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Published in:
Energy Storage Materials

Link to article, DOI:
[10.1016/j.ensm.2019.01.012](https://doi.org/10.1016/j.ensm.2019.01.012)

Publication date:
2019

Document Version
Peer reviewed version

[Link back to DTU Orbit](#)

Citation (APA):
Shangguan, H., Huang, W., Engelbrekt, C., Zheng, X., Shen, F., Xiao, X., Ci, L., Si, P., & Zhang, J. (2019). Well-defined cobalt sulfide nanoparticles locked in 3D hollow nitrogen-doped carbon shells for superior lithium and sodium storage. *Energy Storage Materials*, 18, 114-124. <https://doi.org/10.1016/j.ensm.2019.01.012>

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Well-Defined Cobalt Sulfide Nanoparticles Locked in 3D Hollow Nitrogen-Doped Carbon Shells for Superior Lithium and Sodium Storage

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ABSTRACT: Hollow nanostructured materials present a class of promising electrode materials for energy storage and conversion. Herein, 3D hollow nitrogen-doped carbon shells decorated with well-defined cobalt sulfide nanoparticles (Co₉S₈/HNCS) have been
20 constructed for superior lithium and sodium storage. Two steps are involved in the designed preparation procedure. First, hollow intermediates with preserved cobalt components are controllably fabricated by simultaneously dissociating cobalt containing zeolitic-imidazolate-
frameworks-67 (ZIF-67), and polymerizing dopamine in a Tris-HCl solution (pH = 8.5). The poly-dopamine (PDA) wrapped intermediates inherits the polyhedral structure of the ZIF-67
25 crystals. In the second step, the final Co₉S₈/HNCS composite is obtained via a combined carbonization and sulfurization treatment of the intermediates, allowing the formation of hollow polyhedrons of nitrogen-doped carbon shells (900 ± 100 nm) derived from PDA and the encapsulation of highly uniform cobalt sulfide nanoparticles (11 ± 2 nm). This

configuration is believed to not only shorten the lithium or sodium ion diffusion distance and accommodate volume change during lithium or sodium ion insertion/extraction, but also to enhance the overall electrical conductivity and the number of active sites. As a result, the Co₉S₈/HNCS composite exhibits an impressive reversible capacity of 755 mA h g⁻¹ at 500 mA g⁻¹ after 200 cycles for lithium ion storage, and capacities of 327 mA h g⁻¹ at 500 mA g⁻¹ after 200 cycles and 224 mA h g⁻¹ at 1000 mA g⁻¹ after 300 cycles for sodium ion storage. Essential factors especially the structural stability during cycling have been identified, and the discharge/charge mechanism is discussed.

Keywords: Cobalt sulfide, hollow structure, metal organic framework, lithium ion storage, sodium ion storage.

1. Introduction

To meet the increasing demands for energy storage in renewable energy economy, the development of secondary battery technologies such as lithium and sodium ion batteries (LIBs and SIBs) has invariably gained great attention. Two main reactive modes (i.e. intercalation and conversion) are responsible for LIBs and SIBs [1]. In comparison to the intercalation reaction occurring in carbonaceous materials with no more than one electron transferred, conversion reactions can transfer numerous electrons (2-6 electrons), and thus possess higher theoretical capacity [1-3]. However, cracks and pulverization found in conversion-type materials, as results of significant volumetric change during cycling, alongside with sluggish ion diffusion within the electrode materials, lead to large capacity loss and weak rate capability. Tremendous efforts have been dedicated to developing robust conversion-type materials to replace the traditional intercalation materials [4-10]. Cobalt sulfides (Co_xS_y), a subgroup of transition metal sulfides (TMSs) with excellent electrochemical activity and high theoretical capacity ($> 400 \text{ mA h g}^{-1}$), have been investigated as promising conversion-type electrode materials [11-16].

To shorten the diffusion path for high rate performance, decreasing the particle-sizes of Co_xS_y is a well-recognized approach [17-19]. In addition, incorporating Co_xS_y into a carbonaceous framework can effectively promote electrical conductivity and accommodate its volumetric change for enhanced cycling stability [17-21]. For example, Wu and co-workers have reported a graphene paper / Co_9S_8 nanocomposite for high-performance LIBs, delivering a capacity of $538.69 \text{ mA h g}^{-1}$ at 1090 mA g^{-1} . The good electrochemical performance was benefited from the unique structure with Co_9S_8 nanoparticles (ca. 25 nm) uniformly dispersed on the surface of highly conductive graphene sheets [20]. Wang et al. have prepared CoS_2 /multi-walled carbon nanotubes (MWCNTs) nanocomposites for SIBs with a capacity of $242.3 \text{ mA h g}^{-1}$ at 800 mA g^{-1} [21]. Besides, introducing nitrogen atoms to porous carbon materials can alter the chemical and electronic properties of carbonaceous components for enhanced electrochemical performance [22, 23]. It is not surprisingly to see increasing interest in developing $\text{Co}_x\text{S}_y/\text{N}$ doped carbon hybrids [24, 25]. However, those hybrids are generally fabricated by post-modification processes, lacking integral structural design and excellent rate performance. Furthermore, hollow micro/nanostructured carbonaceous materials with large specific surface area can enable more active sites

displayed and ensure shorter ion/electron diffusion pathways [26-29]. For example, Qian and co-workers have encapsulated Co_{1-x}S nanoparticles in nitrogen-doped porous carbon hollow nanospheres for superior lithium and sodium storage. The materials demonstrated a discharge capacity of 320 mA h g^{-1} for sodium storage at 1000 mA g^{-1} after 130 cycles and 559 mA h g^{-1} for lithium storage at 500 mA g^{-1} after 100 cycles [29]. Inspired by the previous reports, highly homogeneous cobalt sulfide nanoparticles embedded in a nitrogen-doped carbon matrix with integral hollow structure are of significant interest for high-performance LIBs and SIBs.

Metal-organic frameworks (MOFs) formed by assembly of metal units and organic linkers with unique structure and component functionalities, offer great opportunities as templates or precursors for hollow structured materials [30-36]. For example, Chen and co-workers have reported MOFs derived CoP nanoparticle-embedded N-doped carbon nanotube hollow polyhedron for overall water splitting, utilizing the as-prepared ZIF-8@ZIF-67 as the precursor for pyrolysis and following phosphorization [35]. Wang et. al have fabricated the hollow metal (Co or Zn)/N-doped carbon particles with excellent oxygen reduction electrocatalytic activity. The precursors were hollow-structured PDA with coordinated assembly of metal ions (Co or Zn) originated from the ZIF-67 or ZIF-8 [36]. PDA wrapping of the well-structured MOF crystals, which were simultaneously dissolved in a slightly alkaline solution, results in PDA intermediates preserving the leaked metal ions and imprinted hollow structure of MOF crystals (Scheme 1). The intermediates can be subsequently treated for various desired functional materials and the versatile approach allows the preparation of a wide range of metal-based materials. Pioneering works on MOFs derived Co_9S_8 nanoparticles have been reported [37, 38]. However, those nanocomposites did not well inherit the precursor polyhedral configuration, showing limited electrochemical performance. For example, Zhu et. al have synthesized ZIF-67 derived Co_9S_8 nanoparticles encapsulated in nitrogen-doped carbon networks with a constricting polyhedral morphology, without showing a high-current-density cycling ability [37]. Yu and coworkers have fabricated ZIF-67 derived Co_9S_8 @C nanocages with absolute hollow interiors, while only delivers 54 mA h g^{-1} for lithium storage after 30 cycles at 544 mA g^{-1} [38]. To the best of our knowledge, there is no report on utilizing PDA derived nitrogen doped carbon layers to embed ZIF-67 derived Co_9S_8 nanoparticles for enhanced lithium or sodium storage

performance. Moreover, significant challenge lies in the controllable synthesis of MOFs derived Co_9S_8 nanocomposites showing uniform decoration of Co_9S_8 nanoparticles immobilized in hollow nitrogen-doped carbon shells.

Herein, we demonstrate a synthetic strategy of cobalt sulfide nanoparticles homogeneously locked in 3D hollow nitrogen-doped carbon shells ($\text{Co}_9\text{S}_8/\text{HNCS}$) for high-performance lithium and sodium storage. PDA intermediates retaining of the Co cations and polyhedral structure of ZIF-67 crystals are prepared (Scheme 1). Key parameters including the concentration of dopamine hydrochloride (DAH) are examined to evaluate their effects on the resulted intermediate morphology. After carbonization and the subsequent sulfurization (Scheme 1), $\text{Co}_9\text{S}_8/\text{HNCS}$ composite is obtained with highly monodisperse Co_9S_8 nanoparticles (11 ± 2 nm) embedded in 3D hollow nitrogen-doped carbon shells. $\text{Co}_9\text{S}_8/\text{HNCS}$ is tested for batteries, exhibiting an impressive reversible capacity of 755 mA h g^{-1} at 500 mA g^{-1} after 200 cycles for lithium storage, and superior capacities of 327 mA h g^{-1} at 500 mA g^{-1} after 200 cycles and 224 mA h g^{-1} at 1000 mA g^{-1} after 300 cycles for sodium storage. The excellent electrochemical performance is ascribed to the synergistic effects of nanosized cobalt sulfide particles and nitrogen-doped carbon polyhedral shells combined in the unique porous hollow configuration.

2. Experimental

2.1. Chemicals and Reagents

Cobaltous nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 99%), 2-methylimidazole ($\text{C}_4\text{H}_6\text{N}_2$, 98%), dopamine hydrochloride (DAH, $\text{C}_8\text{H}_{11}\text{NO}_2 \cdot \text{HCl}$, 98%), tris(hydroxymethyl)aminomethane hydrochloride (Tris HCl, $\geq 99\%$), thiourea ($\text{CH}_4\text{N}_2\text{S}$, $\geq 99\%$) were purchased from Aladdin, China. Methanol (CH_4O , $\geq 99.5\%$) and ethanol ($\text{C}_2\text{H}_6\text{O}$, $\geq 99.7\%$) were obtained from Sinopharm Chemical Reagent Co., Ltd. All chemicals were used as received without further purification. Ultrapure water ($>18.25 \text{ M}\Omega \text{ cm}$) was used to prepare all the aqueous solutions.

2.2. Synthesis of hollow $\text{Co}_9\text{S}_8/\text{HNCS}$ composite

ZIF-67 crystals were fabricated according to a modified procedure [34]. Briefly, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (498 mg) and 2-methylimidazole (656 mg) were dissolved in 100 mL

methanol to form a uniform solution, which was left at room temperature for 24 h to form ZIF-67 crystals. The obtained ZIF-67 crystals were purified with centrifugation and washing with methanol at least three times.

A poly-dopamine (PDA) layer was subsequently introduced to the surface of the ZIF-67 crystals. 120 mg ZIF-67 crystals were added into DAH solution (with concentrations of 0.5, 1.0 or 2.0 mg mL⁻¹) in 50 mL Tris-HCl (10 mM, pH = 8.5) and sonicated for 10 min. The mixtures were stirred for 24 h at room temperature. The solid products were washed with ultrapure water and ethanol separately more than three times. After vacuum drying, the PDA@ZIF-67 composite was obtained.

As-prepared PDA@ZIF-67 composite was annealed at 550 °C for 1 h under nitrogen gas. Then, the carbonized PDA@ZIF-67 composites were sulfurized at 400 °C for 6 h under Ar/H₂ atmosphere (content of H₂: 5% (v/v)) using thiourea as the sulfur source. Two individual quartz boats containing thiourea and PDA@ZIF-67 (mass ratio 3:1), respectively, were aligned parallel to the direction of gas flow. The final dark powders (Co₉S₈/HNCS) were collected. As a reference material, cobalt sulfide nanoparticles coated with nitrogen-doped carbon (Co₉S₈/NC) composite was synthesized according to the same protocol without PDA modification layers.

2.3. Materials characterization

The crystalline features of the obtained composites were analyzed by X-ray diffraction (XRD, Miniflex 600). Raman spectra were recorded by a Raman spectrometer (Renishaw InVia, 633 nm Laser). X-ray photoelectron spectroscopic (XPS) analysis was performed on samples loaded on a silicon substrate with a Thermo-Scientific system (Al-K α radiation, 1484.6 eV). Microstructure and composition analysis were conducted with scanning electron microscopy (SEM, HITACHI SU-70, 15 kV; Quanta FEG 200 ESEM, 15 kV), atomic-force microscopy (AFM, Agilent Technology 5500, tapping mode, a mica sheet as the substrate), and transmission electron microscopy (TEM, JEOL 2800, 200 kV; Tecnai G2 T20, 200 kV). Surface functional groups were determined by Fourier transform infrared spectroscopy (FTIR, Vector 22 spectrometer, Bruker). The specific surface area was estimated by a Surface Area & Pore Size Analyzer (ASAP 2020, Micromeritics). Thermal

gravimetric analysis (TGA, Mettler-Toledo TGA/SDTA851e Thermo Analyzer) was performed in air from room temperature to 900 °C with a heating rate of 5 °C min⁻¹.

2.4. Electrochemical measurements

The working electrodes of half coin cells were prepared by casting the mixture of active materials (70 wt%), super P (20 wt%) and polyvinylidene fluoride (PVDF) (10 wt%) dissolved in N-methyl-2-pyrrolidone (NMP) onto a copper foil. For lithium and sodium ion storage, lithium and sodium foil were used as the counter electrode, respectively. 1.0 M LiPF₆ dissolved in a solution composed of dimethyl carbonate, ethylene carbonate, diethyl carbonate (1:1:1 by volume) was used as the electrolyte for lithium ion storage. 1.0 M NaClO₄ dissolved in a medium consisting of ethylene carbonate, propylene carbonate (1: 1 wt%) and 5 wt% fluoroethylene carbonate was used as the electrolyte for sodium ion storage. Coin-type (CR 2016) batteries were assembled in a glove box under argon atmosphere at room temperature. Neware-CT-3008 test system (Shenzhen, China) was used for galvanostatic charge/discharge tests in a potential window of 0.01-3.0 V. CHI 660E electrochemical workstation (Shanghai, China) was utilized to record cyclic voltammograms (CVs) in a voltage range of 0.01-3.0 V at a scan rate of 0.1 mV s⁻¹. Electrochemical impedance spectroscopy (EIS) in the frequency range of 0.01 to 100 kHz was carried out at open circuit potential (OCP) using a Metrohm Autolab.

3. Results and discussion

Formation of PDA@ZIF-67 intermediates. The synthetic strategy of Co₉S₈/HNCS composite was shown in Scheme 1. First, as-prepared solid rhombic dodecahedral ZIF-67 crystals with an average particle size of 1100 ± 100 nm (Fig. S1 and Fig. S2) were mixed with different concentrations of dopamine hydrochloride (DAH) in Tris-HCl (10 mM, pH=8.5) solution under magnetic stirring. Two processes were likely to occur simultaneously: (1) the dissolution of ZIF-67 crystals in the weak alkaline environment. The 2-methylimidazole (2-MIM) linkers in the ZIF-67 become protonated, leading to the breakdown of metal-ligand bonds and the subsequent dissolution of ZIF-67 crystals [39, 40], and (2) oxidation and self-polymerization of dopamine forming polydopamine (PDA) layers, onto the polyhedron structure of ZIF-67 while immobilizing liberated Co units [41].

Scheme 1. Schematic illustration of the preparation of the $\text{Co}_9\text{S}_8/\text{HNCS}$ composite. Not drawn to real scale.

Controlling the concentration of DAH is key for the formation of well-defined PDA@ZIF-67 intermediates. When the concentration of DAH is 0.5 mg mL^{-1} , the obtained PDA@ZIF-67 samples show a cracked structure (Fig. S3a and b), which are further confirmed by the TEM characterization (Fig. S3c and d). This is a result of insufficient protection by PDA layers. When treated by 2.0 mg mL^{-1} DAH, the generated PDA@ZIF-67 (Fig. S4) shows the co-existence of both polyhedron-shaped structures and spherical PDA clusters, due to the formation of extra PDA clusters. 1.0 mg mL^{-1} DAH is adopted as the optimal concentration where PDA layers maintain the original polyhedral structure ($1000 \pm 100 \text{ nm}$) without excess PDA for spheres formation (Fig. S5a and b). TEM (Fig. S5c and d) further reveals hollow inner voids of the generated polyhedral structure compared with solid ZIF-67 crystals (Fig. S2). This transformation is also confirmed from changes in crystallography. The X-ray diffraction (XRD) pattern of ZIF-67 crystals shows a characteristic crystalline pattern, which is not found for the amorphous-featured PDA@ZIF-67 composite (Fig. S6a). Moreover, Fourier transform infrared spectroscopy (FTIR) verifies the transformation by the disappearance of the band at 420 cm^{-1} ascribed to Co-N stretching vibrations of the ZIF-67 crystals in the PDA@ZIF-67 composite (Fig. S6b) [42]. The broad band at 3391 cm^{-1} is assigned to the O-H & N-H stretching modes in the PDA@ZIF-67 composite [43].

Structural and morphological characteristics of $\text{Co}_9\text{S}_8/\text{HNCS}$. Subsequent carbonization and sulfurization of PDA@ZIF-67 is applied to generate the final product, i.e. $\text{Co}_9\text{S}_8/\text{HNCS}$. As a reference, a non-PDA-protected material ($\text{Co}_9\text{S}_8/\text{NC}$) is prepared without PDA coating in Scheme 1 directly carbonizing/sulfurizing ZIF-67 crystals. The generated $\text{Co}_9\text{S}_8/\text{HNCS}$

composite is confirmed by XRD (Fig. 1a) where all peaks could be indexed to Co_9S_8 (JCPDS no. 65-1765). A broad low-intensity peak is observed at $20\text{-}25^\circ$ due to the existence of PDA derived carbon [44]. As a control, the broad peak is not found in that of $\text{Co}_9\text{S}_8/\text{NC}$ composite (Fig. S7). The Raman spectra (Fig. 1b) reveal an I_D/I_G intensity ratio of 0.83 for the $\text{Co}_9\text{S}_8/\text{HNCS}$ composite which is smaller than that of $\text{Co}_9\text{S}_8/\text{NC}$ (0.94), suggesting an increased sp^2 hybridization expected to promote electrical conductivity. The presence of cobalt, sulfur, nitrogen and carbon in $\text{Co}_9\text{S}_8/\text{HNCS}$ is identified by X-ray photoelectron spectroscopy (XPS, Fig. S8). The high-resolution Co 2p spectrum (Fig. 1c) shows peaks at 778.5 and 793.6 eV assigned to cobalt sulfide in the composite, with peaks at 781.0 and 796.5 eV mainly attributed to cobalt oxide species, which is originated from the partial oxidation on the surface of composite [45-47]. In the S 2p spectrum (Fig. 1d), a spin-orbit doublet at 161.3/162.5 eV is found due to the presence of S^{2-} . Other peaks are observed at 162.4/163.6 eV corresponding to S_n^{2-} , and 167.6/168.8 eV belong to SO_x from the partial superficial oxidation of the composite [9, 10]. The high-resolution N 1s spectrum (Figure 1e) is deconvoluted into five peaks at 398.5, 399.5, 400.3, 401.3 and 403.3 eV, which are assigned to pyridinic-N, amino-N, pyrrolic-N, graphitic-N and oxidized-N, respectively. In addition, the high pyridinic-N and pyrrolic-N content is likely to provide more active sites for lithium and sodium storage [22, 48]. In the high-resolution C 1s spectrum (Figure 1f), peaks at 284.6 and 285.4 eV from sp^2 and sp^3 C-C indicate both graphitic and amorphous states in the carbon structure, respectively. The peak at 285.9 eV reveals the existence of C-N bonding, with peaks at 286.9 and 289.1 eV corresponding to the C-O and C=O, respectively [49, 50]. The surface elemental Co, S, N and C contents of $\text{Co}_9\text{S}_8/\text{HNCS}$ composite are quantified from XPS, with 3.85 atom% cobalt, 3.41 atom% sulfur, 9.50 atom% nitrogen and 83.24 atom% carbon. The obtained atom ratio of Co/S corroborates the chemical formula of Co_9S_8 . In addition, the high content of nitrogen element on the surface of $\text{Co}_9\text{S}_8/\text{HNCS}$ composite reveals the high nitrogen doping in the PDA derived carbon shells.

Fig. 1. (a) XRD pattern of the $\text{Co}_9\text{S}_8/\text{HNCS}$ composite. (b) Raman spectra of the $\text{Co}_9\text{S}_8/\text{HNCS}$ and $\text{Co}_9\text{S}_8/\text{NC}$ composite. High-resolution XPS Co 2p spectrum (c), S 2p spectrum (d), N 1s spectrum (e) and C 1s spectrum (f) of the $\text{Co}_9\text{S}_8/\text{HNCS}$ composite.

5 The morphology of as-prepared composites is examined using scanning electron microscopy (SEM), atomic-force microscopy (AFM) and transmission electron microscopy (TEM). Highly uniform $\text{Co}_9\text{S}_8/\text{HNCS}$ polyhedrons with an average size of 900 ± 100 nm are shown in Fig. 2a. The high-resolution SEM images (Fig. 2b and c) clearly displayed a typical hollow rhombic-dodecahedron morphology, originating from the structure of the hollow

10 PDA@ZIF-67 intermediates. Moreover, the energy dispersive X-Ray spectrum (EDS) of $\text{Co}_9\text{S}_8/\text{HNCS}$ composite (Fig. S9) indicates the existences of carbon, oxygen, nitrogen, sulfur and cobalt. In contrast, the SEM images of $\text{Co}_9\text{S}_8/\text{NC}$ composite (Fig. S10a, b) shows no obvious polyhedral structure, revealing that the initial structure of the ZIF-67 crystals is destroyed without PDA modification. The EDS of $\text{Co}_9\text{S}_8/\text{NC}$ composite (Fig. S10c) exhibits the

15 expected elements (C, O, N, S and Co). It is noteworthy that the nitrogen content in $\text{Co}_9\text{S}_8/\text{HNCS}$ (12.60 atom%) is much higher than that in $\text{Co}_9\text{S}_8/\text{NC}$ (4.12 atom%), which is close to the calculated value (9.50%) of XPS data of $\text{Co}_9\text{S}_8/\text{HNCS}$. More nitrogen doping in the $\text{Co}_9\text{S}_8/\text{HNCS}$ composite could promote electronic conductivity and generate more defects in the carbon layers, supplying more active sites for the lithium and sodium ion

20 insertion [22, 23]. The surface micromorphology of a single $\text{Co}_9\text{S}_8/\text{HNCS}$ particle is further characterized by AFM (Fig. 2d) exhibiting polyhedral structure. The height of the $\text{Co}_9\text{S}_8/\text{HNCS}$

particle is 780 nm on the central platform and 856 nm on the apex, further confirming the obtained rhombic-dodecahedron structure, in good agreement with the SEM results (Fig. 2a, b and c).

Fig. 2. (a, b, c) SEM images of the $\text{Co}_9\text{S}_8/\text{HNCS}$ composite; inset in (a) shows the particle size distribution. (d) AFM image of a single $\text{Co}_9\text{S}_8/\text{HNCS}$ nanoparticle; (e) height profile of the single $\text{Co}_9\text{S}_8/\text{HNCS}$ nanoparticle, indicated by the red line in (d).

TEM images of $\text{Co}_9\text{S}_8/\text{HNCS}$ (Fig. 3a and b) clearly show ultrafine and monodisperse Co_9S_8 nanoparticles (Fig. 3a) with a size of 11 ± 2 nm encapsulated in PDA derived carbon layers. Moreover, the dark boundary and bright center of the polyhedral shell emphasize the hollow structure. As a control, TEM images of $\text{Co}_9\text{S}_8/\text{NC}$ (Fig. S11) show Co_9S_8 nanoparticles coated on the carbon layers with a fragmented morphology. It is clear that the introduction of PDA in the ZIF-67 precursors leads to the generation of a novel hollow

structure, as well as maintains polyhedral morphology during the carbonization and sulfurization. Fig. 3b displays the porous structure of the composite and the wrapping of Co_9S_8 nanoparticles in the polyhedral carbon framework. High-resolution TEM (Fig. 3c) further confirms that Co_9S_8 nanoparticles embed in the carbon layers rather than attach on the carbon outer surface. Lattice fringes estimated as 0.29 nm (Fig. 3c) are assigned to the (311) plane of Co_9S_8 (JCPDS no. 65-1765) [51, 52]. The nanoscale elemental distribution within the composite structure is investigated with scanning-TEM and EDS mapping (Fig. S12). A line plot across a single $\text{Co}_9\text{S}_8/\text{HNCS}$ particle (Fig. 3d) and elemental maps (Fig. 3f-i) clearly shows a hollow framework of Co and S wrapped in a thin nitrogen-doped carbon matrix (C, N). Co, S, N and C elements are uniformly distributed in the polyhedral shell.

Fig. 3. (a) TEM image of the $\text{Co}_9\text{S}_8/\text{HNCS}$ composite; inset is the corresponding particle size distribution of Co_9S_8 particles. (b) TEM image of the shell of the $\text{Co}_9\text{S}_8/\text{HNCS}$ composite. (c) High-resolution TEM image of the $\text{Co}_9\text{S}_8/\text{HNCS}$ composite. (d) Elemental distribution obtained from a line plot across a single $\text{Co}_9\text{S}_8/\text{HNCS}$ particle; Inset shows the line with the particle. (e) Secondary electron image, and (f-i) EDS elemental map of a single $\text{Co}_9\text{S}_8/\text{HNCS}$ particle.

Surface area and composition analysis of $\text{Co}_9\text{S}_8/\text{HNCS}$. Typical nitrogen adsorption-desorption isotherms of as-prepared composites are shown in Fig. 4. The specific surface area of the $\text{Co}_9\text{S}_8/\text{HNCS}$ composite is $63.5 \text{ m}^2 \text{ g}^{-1}$, while the $\text{Co}_9\text{S}_8/\text{NC}$ composite only

registers a value of $24.6 \text{ m}^2 \text{ g}^{-1}$. The inset in Fig. 4a present the pore-size distribution of $\text{Co}_9\text{S}_8/\text{HNCS}$ in the range of 23-95 nm. This observation reveals that abundant mesopores (2-50 nm) and macropores (> 50 nm) simultaneously exist in the composite, most likely originating from the stacking of Co_9S_8 nanoparticles and the hollow interior structure, respectively. In contrast, the pore size of $\text{Co}_9\text{S}_8/\text{NC}$ composite (Fig. 4b) distributes at about 32 nm and no obvious macropores are found. The components of synthesized composites are investigated by thermal gravimetric analysis (TGA) in air. A typical TGA curve of $\text{Co}_9\text{S}_8/\text{HNCS}$ composite (Fig. S13a) shows a weight loss below 150 °C, attributed to the removal of adsorbed H_2O and gaseous components in the composites. A weight increase is observed up to 320 °C, due to the partial formation of cobalt sulfate [53]. A rapid loss in the range of 320-550 °C is mainly attributed to the oxidation of carbon species. A constant platform in the region of 550-700 °C is ascribed to the balance from decomposition of carbon materials and generation of cobalt sulfate. A dramatic weight loss then occurs from 700-850 °C, revealing the formation of Co_3O_4 . Above 850 °C, the weight remains constant. The total weight loss in the TGA curve of $\text{Co}_9\text{S}_8/\text{HNCS}$ composite (Fig. S13a) is about 49.6%, indicating the percentage of cobalt sulfide to be 54.9%. As a control, TGA of the $\text{Co}_9\text{S}_8/\text{NC}$ composite (Fig. S13b) provides a total weight loss of 29.2%, and a cobalt sulfide content of 77.1%. TGA of $\text{Co}_9\text{S}_8/\text{NC}$ (Fig. S13b) does not provide a visible weight loss from carbon as the region 320-550 °C. This is different from that of $\text{Co}_9\text{S}_8/\text{HNCS}$, which is due to the weight increase from sulfide to sulfate over the weight loss from carbon dominates in the $\text{Co}_9\text{S}_8/\text{NC}$ composite.

Fig. 4. Typical nitrogen adsorption-desorption isotherms of the Co₉S₈/HNCS (a) and Co₉S₈/NC (b) composite; Insets were the corresponding pore-size distribution.

Lithium storage performance. The lithium storage properties of Co₉S₈/HNCS and Co₉S₈/NC composites were evaluated in coin-type half cells. Cyclic voltammograms (CVs) of the first five cycles of Co₉S₈/HNCS composite in a potential window of 0.01–3.0 V are demonstrated in Fig. 5a. Two peaks at ca. 1.0 and 0.40 V are found in the initial cathodic cycle, respectively. The peak at 1.0 V is assigned to the conversion of Li₂S and metallic cobalt, while the peak at 0.40 V is attributed to the formation of solid electrolyte interphase (SEI) film and partial decomposition of the electrolyte [12, 54]. In the initial anodic cycle, a peak at about 2.1 V is clearly observed, corresponding to the sulfurization of metallic cobalt [12]. The conversional reaction can be described as following:

After the first two scans, the cathodic peak and anodic peak shift to 1.1 and 2.5 V, respectively. Moreover, the well-overlapping CVs after the first cycle reveal considerable electrochemical reversibility and stability of Co₉S₈/HNCS composite. Differently, the CVs of Co₉S₈/NC composite (Fig. S14a) decrease irreversible, indicating instability of Co₉S₈/NC composite during cycling. Galvanostatic discharge/charge profiles of the first three, 10th and 20th cycles of Co₉S₈/HNCS at a current density of 100 mA g⁻¹ are shown in Fig. 5b. The observed voltage platforms in the first three cycles correspond to the peaks found in the CVs of Co₉S₈/HNCS. A small decrease of discharge and charge capacities is found in the 10th and 20th cycles, revealing considerable cycling stability. In comparison, the Co₉S₈/NC (Fig. S14b) demonstrates a non-overlapping curve, indicating a poor cycling stability of Co₉S₈/NC during cycling.

Fig. 5c shows the cycling performance of the Co₉S₈/HNCS and Co₉S₈/NC composites at a current density of 100 mA g⁻¹. The first discharge and charge capacities of Co₉S₈/HNCS are 1105 and 879 mA h g⁻¹, respectively, with an initial Coulombic efficiency of 80%. The irreversible capacity loss (i.e. the lower initial charge capacity than the initial discharge capacity), is likely due to the irreversible consumption of Li⁺ from side reaction with the electrolyte, partially irreversible Li⁺ trapping in the amorphous carbon of the composite, and generation of the SEI film as a considerable amount of Li⁺ irreversibly reacted with the surface of active materials [12, 54, 55]. The formation of SEI film has been identified by TEM images (Fig. S20c and d), which clearly show that the surface of the active material is coated by a SEI film after discharge-charge cycling. In contrast, Co₉S₈/NC delivers an initial discharge/charge capacity of 1140/814 mA h g⁻¹, with a lower initial Coulombic efficiency of 71%. Co₉S₈/HNCS maintains a stable discharge capacity of 768 mA h g⁻¹ at 100 mA g⁻¹ after 100 cycles, with a retained capacity of 70%. The Coulombic efficiency is over 97% after the first three cycles. The good cycling stability of Co₉S₈/HNCS is attributed to the integral structural stability of Co₉S₈/HNCS with PDA derived carbon-shells modification. In converse, Co₉S₈/NC shows a rapid capacity loss in discharge capacity and only delivers 345 mA h g⁻¹ at 100 mA g⁻¹ after 100 cycles, with a lower retained capacity of 30%. The rate capabilities of Co₉S₈/HNCS and Co₉S₈/NC composites at different current densities are shown in Fig. 5d. Co₉S₈/HNCS (Fig.5d) delivers the first discharge/charge capacity of 1171/798 mA h g⁻¹. In comparison, the initial discharge and charge capacities of Co₉S₈/NC (Fig.5d) are 1140 and

632 mA h g⁻¹, respectively. The higher initial Coulombic efficiency (Fig. 5c and d) of Co₉S₈/HNCS than Co₉S₈/NC indicates that Co₉S₈ nanoparticles locked in the hollow PDA derived carbon shells, and the higher nitrogen-doping level in the Co₉S₈/HNCS composite can efficiently improve the integral electrical conductivity of the composite for Li⁺ transport and significantly prevent detrimental reactions between active materials and electrolyte. Thus, the extent of first-cycle irreversible capacity loss of Co₉S₈/HNCS is reduced [17, 22]. In addition, Co₉S₈/HNCS delivers discharge capacities of 734, 613, 579, 539, 447, 287 mA h g⁻¹ at 100, 200, 300, 500, 1000, 2000 mA g⁻¹, respectively. Remarkably, setting the current density back to 100 mA g⁻¹ after the 60th cycle, the discharge capacity of Co₉S₈/HNCS composite shows a stable performance and regains a value of 734 mA h g⁻¹ after 90 cycles, suggesting an excellent rate capability originated from the structural stability of Co₉S₈/HNCS during cycling. In contrast, Co₉S₈/NC composite registers discharge capacities of 518, 323, 216, 146, 96, 65 mA h g⁻¹ at 100, 200, 300, 500, 1000, 2000 mA g⁻¹, respectively. Upon resetting the current density to 100 mA g⁻¹, the discharge capacity of Co₉S₈/NC composite decreases to 204 mA h g⁻¹ after 90 cycles upon resetting current density to 100 mA g⁻¹, 39% of the initial capacity (518 mA h g⁻¹). The results indicate the Co₉S₈/NC composite without PDA modification cannot buffer the large volume expansion during high-rate cycling, leading to a poor rate performance.

Fig. 5. Electrochemical behavior of as-prepared composites for lithium ion storage: (a) Cyclic voltammograms of the first five cycles of Co₉S₈/HNCS composite with a scan rate of 0.1 mV s⁻¹. (b) Galvanostatic discharge/charge profiles of the first three, 10th and 20th cycles of Co₉S₈/HNCS composite at a current density of 100 mA g⁻¹. (c) Cycling performance of the Co₉S₈/HNCS and Co₉S₈/NC composites at a current density of 100 mA g⁻¹. (d) Rate capabilities at different current densities. (e) Cycling performance of Co₉S₈/HNCS composite at a high current density of 500 mA g⁻¹ after cycling with first three cycles at 100 mA g⁻¹.

Fig. 5e displays the cycling performance of Co₉S₈/HNCS composite at a high current density of 500 mA g⁻¹ after discharge-charge cycling with first three cycles at 100 mA g⁻¹. The

initial discharge and charge capacities are 1217 and 806 mA h g⁻¹, respectively, with a low initial Coulombic efficiency of 66%. Besides, Co₉S₈/HNCS shows the low Coulombic efficiencies during first four cycles, which are attributed to the partial decomposition of the electrolyte and activation process of electrode materials during the low current density of 100 mA g⁻¹. In addition, the low Coulombic efficiency of the forth cycle is mainly due to the change from the low current density (100 mA g⁻¹) to the high current density (500 mA g⁻¹), since the lithium ion requires time to complete insertion or extraction in the Co₉S₈/HNCS electrode materials. Then, the discharge capacity of Co₉S₈/HNCS decreases to 428 mA h g⁻¹ at the 13th cycle. After that, the discharge capacity gradually increases and stabilizes at 755 mA h g⁻¹ after 200 cycles, with a Coulombic efficiency of over 98%. The unique behavior is ascribed to structural rearrangement of electrode materials due to long-term activation effects. In addition, it is noteworthy that the discharge capacity of Co₉S₈/HNCS composite is higher than the theoretical specific capacity of Co₉S₈ (544 mA h g⁻¹), which could be ascribed to the formation of electroactive polymeric gel-like film on the surface of hollow porous structure, as well as the insertion of lithium ions into interfacial storage [7, 44]. As a reference, the long-term cycle performance of Co₉S₈/NC is tested under the same condition (Fig. S15). The discharge capacity of Co₉S₈/NC composite only reaches 321 mA h g⁻¹ after 200 cycles. Moreover, compared with previously reported cobalt sulfides based systems for lithium storage (Table S1), the Co₉S₈/HNCS composite exhibits superior cycling stability and rate capability.

Sodium storage performance. To test the sodium storage of Co₉S₈/HNCS and Co₉S₈/NC composites, coin-type half-cells with metallic sodium as the counter electrode were assembled. Fig. 6a demonstrates the cyclic voltammograms (CVs) of the first five cycles of Co₉S₈/HNCS in a voltage range of 0.01–3.0 V at 0.1 mV s⁻¹. A main reductive peak at about 0.40 V is observed, revealing the conversion reaction of cobalt sulfide with sodium ion. Another small peak at about 0.90 V is ascribed to partial decomposition of the electrolyte and the formation of SEI film. The oxidative peak at about 1.75 V is ascribed to the oxidation of metallic Co [15, 56]. The detailed electrochemical reaction could be shown as following [15]:

Where $x = (n + m)/2$. After the initial scans, the reductive and oxidative peaks shift to 0.84 and 1.78 V, respectively. Moreover, the CVs overlap well in the subsequent cycles, indicating excellent cycling stability of the Co₉S₈/HNCS composite for sodium ion storage. In comparison, the CVs of Co₉S₈/NC composite (Fig. S16a) shows a continuous degenerative process from the first five cycles, revealing the instability of Co₉S₈/NC during cycling. Fig. 6b shows the galvanostatic discharge/charge profiles of the cycles 1-3, 10 and 20 of Co₉S₈/HNCS at a current density of 100 mA g⁻¹. The potential slopes found in the first three cycles agree with the peaks in the CVs of Co₉S₈/HNCS. The Co₉S₈/HNCS registers the initial discharge and charge capacity of 713 and 368 mA h g⁻¹, respectively. The relatively low Coulombic efficiency of 52% is attributed to generation of SEI film and partial decomposition of the electrolyte [15, 56]. The lower initial Coulombic efficiency (52%) of Co₉S₈/HNCS for SIBs than that (80%) for LIBs is mainly attributed to the larger ionic radius of sodium ion (1.02 Å) comparing to that of lithium ion (0.76 Å), resulting in more sluggish sodium ion diffusion kinetics than lithium ion. Good overlap is observed during the 10th and 20th cycles, confirming the superior cycling stability. Differently, the initial discharge and charge capacity of Co₉S₈/NC composite (Fig. S16b) is 679 and 418 mA h g⁻¹. Besides, no overlapping curves (Fig. S16b) are observed, implying inferior cycling stability.

The cycling performance of the Co₉S₈/HNCS and Co₉S₈/NC composites at a current density of 100 mA g⁻¹ is showed in Fig. 6c. Co₉S₈/HNCS shows a small capacity decrease during the first five cycles, with a discharge capacity of 372 mA h g⁻¹ of the fifth cycle. A gradual capacity increase (Fig. 6c) is found after the 5th cycle, indicating structural rearrangement of electrode materials originating from activation of the materials, which provides more active sites during cycling [9, 10]. Co₉S₈/HNCS delivers a stable discharge capacity of 421 mA h g⁻¹ at 100 mA g⁻¹ after 50 cycles, and a Coulombic efficiency above 96% after the first five cycles. In contrast, Co₉S₈/NC exhibits a dramatic capacity decay and only retains a discharge capacity of 63 mA h g⁻¹ at 100 mA g⁻¹ after 50 cycles, with a lower retained capacity of 9%. It is noteworthy that the obvious higher capacities (Fig. 6c) for Co₉S₈/NC than that of Co₉S₈/HNCS during the beginning several cycles are mainly attributed to the higher Co₉S₈ ratio of Co₉S₈/NC (77.1%, Fig. S13a) than that of Co₉S₈/HNCS (54.9%, Fig. S13b). The results further indicate the high extent of utilization of active materials in the Co₉S₈/HNCS electrode. Fig. 6d displays the rate capabilities of the Co₉S₈/HNCS and Co₉S₈/NC composites at different

current densities. Co₉S₈/HNCS exhibits discharge capacities of 386, 340, 330, 311, 288, 252 mA h g⁻¹ assigning to current densities of 100, 200, 300, 500, 1000, 2000 mA g⁻¹, respectively. When the current density is reset 100 mA g⁻¹ after 60 cycles, the discharge capacity of Co₉S₈/HNCS restores to 394 mA h g⁻¹ after 90 cycles with a good capacity retention, indicating a promising rate capability. In contrast, the discharge capacities of Co₉S₈/NC composite are 347, 188, 87, 46, 25, 12 mA h g⁻¹ at current densities of 100, 200, 300, 500, 1000, 2000 mA g⁻¹, respectively. Co₉S₈/NC only delivers a discharge capacity of 62 mA h g⁻¹ after 90 cycles when reverting the current density to 100 mA g⁻¹, showing a sharp capacity loss. The better rate performance of Co₉S₈/HNCS is mainly attributed to the integral hollow nanostructure, which could provide more active sites and space for sodium ion insertion/extraction. Further, the hollow interior structure of Co₉S₈/HNCS could offer extra inner void to accommodate large volume change during high current-density cycling.

Fig. 6. Electrochemical behavior of as-prepared composites as sodium ion storage materials: (a) Cyclic voltammograms of the first five cycles of Co₉S₈/HNCS composite at a scan rate of 0.1 mV s⁻¹. (b) Galvanostatic discharge/charge profiles of the first three, 10th and 20th cycles of Co₉S₈/HNCS composite at a current density of 100 mA g⁻¹. (c) Cycling performance of the Co₉S₈/HNCS and Co₉S₈/NC composites at a current rate of 100 mA g⁻¹. (d) Rate capabilities at various current densities. (e) Cycling performance of the Co₉S₈/HNCS composite at a current density of 1000 mA g⁻¹ after cycling with first three cycles at 100 mA g⁻¹.

Cycling performance of Co₉S₈/HNCS for sodium ion storage at high current densities of 500 and 1000 mA g⁻¹ after discharge-charge cycling with the first three cycles at 100 mA g⁻¹

is further studied. Fig. S17 shows that $\text{Co}_9\text{S}_8/\text{HNCS}$ registers a discharge capacity of 327 mA h g^{-1} at 500 mA g^{-1} after 200 cycles, with a Coulombic efficiency of more than 97% after first fifth cycles. In contrast, $\text{Co}_9\text{S}_8/\text{NC}$ only demonstrates a discharge capacity of 26 mA h g^{-1} at 500 mA g^{-1} after 200 cycles. Fig. 6e shows the long-term cycling performance of $\text{Co}_9\text{S}_8/\text{HNCS}$ composite at 1000 mA g^{-1} . The discharge capacity of $\text{Co}_9\text{S}_8/\text{HNCS}$ is initially 729 mA h g^{-1} , and decreases to 231 mA h g^{-1} after 27 cycles. After that, the discharge capacity gradually increases, and finally stabilizes and remains a discharge capacity of 224 mA h g^{-1} after 300 cycles. The Coulombic efficiency is over 97% after the first fifth cycles. Interestingly, Compared to the distinct increased capacity of $\text{Co}_9\text{S}_8/\text{HNCS}$ for lithium ion storage (Fig. 5e) at a high current density of 500 mA g^{-1} , the $\text{Co}_9\text{S}_8/\text{HNCS}$ shows a relatively stable cyclic ability for sodium ion storage (Fig. 6e). This phenomenon could be mainly result from the larger ionic radius of sodium ion than that of lithium ion, leading to the decrease of sodium-ions insertion into interfacial storage between the cobalt sulfide and hollow carbon shells [7, 10]. The $\text{Co}_9\text{S}_8/\text{NC}$ composite shows poor long-term cycling performance (Fig. S18) with a discharge capacity of only 19 mA h g^{-1} after 300 cycles. In contrast to previous reports on cobalt sulfides related systems for sodium storage (Table S2), the $\text{Co}_9\text{S}_8/\text{HNCS}$ composite exhibits a promising sodium ion storage, which is attributed to the integral hollow structure associated with the uniform cobalt sulfide nanoparticles and nitrogen-doped carbon networks.

Scheme 2. Schematic illustration of the electrochemical process of $\text{Co}_9\text{S}_8/\text{HNCS}$ composite for lithium or storage ion storage. Not drawn to real scale.

To obtain a better understanding of the superior lithium and sodium ion storage properties of $\text{Co}_9\text{S}_8/\text{HNCS}$, electrochemical impedance spectroscopy (EIS) studies of the

Co₉S₈/HNCS and Co₉S₈/NC composites as lithium and sodium ion storage materials before cycling and after the 1st, 3rd and 10th cycles were performed (Fig. S19). The semicircle at medium frequency region corresponds to the charge-transfer resistance (R_{ct}) between the electrolyte and electrode. The fitted R_{ct} values are listed in Table S3. Fresh cells based on the Co₉S₈/HNCS composite (172 Ω for LIBs and 447 Ω for SIBs) show lower R_{ct} values than that of the Co₉S₈/NC composite (400 Ω for LIBs and 915 Ω for SIBs), indicating faster charge transfer kinetics for Co₉S₈/HNCS. This is attributed to the encapsulation effect of PDA derived carbon layers, which could cross-link monodisperse Co₉S₈ nanoparticles to improve inter-particle connection of Co₉S₈/HNCS for fast charge transfer. Besides, higher nitrogen doping level of Co₉S₈/HNCS (12.60 atom%, Fig. S9) over Co₉S₈/NC (4.12 atom%, Fig. S10c) is likely to decrease R_{ct} . This is because higher nitrogen-doping extent not only facilitates the electronic conductivity of carbon coating layer, but also enhances the interactions between the nitrogen-doped carbon structure and lithium or sodium ions [22, 23]. After the first cycle, Co₉S₈/HNCS shows a relatively stable charge-transfer resistance (Fig. S19 a, c) compared with the R_{ct} of fresh cells, in contrast, a large change of R_{ct} value for Co₉S₈/NC electrode (Fig. S19 b, d) after the initial cycle demonstrates the structural instability of the Co₉S₈/NC materials. After the 3rd and 10th cycle, the R_{ct} of Co₉S₈/HNCS gradually levels off (Fig. S19 a, c and Table S3), due to the activation of the Co₉S₈/HNCS electrode [34, 57]. While, Co₉S₈/NC (Fig. S19 b, d and Table S3) exhibits increased R_{ct} , further confirming the structural fragmentation of Co₉S₈/NC electrode during cycling. Moreover, the morphology and structural changes of Co₉S₈/HNCS during lithium and sodium ion storage are also investigated. First, the cycled batteries for lithium storage were disassembled after 50 cycles at 100 mA g⁻¹. SEM and TEM images (Fig. S20) show that the hollow structure with Co₉S₈ nanoparticles embedded in the carbon matrix is maintained in the electrode materials after cycling, revealing excellent structural stability of the Co₉S₈/HNCS composite during lithium ion insertion/extraction. Interestingly, the thick layer covering Co₉S₈/HNCS formed after cycling in Fig. S20c and d is believed to be the solid electrolyte interphase (SEI) film. The thickness of SEI film is measured to be in the range of 100 – 120 nm, which is comparable to the previous reports [58, 59]. The stable SEI film could prevent the further decomposition of electrolyte and maintain effectively the structural stability of Co₉S₈/HNCS during cycling for the promising electrochemical performance [58]. We also disassembled the cycled coin cells for sodium storage after 50 cycles at 100 mA g⁻¹. No pulverization and aggregation (Fig. S21)

were observed, and Co_9S_8 nanoparticles are tightly interconnected by carbon layers during sodium ion insertion/extraction. These results were further demonstrated as illustrated in Scheme 2. The promising electrochemical performance of $\text{Co}_9\text{S}_8/\text{HNCS}$ for lithium and sodium storage could be regarded as the result of the combined effect of homogenously ultrafine Co_9S_8 nanoparticles associated with hollow nitrogen-doped carbon polyhedral shells. Firstly, ultrafine Co_9S_8 nanoparticles (11 ± 2 nm) effectively shorten the diffusion distance during lithium or sodium insertion/extraction; the entire electrode can efficiently accommodate the strain generated from cycling due to the highly uniform Co_9S_8 nanoparticles, thus facilitating good rate capability and cycling performance. Secondly, the hollow nitrogen-doped carbon networks not only promote electronic conductivity and provide more active sites for lithium and sodium storage, but also play a critical role as a buffer for volume expansion maintaining the structural integrity during cycling. Thirdly, the encapsulation of monodispersed Co_9S_8 nanoparticles in the nitrogen-doped carbon polyhedral shells prevent Co_9S_8 nanoparticles from aggregation and pulverization. More importantly, the hollow structure provides extra interior space with abundant active sites and contact area between active material and electrolyte, enhancing lithium or sodium ion diffusion and conversional reaction for superior cyclic stability and rate capability.

4. Conclusions

Well-defined cobalt sulfide nanoparticles encapsulated in 3D hollow nitrogen-doped carbon shells ($\text{Co}_9\text{S}_8/\text{HNCS}$) were successfully constructed by utilizing nitrogen doped carbon layers derived from PDA layers to wrap and interconnect the monodisperse cobalt sulfide nanoparticles (11 ± 2 nm). The composite inherited the hollow polyhedral structure of the MOF (ZIF-67) skeleton. The remarkable synergistic effects between chemical and structural properties of the $\text{Co}_9\text{S}_8/\text{HNCS}$ composite give rise to superior electrochemical performance for lithium and sodium storage. As tested for lithium ion storage, $\text{Co}_9\text{S}_8/\text{HNCS}$ exhibits an impressive reversible capacity of 755 mA h g^{-1} at 500 mA g^{-1} after 200 cycles. When utilized for sodium ion storage, the $\text{Co}_9\text{S}_8/\text{HNCS}$ composite delivers superior capacities of 327 mA h g^{-1} at 500 mA g^{-1} after 200 cycles and 224 mA h g^{-1} at 1000 mA g^{-1} after 300 cycles. These results highlight this composite as a promising electrode material for lithium and sodium

storage. Moreover, the designed strategy of the Co₉S₈/HNCS composite could be applied for other hollow metal sulfides for electrochemical energy conversion and storage technology.

5 Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version.

Declaration of interests

The authors declare no competing financial interest.

10 Acknowledgments

Finance support from Shandong Provincial Science and Technology Major (2018JMRH0211, 2016GGX104001, 2017CXGC1010 and ZR2017MEM002), the Fundamental Research Funds of Shandong University (2016JC005, 2017JC042 and 2017JC010) and 1000 Talent Plan program (No. 31370086963030), Chinese Scholarship Council (201706220080), Danish Council for Independent Research (DFT-1335-00330), H. C. Ørsted COFUND fellowship, Independent Research Fund Denmark (DFF-5054-00107) are acknowledged. TEM work was partly performed at the UC Irvine Materials Research Institute (IMRI).

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Well-Defined Cobalt Sulfide Nanoparticles Locked in 3D Hollow Nitrogen-Doped Carbon Shells for Superior Lithium and Sodium Storage

Supporting Information

Well-Defined Cobalt Sulfide Nanoparticles Locked in 3D Hollow Nitrogen-Doped Carbon Shells for Superior Lithium and Sodium Storage

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I. Supplementary figures and table

Fig. S1. (a, b, c) SEM images of ZIF-67 crystals. (d) The particle size distribution of ZIF-67 crystals corresponding to Fig. S1a.

Fig.S2. (a, b) TEM images of ZIF-67 crystals.

Fig. S3. SEM (a, b) and TEM (c, d) images of the PDA@ZIF-67 composite prepared with 0.5 mg mL⁻¹ DAH.

Fig. S4. SEM (a, b) and TEM (c, d) images of the PDA@ZIF-67 composite prepared with 2.0 mg mL⁻¹ DAH.

Fig. S5. SEM (a, b) and TEM (c, d) images of PDA@ZIF-67 composite prepared with 1.0 mg mL^{-1} dopamine hydrochloride. Insert is the particle size distribution of PDA@ZIF-67 composite corresponding to Fig. S5a.

Fig. S6. (a) The XRD pattern of ZIF-67 crystals and PDA@ZIF-67 composite (1.0 mg mL^{-1} dopamine hydrochloride). (b) FT-IR spectrum of the ZIF-67 crystals and PDA@ZIF-67 composites (1.0 mg mL^{-1} dopamine hydrochloride).

Fig. S7. The XRD pattern of $\text{Co}_9\text{S}_8/\text{NC}$ composite.

Fig. S8. The XPS survey spectrum of $\text{Co}_9\text{S}_8/\text{HNCS}$ composite.

Fig. S9. EDS mapping image of the $\text{Co}_9\text{S}_8/\text{HNCS}$ composite. Inset is SEM image of the scanning area of the $\text{Co}_9\text{S}_8/\text{HNCS}$ composite.

Fig. S10. (a, b) SEM images of Co₉S₈/NC composite. (c) EDS mapping image of the Co₉S₈/NC composite. Inset is the scanning area.

Fig. S11. (a, b) TEM images of Co₉S₈/NC composite.

Fig. S12. (a) Bright-field, (b) dark-field, (c) secondary electron images and (d-g) EDS elemental map of large-scale $\text{Co}_9\text{S}_8/\text{HNCS}$ composite for TEM test.

Fig. S13. (a, b) TGA curves of the Co₉S₈/HNCS (a) and Co₉S₈/NC (b) composites.

The component calculation of Co₉S₈/HNCS composite:

$$1 \times 787 \sim 3 \times 241 \quad (\text{mass conservation})$$

$$Y \sim 50.4\%$$

Calculated the percentage of cobalt sulfide (Co₉S₈) $Y = 50.4\% \times 1 \times 787 / (3 \times 241) = 54.9\%$.

The component calculation of Co₉S₈/NC composite:

$$1 \times 787 \sim 3 \times 166 \quad (\text{mass conservation})$$

$$Y \sim 70.8\%$$

Calculated the percentage of cobalt sulfide (Co₉S₈) $Y = 70.8\% \times 1 \times 787 / (3 \times 241) = 77.1\%$.

Fig. S14. (a) Cyclic voltammograms of the first five cycles of Co₉S₈/NC composite in a voltage range of 0.01–3.0 V with a scanning rate of 0.1 mV s⁻¹. (b) Galvanostatic discharge/charge profiles of the first three, 10th and 20th cycles of Co₉S₈/NC composite at a current density of 100 mA g⁻¹.

Fig. S15. The long-term cycle performance of Co₉S₈/NC composite at a current rate of 500 mA g⁻¹.

Table S1. Comparison of electrochemical performances of Co₉S₈/HNCS composite with previously reported cobalt sulfides related systems for lithium storage.

Composites	Current (mA g ⁻¹)	Cycle number	Capability (mAh g ⁻¹)	Ref.
Co ₉ S ₈ hollow sphere	100	100	254.9	[1]
CoS ₂ nanobubble hollow prisms	1000	200	737	[2]
Co ₉ S ₈ /MoS ₂	1000	70	756	[3]
Co _{1-x} S/BC	100	120	630	[4]
C@Co ₉ S ₈	1000	50	520	[5]
Co ₉ S ₈ /C	200	150	709	[6]
Co ₉ S ₈ @C	539	300	606	[7]
Co ₃ S ₄ /MWCNT	2000	500	976.5	[8]
Co ₉ S ₈ -GNS	500	100	414	[9]
RGO/Co ₉ S ₈	545	500	382.2	[10]
C & graphene Co ₉ S ₈	200	50	609	[11]
Co ₉ S ₈ @NMCN	100	80	988	[12]
Co ₉ S ₈ @C nanocages	544	30	54	[13]
Co ₉ S ₈ /NC	500	200	321	This work
Co ₉ S ₈ /HNCS	500	200	755	This work

Fig. S16. (a) Cyclic voltammograms of the first five cycles of $\text{Co}_9\text{S}_8/\text{NC}$ composite in a voltage range of 0.01–3.0 V with a scanning rate of 0.1 mV s^{-1} . (b) Galvanostatic discharge/charge profiles of the first three, 10th and 20th cycles of $\text{Co}_9\text{S}_8/\text{NC}$ composite at a current density of 100 mA g^{-1} .

Fig. S17. The long-term cycle performance of $\text{Co}_9\text{S}_8/\text{HNCS}$ and $\text{Co}_9\text{S}_8/\text{NC}$ composites at a current density of 500 mA g^{-1} .

Fig. S18. The long-term cycle performance of $\text{Co}_9\text{S}_8/\text{NC}$ composite at a current density of 1000 mA g^{-1} .

Table S2. Comparison of electrochemical performances of Co₉S₈/HNCS composite with previously reported cobalt sulfides related systems for sodium storage.

Composites	Current (mA g⁻¹)	Cycle number	Capability (mAh g⁻¹)	Ref.
Co _{1-x} S/C	1000	130	320	[14]
CoS/rGO	100	100	230	[15]
CoS ₂ –MWCNT	100	100	568	[16]
Co ₃ S ₄ @PANI	200	100	252.5	[17]
cs-Co _x S _y /DPC	500	50	300	[18]
Co ₉ S ₈ –carbon	500	50	404	[19]
Co ₉ S ₈ /C	5	30	320	[20]
Co ₉ S ₈ @C nanospheres	500	100	405	[21]
Co ₉ S ₈ @CNNs	100	50	249	[22]
Co ₉ S ₈ /NC	500	200	26	This work
Co ₉ S ₈ /NC	1000	300	19	This work
Co ₉ S ₈ /HNCS	500	200	327	This work
Co ₉ S ₈ /HNCS	1000	300	224	This work

Fig. S19. (a, b) Nyquist impedance plots of $\text{Co}_9\text{S}_8/\text{HNCS}$ and $\text{Co}_9\text{S}_8/\text{NC}$ composites as lithium-ion storage materials before the 1st cycle and after the 1st, 3rd and 10th cycles. (c, d) Nyquist impedance plots of $\text{Co}_9\text{S}_8/\text{HNCS}$ and $\text{Co}_9\text{S}_8/\text{NC}$ composites as sodium-ion storage materials before the 1st cycle and after the 1st, 3rd and 10th cycles.

Table S3. The corresponded R_{ct} values of $\text{Co}_9\text{S}_8/\text{HNCS}$ and $\text{Co}_9\text{S}_8/\text{NC}$ in different cycles for lithium and sodium ion storage.

	R_{ct} of Lithium ion storage (Ω)		R_{ct} of Sodium ion storage (Ω)	
	$\text{Co}_9\text{S}_8/\text{HNCS}$	$\text{Co}_9\text{S}_8/\text{NC}$	$\text{Co}_9\text{S}_8/\text{HNCS}$	$\text{Co}_9\text{S}_8/\text{NC}$
Fresh	172	400	447	915
1 st	179	71	445	566
3 rd	121	103	283	409
10 th	94	97	270	459

Fig. S20. SEM (a, b) and TEM (c, d) images of $\text{Co}_9\text{S}_8/\text{HNCS}$ composite based lithium-ion storage material after 50 charge-discharge cycles at 100 mA g^{-1} .

Fig. S21. SEM (a, b) and TEM (c, d) images of Co₉S₈/HNCS composite based sodium-ion storage material after 50 charge-discharge cycles at 100 mA g⁻¹.

II. Supporting references

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