Electronic Supplementary Material (ESI) for ChemComm. This journal is © The Royal Society of Chemistry 2020

Supporting Information

Metal-organic Framework-derived Hollow structure CoS₂/nitrogen-doped Carbon Spheres for High-performance Lithium/Sodium ion Batteries

Lin Chen, ^a Ningjing Luo, ^a Shuping Huang, ^{*a} Yafeng Li, ^{a, c} Mingdeng Wei ^{*a, b}

- ^a Fujian Provincial Key Laboratory of Electrochemical Energy storage Material, Fuzhou University, Fuzhou, Fujian 350002, China
- ^b Jiangsu Collaborative Innovation Center of Photovoltaic Science and Engineering, Changzhou University, Changzhou, 213164 Jiangsu, China.
- ^c Hainan Provincial Key Laboratory of Research on Utiliation of Si-Zr-Ti Resources, Hainan University, Haikou, 570228 Hainan, China.

E-mail address: wei-mingdeng@fzu.edu.cn; huangshp@gmail.com;

Experimental Section

2.1 Preparation of porous Co-MOF spheres precursor

All chemicals were purchased commercial and used as received without further purification. In a typical synthesis, 0.21g (1.0 mM) 1,3,5-benzenetricarboxylic acid (H_3BTC), 0.436 g (1.5 mM) of Co(NO_3)₂.6H₂O and 0.5g of polyvinyl pyrrolidone (PVP) were dissolved in 35 mL methanol. After stirring for 30 min, the resulting solution was transferred into a Teflon-coated stainless-steel autoclave (50 mL) and kept at 150 °C for 12h. The product was naturally cooled to room temperature, then washed by ethanol and collected after dried at 70 °C for 12 h under air.

2.2 Preparation of hollow structure CoS₂/NC spheres

The porous Co-MOF spheres precursors were uniformly mixed with sublimed sulfur powder at a mass ratio of 1:2. Then, the mixture was heated at 550 °C for 2h in a tube furnace under the N₂ gas flow (heating ramp: 2 °C min⁻¹). Finally, the furnace was naturally cooled to room temperature, and the hollow structure CoS_2/NC spheres were obtained.

2.3 Structural characterization

The X-ray diffraction (XRD) of the samples were determined using a Rigaku Ultima IV using Cu K α radiation. The morphologies information was carried out by scanning electron microscopy (SEM, Hitachi 4800) and transmission electron microscopy (TEM, TECNAI G2 F20). The Thermogravimetric analysis (TGA) was recorded using a NETZSCH STA 449 C with a rate of 10 °C min⁻¹ in air atmosphere. X-ray photoelectron spectroscopy (XPS, ESCALAB 250) was measured to analyze the elements and Oxidation states. Raman spectroscopy was collected using a Renishaw in Via Reflex Raman system with a 532 nm Nd:YAG excitation source. FT-IR spectra were performed on a BRUKER-EQUINOX-55 IR spectrophotometer. N₂ adsorption/desorption analysis were obtained on a Micromeritics ASAP 2020 instrument, Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) analyses were used to calculate the specific surface area, and the corresponding pore size distribution.

2.4 Electrochemical measurement

Electrochemical measurements of the samples were carried out in CR2025 type coin cells. The working electrode were made by coating a mixture slurry which composed of 70 wt% the samples, 20 wt% acetylene black carbon (AC) and 10 wt% polyvinylidene difluoride (PVDF) on the copper foil and dried at 110 °C in vacuum overnight. The average active material mass loading was around 0.8-1.0 mg cm⁻². For lithium ion battery, lithium foils were used as the counter electrodes, and Celgard 2400 microporous polypropylene membrane was used as a separator. The electrolyte was a 1 M LiPF₆ in a 1:1 (volume ratio) mixture of ethylene carbonate (EC) and diethyl carbonate (DEC), including 10% (volume) fluoroethylene carbonate (FEC) and 1% vinylene carbonate (VC). For sodium ion battery, the electrolyte was 1M solution of NaPF₆ in dimethoxyethane (DME). Also, the metallic sodium and glass fiber (Whatman) was used as the counter electrode and the separator. Cell assembly was carried out in a glove box filled with highly pure argon gas (O₂ and H₂O levels < 0.1 ppm). Galvanostatic charge-discharge were measured by an electrochemical workstation (Land CT 2001A, Wuhan, China) within a voltage range of 0.01 to 3.0 V (vs. Li⁺/Li or Na⁺/Na) at room temperature. Electrochemical impedance spectroscopy (EIS) measurements were carried out on an electrochemical workstation (Chenhua CHI660c, Shanghai, China). Cyclic voltammograms (CV) were performed on an electrochemical workstation (Chenhua CHI660c, Shanghai, China).

2.5 Computation details

The DFT calculations were performed using the Vienna Ab Initio Simulation Package (VASP) with generalized gradient approximations (GGA). ^{S1-S3} The exchange-correlation (XC) term used the Perdew-Burke-Ernzerhof (PBE) functional. The projector augmented wave (PAW) method was used to model the valence-electron configuration of C, Co and S with an energy cut-off of 500 eV. ^{S4} For the conventional cell of CoS₂, a 5×5×5 k-point mesh was used. The (200) surface of CoS₂ derives from fully relaxed CoS₂ bulk, among it, three bottom layers of the six-layered slabs model were fixed and used for modelling bulk property with a 2×2×1 k-point mesh. The k-point grids of 12×12×4 were used for precise calculations of the densities of states (DOS) of graphene.^{S5} The convergence criteria were set to less than 0.02 eV/Å for the force and 10^{-4} eV/atom for the energy, respectively. All structure schematic diagrams were visualized by VESTA.^{S6}



Fig. S1 (a) SEM image, (b-d) TEM images of porous Co-MOF precursor, respectively.

The morphology of porous Co-MOF spheres was observed by SEM and TEM measurements. As depicted in Fig. S1 (a-c), the Co-MOF precursor shows a uniform structure of porous sphere with an average diameter of about 500-800 nm and a slightly rough surface. It can also be found that hollow spheres are composed of nanoparticles. As shown in Fig. S1d, the lattice fringe of the precursor cannot be observed clearly, indicating the amorphous was formed.



Fig. S2 (a) XRD pattern and (b) IR spectrum of porous Co-MOF precursor.

The XRD pattern and FTIR spectrum of precursor are shown in Fig. S2. Obviously, the well-defined diffraction peak is not detected in the former (Fig. S2a), presenting a low degree of crystallinity, which is consistent with the result of HRTEM.⁵⁷ The FTIR spectrum exhibits the characteristic peaks of the asymmetric and symmetric stretching vibrations of -COO⁻ in the range of 1613-1361cm⁻¹, and the band at 720 cm⁻¹ can be ascribed to plane vibration of the benzene and the band at 1290 cm⁻¹ can be contributed to the stretching vibration of C-N in PVP molecule.⁵⁸



Fig. S3 (a) XRD pattern, (b) N₂ adsorption-desorption isotherms, (c) Raman spectrum and (d) TGA curve of hollow structure COS_2/NC spheres.



Fig. S4 XRD pattern of hollow CoS_2/NC spheres after calcination under air at 900 °C.



Fig. S5 (a) Typical XPS survey spectrum and the corresponding: (b) Co 2p, (c) S 2p, (d) C 1s and (e) N 1s of the hollow structure CoS₂/NC spheres.

To further identify the surface composition and chemical state of hollow structure CoS₂/NC spheres, the XPS measurement was carried on and the results are shown in Fig. S5a. It can be found from the survey spectrum that the elements Co, S, N and C can be detected. In the presence of the O 1s peak, this might be oxygen adsorption and partial oxidation on the surface of CoS₂. The high-resolution spectrum of Co 2p is shown in Fig. S5b, two binding energies at 778.6 and 780.6 eV can be ascribed to Co 2p_{3/2}, and the peaks of Co 2p_{1/2} locate at 793.5 and 797.7 eV. Meanwhile, the binding energies at 783.5 and 803.2 eV can be contributed to the shake-up statellite peaks.⁵⁹ Also, the four peaks at 162.1, 163.5, 164.8 and 168.2 eV are well fitted with the location of S 2p_{3/2}, S 2p_{1/2}, C-S-C bonds and sulfate in Fig. S5c, respectively.^{S10} As for the C 1s core level spectrum displayed in Fig. S5d, the strong peak located at 284.7 is recognized as C-C bond, and another two peaks at 286.0 and 288.2 eV can be attributed to C-N bond, and C=O groups, respectively.^{S11} As shown in Fig. S5e, the N 1s spectrum presents the existence of pyridinic N (398.3 eV), pyrrolic N (399.5 eV) and graphitic N (400.9 eV) types of nitrogen, indicating that the N element was doped into carbon successfully.^{S12} It is believed that the nitrogen doping can benefit to the electron transport and improvement of the electrochemical performance.



Fig. S6 XRD pattern of hollow structure CoS₂/NC spheres electrode at first discharge to 0.01V.



Fig. S7 (a) the equivalent circuit used to fit the experimental data, (b) impedance plots of hollow structure CoS_2/NC spheres electrode after different lithium storage cycles.

With increasing cycle number, the gradual decrease in Rct for hollow CoS₂/NC spheres electrode can be ascribed to the following: i) the hollow structure spheres combined with the amorphous N-doped carbon layer is favorable for the delocalization of electrons and ions; ii) the permeation of electrolyte to the electrode material improves electrochemical kinetics and reduces the impedance between electrode and electrolyte; iii)with the repetition of discharge/charge process, the structure of the electrode material is more suitable for lithiation/delithiation, and the electrochemical kinetics is enhanced, which is conducive to charge transfer.



Fig. S8 SEM images of hollow structure CoS_2/NC spheres after 200 cycles.



Fig. S9 Kinetics analysis of the electrochemical behavior toward Li⁺ for hollow structure CoS₂/NC spheres electrode: (a) CV curves at different scan rates from 0.2 to 5 mV s⁻¹; (b) determination of the b-value using the relationship between peak current and scan rate, (c) separation of the capacitive and diffusion currents to the total at of 1.0 mV s⁻¹ and (d) contribution ratio of the capacitive and diffusion-controlled capacities at different scan rates.

To investigate the possible Li-ion reaction kinetics of CoS_2/NC anode, CV curves were performed at various scan rates from 0.2 to 5.0 mV s⁻¹ and the results are shown in Fig S9a. It is observed that CV curves show similar shape, and the peaks are also strengthened along with the increased scan rate, indicating low polarization of CoS_2/NC electrode.⁵¹³ According to the previous studies, the type of capacity contribution could be qualitatively analyzed by following equations (1-2):^{S14-S15}

$$i = a v^b \tag{1}$$

$$\log i = b \log v + \log a \tag{2}$$

where *a* is a constant and the value of *b* can be determined by the slop of log *i* -log *v* plots. When the value of *b* is 0.5 or 1.0, it represents an ideal diffusion-controlled process or a capacitive-dominated behavior, respectively. The plot of log *i* -log *v* is shown in Fig. S9b, the slope (*b* value) of 0.627, 0.730, 0.677, 0.642 are corresponded to oxidation and reduction peaks from 1 to 4, respectively, suggesting that the electrochemical reaction of CoS_2/NC composite has the diffusion-controlled process and capacitive behavior. Where, the capacity contribution of capacitive effect (k_1v) and diffusion-controlled reaction ($k_2v^{1/2}$) can be calculated based on the following equation (3):

$$i = k_1 v + k_2 v^{1/2} \tag{3}$$

As shown in Fig. S9c, the capacitive-dominated reaction contribution in the total capacity for the hollow structure CoS_2/NC spheres (the red zone) is about 52.1% at a scan rate of 1.0 mV s⁻¹. With increasing scan rate, the capacitive contribution increased gradually, as shown in Fig. S9d. When the scan rate was increased to 5 mV s⁻¹, the contribution of capacitive-dominated is as high as 77.2%.



Fig. S10 Impedance plots of hollow structure CoS₂/NC spheres electrode after different sodium storage cycles.

The gradual decrease in semi-circles diameters at high frequency of the EIS spectra upon cycling can be attributed to the following: i) the hollow structure spheres combined with the amorphous N-doped carbon layer is favorable for the delocalization of electrons and ions; ii) the ether electrolyte is easier to permeate the active material, which improves the electrochemical kinetics and reduces the impedance between the electrode and electrolyte; iii) with the repetition of discharge/charge process, the structure of the electrode material is more suitable for sodiation/desodiation, and the electrochemical kinetics is enhanced, which is conducive to charge transfer.



Fig. S11 SEM images of hollow structure CoS_2/NC spheres after 200 cycles.



Fig. S12 Kinetics analysis of the electrochemical behavior toward Na⁺ for hollow structure CoS₂/NC spheres electrode: (a) CV curves at different scan rates from 0.2 to 5 mV s⁻¹; (b) determination of the b-value using the relationship between peak current and scan rate, (c) separation of the capacitive and diffusion currents to the total at of 1.0 mV s⁻¹ and (d) contribution ratio of the capacitive and diffusion-controlled capacities at different scan rates.

According to results of CV curves, the contribution of total Na-ion storage by diffusion controlled and capacitive behavior could be calculated quantitatively.^{S16} As shown in Fig. S12a, the reaction kinetic of hollow structure CoS₂/NC spheres was performed via the CV curves at different scan rates from 0.2 to 5.0 mV s⁻¹. The shape of CV curves is retained, demonstrating the minor polarization. In plot of Log *i* - Log *v*, as displayed in Fig. S12b, the fitting b values of corresponding peaks 1 and 2 are 0.764 and 0.881, respectively, demonstrating the partial capacitive behavior during electrochemical reaction process. The contribution of capacitive behavior (red zone) in total capacity was conducted at 1.0 mV s⁻¹ in Fig. S12c, which could be reached to 75.7%. The pseudocapacitive behavior promotes the rapid sodiation and desodiation process and improves the rate capability.^{S17-S18} The detailed results of contribution degree at different scan rates are shown in Fig. S12d. As expected, the capacitive behavior contribution rose gradually with increasing scan rates.



Fig. S13 The total density of states of graphene. The dotted line means the Fermi level.



Fig. S14 The total density of states of the CoS_2 (200) surface with spin polarization. The dotted line means the Fermi level.



Fig. S15 The top and side views of (a) a C atom and (b) a C6 ring adsorbed on CoS₂ (200) surface. In (a), the C-S distances are 1.658 and 1.715 Å, and the Co-C distance is 1.814 Å. In (b), the Co-C distance is 1.932 Å.



Fig. S16 (a) DOS and (b) PDOS of C for a C atom adsorbed on CoS₂ (200) surface. (c) DOS and(d) PDOS of C6 for a C6 ring adsorbed on CoS₂ (200) surface.

Based on the strongest peak of X-Ray powder diffraction data, we also used CoS_2 (200) surface (Fig. 4c) to model electrode conductivity change on a nanoscale. From in Fig. S13, the CoS_2 (200) surface also presents an excellent metallicity due to the formation of surface states. Given the work functions of CoS_2 (4.65 eV) and graphene (4.21 eV) calculated by the GGA functional, in the CoS_2/C , the electrons of graphene with delocalized π bonds will transfer to CoS_2 and enhance the total conductivity of CoS_2 . We also studied the electronic structure of a C atom or a C6 ring adsorbed on CoS_2 (200) surface (The adsorbed structures are shown in Fig. S14). From the DOS and partial DOS of a C atom or a C6 ring adsorbed on CoS_2 surface as shown in Fig. S15, it can be seen that the C atom or the C6 ring contribute to the DOS at the Fermi level, in other words, the DOS of CoS_2 surface at the Fermi level increases after interaction with carbon.

Materials	Voltage window (V vs. Li*/Li)	Current rate (mA g ⁻¹)	Capacity retention (mA h g ⁻¹)	Cycle number	References
Hollow structure CoS ₂ /NC spheres	0.01-3.0	200 2000	850.6 721	200 1000	Our work
CoS ₂ /NC	0.01-3.0	100 2000	1083 696	200	J. Alloy. Compd., 2019, 809 , 151854
CoS₂-NF/rGO-NS	0.01-3.0	500 1000	769 539	200 260	Electrochim. Acta, 2019, 326 , 134992
CoS ₂ /NSCNHF	0.01-3.0	1000	549.9	200	Nanoscale, 2019, 11 , 20996-21007
CoS _x @PC	0.01-3.0	100 1000	781.2 717	100 500	<i>Adv. Sci.,</i> 2018, 5 , 1800829
NiS ₂ @CoS ₂ @C@C nanocubes	0.005-3.0	1000	680	100	Energy Storage Mater., 2018, 11 , 67-74
CoS ₂ -C/CNT	0.01-3.0	100	1030	120	ACS Nano,
CoS_2 -in-wall-NCSs	0.01-3.0	200	1080.6	500	2018, 12 , 7220-7231 J. Mater. Chem. A, 2018, 6 , 7148-7154
Hierarchical Co _{1-x} S/C	0.01-3.0	200 1000	791 667	100 700	Electrochim. Acta, 2018, 290 , 193-202
Co _{1-x} S/C	0.01-3.0	500	559	100	Nanoscale, 2018, 10 , 2804-2811
(Ni _{0.3} Co _{0.7}) ₉ S ₈ / N-CNTs/rGO	0.01-3.0	100 1000	800 746	100 400	Chem. Commun., 2018, 54 , 8909-8912
Graphene-anchored Co_9S_8	0.01-3.0	500 1000	910 622	100 200	Electrochim. Acta, 2017, 250 , 196-202
Hierarchal CoS _x hollow spheres	0.01-3.0	500	1012.1	1000	Nano Energy, 2017, 32 , 320-328

Table S1. Comparison of the electrochemical properties of CoSx based anode materials for LIBs.

Table S2. Comparison of the electrochemical properties of CoSx based anode materials for SIBs.								
Materials	Voltage window (V vs. Na⁺/Na)	Current rate (mA g ⁻¹)	Capacity retention (mA h g ⁻¹)	Cycle numbe r	References			
Hollow structure	0.01-3.0	500 2000	775.6 581.4	100 900	Our work			
AGC-CoS ₂ @NCNFs	0.01-3.0	100 3200	357 148	200 1000	<i>Chem. Eng. J.,</i> 2020, 380 , 122548			
Co ₉ S ₈ -C/Co ₉ S ₈	0.01-3.0	500 1000	616 451	150 500	Angew. Chem. Int. Ed. 2019, 58 , 6239 -6243			
Co ₉ S ₈ @S-CF	0.01-3.0	100	373	1000	ACS Appl. Mater. Inter., 2019, 11 , 19218-19226			
Co₃S ₈ @CYSNs	0.2-2.5	100 1000	549.4 342.5	50 400	Energy Storage Mater., 2019, 18 , 51-58			
CoS ₂ /NSCNHF	0.01-3.0	1000	400	170	<i>Nanoscale,</i> 2019, 11 , 20996-21007			
CoS ₂ -C/CNT	0.01-3.0	100	403	200	ACS Nano, 2018, 12 , 7220-7231			
CoS₂/BNG	0.4-2.9	500 1000	470 392	200 2500	Small Methods, 2018, 1800170			
N-CoS₂@C	0.4-2.9	500 1000	782.9 559	- 1000	J. Mater. Chem. A, 2018, 6 , 18967-18978			
N-C/CoS ₂	0.4-2.9	1000	698	500	<i>Nanoscale,</i> 2018, 10 , 20813-20820			
CoS ₂ @MCNFs	0.4-2.9	1000	620	900	ACS Appl. Mater. Inter., 2018, 10 , 31441-31451			
Co _{1-x} S/C	0.01-3.0	1000	320	130	Nanoscale, 2018, 10 , 2804-2811			
Hierarchal CoS _x hollow spheres	0.01-3.0	500	572	100	Nano Energy, 2017, 32 , 320-328			
(Co ₉ S ₈ QD@HCP) @rGO	0.01-3.0	300	628	500	Adv. Funct. Mater., 2017, 27 , 1702046			
CoS/C	0.01-3.0	1000 5000	542 510	2000	Nano Energy, 2017, 35 , 281-289			

Reference

- S1 P. E. Blöchl, Phys. Rev. B, 1994, 50, 17953-17979.
- S2 G. Kresse and J. Furthmüller, Comput. Mat. Sci., 1996, 6, 15-50.
- S3 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, 77, 3865-3868.
- S4 G. Kresse and D. Joubert, Phys. Rev. B, 1999, 59, 1758-1775.
- S5 H. J. Monkhorst and J. D. Pack, Phys. Rev. B, 1976, 13, 5188-5192.
- S6 K. Momma and F. Izumi, J. Appl. Crystallogr., 2011, 44.
- S7 D. Ge, J. Peng, G. Qu, H. Geng, Y. Deng, J. Wu, X. Cao, J. Zheng and H. Gu, New J. Chem., 2016, 40, 9238-9244.
- S8 C. Li, X. Lou, M. Shen, X. Hu, Z. Guo, Y. Wang, B. Hu and Q. Chen, ACS Appl. Mater. Interfaces, 2016, 8, 15352-15360.
- S9 S.-Y. Liao, T.-T. Cui, S.-Y. Zhang, J.-J. Cai, F. Zheng, Y.-D. Liu and Y.-G. Min, Electrochim. Acta, 2019, 326, 134992.
- S10 F. Han, C. Zhang, B. Sun, W. Tang, J. Yang and X. Li, *Carbon*, 2017, **118**, 731-742.
- S11 D. Cao, W. Kang, S. Wang, Y. Wang, K. Sun, L. Yang, X. Zhou, D. Sun and Y. Cao, J. Mater. Chem. A, 2019, 7, 8268-8276.
- S12 C. Zheng, N. Luo, S. Huang, W. Wu, H. Huang and M. Wei, ACS Sustainable Chem. Eng., 2019, 7, 10198-10206.
- S13 C. Dong, J. Liang, Y. He, C. Li, X. Chen, L. Guo, F. Tian, Y. Qian and L. Xu, ACS Nano, 2018, **12**, 8277-8287.
- S14 T. Brezesinski, J. Wang, S. H. Tolbert and B. Dunn, Nature Mater., 2010, 9, 146-151.
- S15 F. Liu, X. Cheng, R. Xu, Y. Wu, Y. Jiang and Y. Yu, Adv. Funct. Mater., 2018, 28, 1800394.
- S16 X. Cheng, D. Li, F. Liu, R. Xu and Y. Yu, Small Methods, 2019, 3, 1800170.
- S17 S. Li, L. Xie, H. Hou, H. Liao, Z. Huang, X. Qiu and X. Ji, J. Power Sources, 2016, 336, 196-202.
- S18 Q. Guo, Y. Ma, T. Chen, Q. Xia, M. Yang, H. Xia and Y. Yu, ACS Nano, 2017, 11, 12658-12667.