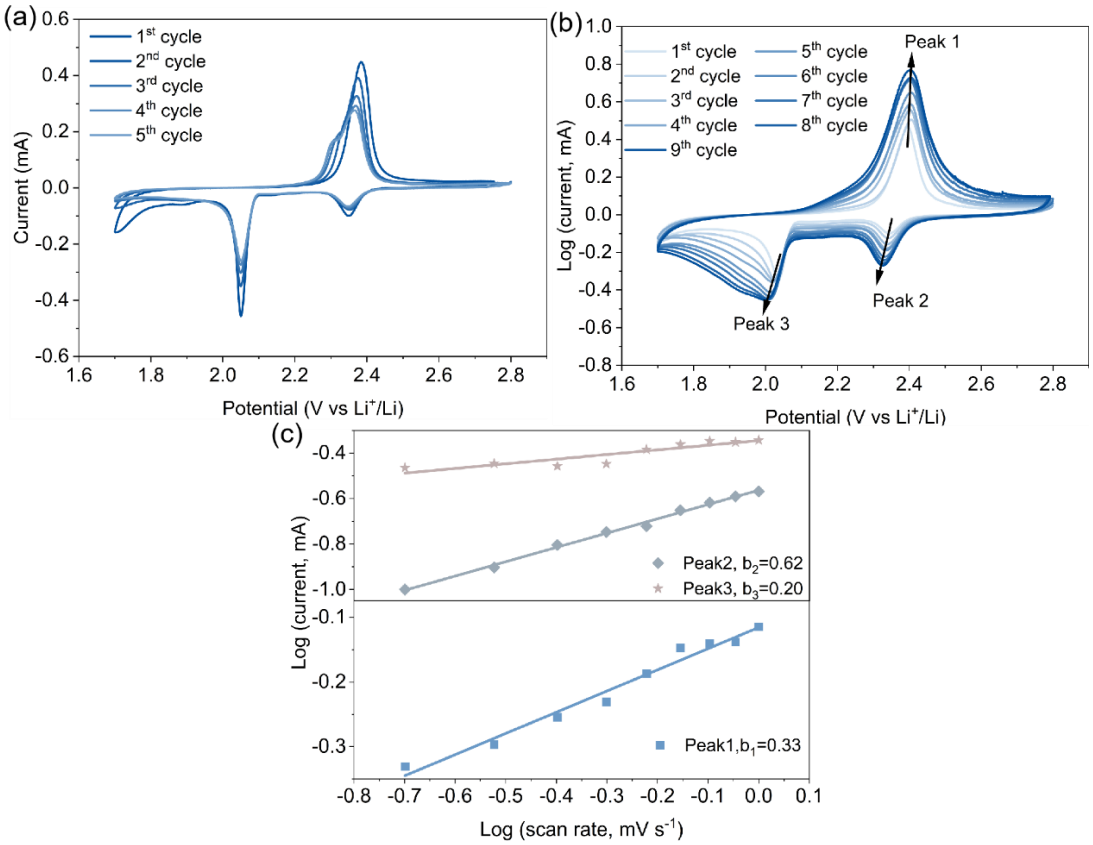

Fig. S5 (a) CV plots of Co_3O_4@S in the initial five cycles at 0.1 mV s^{-1}. (b) CV curves of Co_3O_4@S in the range of 0.1-1 mV s^{-1}. (c) Relationships between log(i) and log(v).

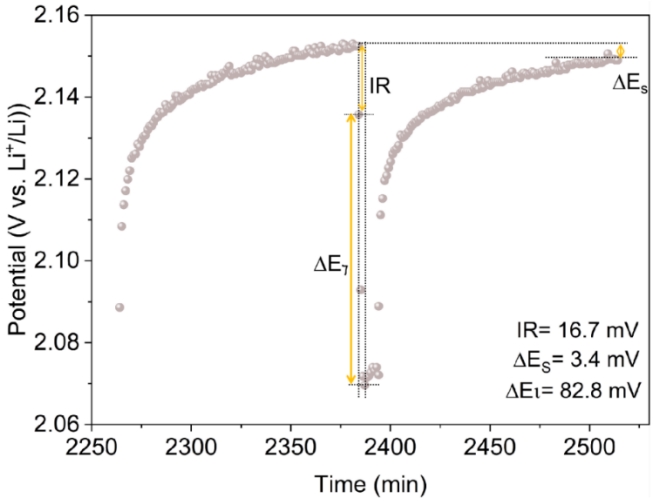

Fig. S6 IR drop of Co_3O_4@S.

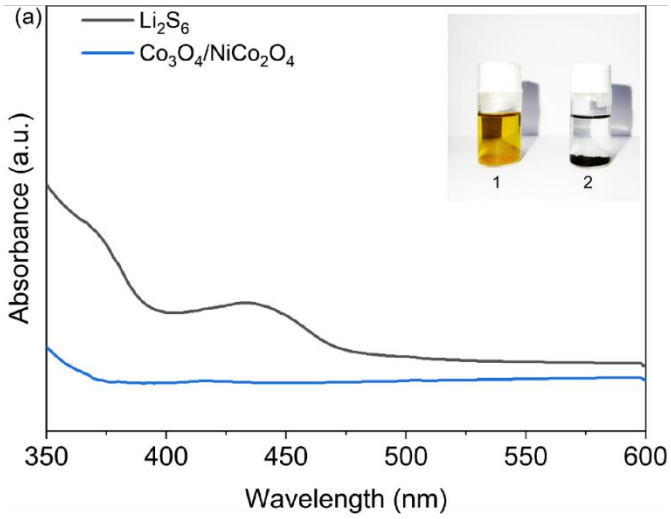

Fig. S7 UV-vis spectra of the Li_2S_6 solution before and after adsorption by $Co_3O_4/NiCo_2O_4$/GQDs. Inset shows the photos: Li_2S_6 solution (1) before and (2) after adsorption.

Table S1. Comparison on electrochemical performance of some hollow host-based sulfur cathodes.

Cathode	Cycling rate	Cycle number	Capacity (mAh g^{-1})	References
NiO-$NiCo_2O_4$@PPy hollow polyhedrons	1 C	200	411	[1]
MnO_2@carbon hollow nanoboxes	2 A/g	200	~200	[2]
CoO/SnO_2@NC/S	0.2 C	100	327	[3]
$NiCo_2O_4$ hollow nanoflowers	0.5 C	100	610	[4]
Co_3O_4/S/carbon nanotubes	0.5 C	550	496	[5]
$Co_3O_4/NiCo_2O_4$/GQDs@S	0.2 C 1 C	100 600	727 508	This work

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