Hollow N-doped Carbon Polyhedrons with Hierarchically Porous Shell for Confinement of Polysulfides in Lithium–Sulfur Batteries

Dong-Hui Yang, Hang-Yu Zhou, Hu Liu, Bao-Hang Han

HIGHLIGHTS
- A hollow N-doped carbon polyhedron is newly developed as sulfur host
- The host provides both physical confinement and chemical interaction for polysulfides
- The host displays a fast polysulfide trapping by hierarchical pores
- The host enables a high sulfur loading and achieves better electrochemical performance

Yang et al., iScience 13, 243–253
March 29, 2019 © 2019 The Author(s).
https://doi.org/10.1016/j.isci.2019.02.019
Hollow N-doped Carbon Polyhedrons with Hierarchically Porous Shell for Confinement of Polysulfides in Lithium–Sulfur Batteries

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SUMMARY

Herein, hollow N-doped carbon polyhedrons with hierarchical pores were fabricated by etching ZIF-8 crystals and were first used as the host of sulfur for lithium-sulfur batteries. This host possesses both micropores and mesopores, and inner wide cavities, which enable the sulfur to effectively immerse into the polyhedrons without obstacles and simultaneously restrict the escaping of polysulfides by outer carbon shell and abundant N sites. Hence, the polyhedron host combines the physical confinement and chemical interaction for polysulfides by virtue of the unique architecture. As a result, the hierarchically porous polyhedron enables a sulfur content of 72 wt% and achieves a faster polysulfide trapping and better electrochemical performance than the ZIF-8-derived microporous host at the sulfur loading of 1 and 5 mg cm$^{-2}$.

INTRODUCTION

High energy density, low cost, and environmental benignity enable the Li–S battery to become a promising next-generation energy supplier (Evers and Nazar, 2013; Fang et al., 2017; Manthiram et al., 2014). However, the performance of Li–S battery is strongly plagued and restrained by poor electrical conductivity and volume variation of sulfur, especially the dissolution of lithium polysulfides (Ji et al., 2009; Li et al., 2018a; Zhang et al., 2018a). Resolving these problems is thus essential to meet the practical requirements of commercial applications (Zhang et al., 2019a). The key approach to figure out these obstructions is exploring appropriate host materials to serve as the conductive networks and immobilize sulfur effectively, such as the host materials with porous structures and chemical polar sites to suppress polysulfide shuttling by physical confinement and chemical adsorption (He et al., 2018; Li et al., 2016a, 2016b; 2017; Seh et al., 2016; Sui et al., 2017; Zhang et al., 2019b; Zhou et al., 2014). N-doped porous carbon hosts have attracted great attention for sulfur cathodes because these hosts not only enhance the conductivity of sulfur cathodes but also increase the interaction of the polar N sites and polysulfides through the Li–N bond, which can alleviate polysulfide shuttling through physical and chemical confinement using the porous structure and chemisorption (Guo et al., 2017; Pang and Nazar, 2016; Su et al., 2017). Therefore, great efforts have been devoted to fabricate the N-doped carbon materials by using different precursors, such as urea, pyrrole, amines, carbohydrates, and porous organic polymers (Inagaki et al., 2018; Li et al., 2018b; Niu et al., 2015; Pei et al., 2016; Yang et al., 2014). Furthermore, the composites of the above-mentioned precursors with carbon nanotubes or graphene are also extensively designed to construct N-doped carbon hosts (Pan et al., 2017; Zhang et al., 2018b). However, the uncontrollability of pore structure or N-doping for the above-mentioned precursors brings some inconclusive or adverse effects on the practical electrochemical performances.

Recently, it has been found that metal-organic frameworks (MOFs) are effective precursors to construct N-doped carbon hosts because of their great superiority in compositions and structures (Chen et al., 2014; Jiang et al., 2017; Li et al., 2016c; Liu et al., 2017; Tan et al., 2017a; Wu et al., 2013; Yang et al., 2017a). Compared with conventional precursors, MOFs possess regular porous structures, large specific surface areas, and controllable structure and composition, which have helped achieve the improved electrochemical performance in Li–S batteries by using MOFs as the carbon precursors (Chang et al., 2018; Chen et al., 2018; Li and Yin, 2015; Tan et al., 2017b; Zhang et al., 2018c, 2018d). Nevertheless, the majority of MOF-derived N-doped carbon materials are almost microporous structures and have limited pore volumes, which are unfavorable for the large mass transport and the release of volume strain. In addition, the solid structure with micropores generally causes the slow adsorption kinetics for long-chain polysulfides.

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https://doi.org/10.1016/j.isci.2019.02.019
owing to the physical barriers of diffusion pathways. Although the large pore volumes or hollow structures could be obtained through template strategies, the removal of template always uses highly corrosive agents (such as HF, NaOH), and the cavity size is largely dependent on the size of the template. Therefore, a straightforward method with mild condition is highly expected to create porous N-doped carbon hosts with large cavity.

Herein, we fabricate a hollow N-doped carbon (HNC) material with hierarchical pores by simple etching and carbonizing of ZIF-8 particles. ZIF-8 can be mildly etched by tannic acid to easily get a shelled polyhedron precursor (Zhang et al., 2017). This polyhedron precursor-derived HNC particle efficiently combines the micropores, mesopores, and internal void space, which is first used as the sulfur host for Li–S battery. Different from the ZIF-8-derived solid microporous host, HNC polyhedron with hollow structure is favorable for sulfur immersion and polysulfide encapsulation via the void space and porous outer shell. With HNC serving as the sulfur host, the S@HNC cathode enables a 72 wt% sulfur loading. Additionally, this hybrid cathode combines the ingenious physical confinement with appropriate chemical adsorption for polysulfide anions, synergistically providing multilayered barriers for polysulfide diffusion by means of the interconnected carbon network and strong interaction between nitrogen and lithium polysulfides. These two functions work well together to not only increase the reversible capacity of hybrid cathode but also display fast adsorption for polysulfides compared with the ZIF-8-derived solid microporous carbon material.

RESULTS AND DISCUSSION

Morphology and Structure Characterization

The synthetic procedure of S@HNC hybrid is illustrated in Figure 1A (see Transparent Methods for details). First, ZIF-8 particles were prepared through a facile method as reported previously (Yang et al., 2017b) and then subjected to a chemical etching process by using tannic acid as the etchant (Hu et al., 2016; Zhang et al., 2018e). The final structure of ZIF-8 was determined by the etching time (Figures S1–S3), and a hollow structure was obtained at the etching time of 10 min. The as-synthesized hollow ZIF-8 was converted into HNC in the subsequent carbonization process. The S@HNC hybrid was finally obtained through melting and infusing sulfur into HNC at 155°C in a sealed vessel. For reference, the
composite (S-NC) of sulfur and ZIF-8-derived N-doped carbon was also prepared without the etching process.

Field emission scanning electron microscopy (FESEM) shows that the prepared ZIF-8 particles are around 300 nm with a uniform rhombic dodecahedral morphology (Figure 1B). X-ray diffraction (XRD) pattern of the prepared ZIF-8 sample is consistent with the simulation diffraction peaks, indicating the successful synthesis of ZIF-8 (Figure S4). After calcination at 900°C under nitrogen atmosphere, Zn^{2+} of ZIF-8 is reduced to Zn^{0} and vaporized rapidly at the high temperature. In the meantime, the organic ligands of ZIF-8 are converted into N-doped carbon (NC) material. The obtained NC particles maintain the typical polyhedral shape of ZIF-8 (Figure 1C). The difference is the NC particles shrink slightly and the surface becomes rough, compared with ZIF-8 with a smooth surface. When ZIF-8 was subjected to chemical etching, the hollow ZIF-8 polyhedrons were obtained (Figure 1D). The XRD pattern of hollow ZIF-8 polyhedrons shows the high crystallinity and typical diffraction peaks of ZIF-8 (Figure S4), which confirm the same crystal structure as ZIF-8 precursors. The absence of new diffraction peaks in the XRD pattern suggests that the chemical etching does not have any effect on the crystalline phase and structure. The HNC particles were then obtained by carbonizing the hollow ZIF-8 polyhedrons. The FESEM image given in Figure 1E demonstrates that the HNC sample perfectly inherits the pristine rhombic dodecahedron of ZIF-8. The characteristic of carbon materials is also provided by XRD signals. Both NC and HNC present a broad and a weak diffraction peak at around 24° and 44°, corresponding to (002) and (101) planes of graphitic carbon with low graphitization (Figure S5) (Wu et al., 2013). Figures 1F and 1G show that the obtained S-NC is supported by aggregating a mass of sulfur and NC particles, where NC particles are trapped in the bulk sulfur. In contrast, the origin morphology is well preserved for S@HNC after sulfur loading (Figures 1H and 1I), and no obvious sulfur aggregation exposes on the polyhedron surface. This result indicates that the sulfur is widely immersed into the HNC and distributes evenly in the HNC host, which is further confirmed by transmission electron microscopy (TEM).

As revealed by TEM images, the NC sample displays a solid texture, whereas HNC shows a unique shelled hollow structure with void space in the interior of polyhedron (Figures 2A and 2B). Figure 2C reveals that the S-NC composite huddles together and causes the confusion between sulfur and NC particles, agreeing with the result of FESEM. By contrast, the well-defined polyhedrons are clearly discerned in TEM images of S@HNC hybrid (Figure 2D). The absence of large cavity illustrates that the interior space has been successfully occupied by sulfur. It is worth noting that the polyhedrons still possess some small voids after sulfur diffusion, which is favorable for the fast migration of Li^{+} (Figure S6). Moreover, the elemental mapping images of S@HNC imply the excellent dispersion of sulfur in the whole polyhedron particle (Figures 2E–2G).

Figure 2. Structure and Composition Characterization
(A–D) TEM images of NC (A), HNC (B), S-NC (C), and S@HNC (D).
(E–G) The overlapped element image (E) and corresponding elemental mappings of S (F) and C (G) elements of S@HNC hybrid.
(H) XRD patterns of S-NC and S@HNC.
The crystalline phase and structural composition of S-NC and S@HNC are also affirmed by XRD. Figure 2H displays the XRD patterns of two samples and the sublimed sulfur, revealing the existence of crystalline sulfur in both samples.

The structural information of S@HNC and S-NC materials was further investigated by Raman spectroscopy (Figures 3A and S7). From Figure 3A, it is confirmed that both HNC and S@HNC display the D-band peak of 1,352 cm\(^{-1}\) and G-band peak of 1,587 cm\(^{-1}\), which represent the typical disordered carbon and graphitic carbon, respectively. Based on the intensity of D and G bands, the intensity ratio (I\(_D\)/I\(_G\)) of S@HNC is about 0.95, implying that there are numerous defects in the carbon matrix. A similar phenomenon is commonly

Figure 3. Structural Analyses of the Samples
(A) Raman spectra of HNC and S@HNC.
(B) \(\text{N}_2\) adsorption/desorption isotherms of NC, HNC, S-NC, and S@HNC samples.
(C) Full XPS spectra of S-NC and S@HNC samples.
(D–F) Deconvoluted spectra of C 1s (D), N 1s (E), and S 2p (F) of S@HNC.
observed in the ZIF-8-derived carbon material after high-temperature carbonization, suggesting the edge modification of carbon matrix with N atoms (Zheng et al., 2014). The plentiful N-doping is also verified by elemental analysis, which manifests the N content of about 6.08 wt% in HNC. It is known that N atoms can serve as the active sites to anchor polysulfides and then enhance the sulfur utilization in a chemical way. A similar intensity ratio ($I_D/I_G$) is also found in NC and S-NC samples, indicating that the structure of carbon material is similar for the four samples.

The infiltration of sulfur can be adequately illustrated by N2 adsorption-desorption isotherm measurements. It is generally known that the pores of ZIF-8 are mostly micropores (Park et al., 2006). As calculated by the nonlocalized density functional theory method, ZIF-8 possesses micropores of uniform size in conjunction with a large Brunauer-Emmett-Teller (BET) specific surface area of 1,640 m² g⁻¹ (Figure S8). After chemical etching, the hollow ZIF-8 perfectly preserves the microporous structure of ZIF-8, only the BET specific surface area lowers to 710 m² g⁻¹ (Figure S9), indicating that the etching has no evident impact on the microporous structure of ZIF-8. The lower BET specific surface area of hollow ZIF-8 is possibly because of the partial amorphization and introduction of tannic acid after chemical etching (Hu et al., 2016). Notably, the microporosity is also well reserved in the derived NC sample with a BET specific surface area of 750 m² g⁻¹, and the pore size distribution has a slight increase with the evolution of Zn (Figures 3B and S10). However, entirely different from the NC sample, the derived HNC from hollow ZIF-8 displays a combined characteristic of Type I and Type IV isotherms with a BET specific surface area of 620 m² g⁻¹, corresponding to the hierarchical pores with micropore and mesopore adsorption (Figure S11). The pore size distribution of HNC is similar to that of the NC sample at the micropore range, but HNC exhibits additional abundant mesopores located at the range from 4 to 20 nm. Furthermore, compared with the NC sample, HNC shows a very steep hysteresis hoop in the desorption branch, which can be attributed to the characteristic feature of a Type H2a with the ink-bottle pores according to the International Union of Pure and Applied Chemistry (IUPAC) definition (Thommes et al., 2015). Such pores possess narrow pore necks but wide bodies, and this construction feature is more beneficial to accommodate more sulfur molecules and polysulfide intermediates and suppress the escaping of polysulfides (Li et al., 2018c). A high pore volume also helps to account for the hierarchical pore structure of HNC (Table 1). After infiltrating sulfur, the BET specific surface area values of S-NC and S@HNC are vastly reduced to 3 and 6 m² g⁻¹, respectively, which is primarily because the sulfur molecules fill the pores and occupy the internal space.

X-ray photoelectron spectroscopy (XPS) survey further confirms the existence of sulfur. As presented in Figure 3C, five well-defined peaks around 1,022.1, 532.5, 400.3, 284.5, and 164.6 eV are attributed to Zn, O, N, C, and S elements, respectively. Comparing the spectra of two samples, it is easy to find that the sulfur has a higher proportion in S-NC than in S@HNC. Thermal gravimetric analysis indicates that the sulfur content of S@HNC is about 72.7 wt% (Figure S12). According to the results of elemental analysis, the sulfur content of two samples is nearly identical, 72.55 wt% for S-NC and 72.54 wt% for S@HNC, respectively. Therefore, it can be concluded that there is more sulfur on the surface of S-NC than on that of S@HNC because of the higher sulfur proportion in the XPS spectrum of S-NC, and this is highly consistent with the descriptions of FESEM and TEM images. The high-resolution spectra of C, N, and S for S@HNC are very similar to those of S-NC (Figure S13), revealing that the chemical composition remains unchanged after etching. The C 1s spectrum can be fitted into three peaks of 284.6, 285.3, and 286.5 eV, corresponding to C–C, C–O, and C–N–C groups (Figure 3D) (Mi et al., 2017). In the N 1s spectrum, the peaks located at 398.6, 400.4, and 401.5 eV can be attributed to pyridinic N, pyrrolic N, and graphitic N, respectively (Figure 3E).

Table 1. The Surface Area and Pore Volume of Four Samples

| Samples      | $S_{BET}$ (m² g⁻¹) | $S_{micropore}$ (m² g⁻¹) | $V_{total}$ (cm³ g⁻¹) | $V_{mesopore}$ (cm³ g⁻¹) | $V_{micropore}$ (cm³ g⁻¹) |
|--------------|--------------------|--------------------------|----------------------|--------------------------|---------------------------|
| ZIF-8        | 1,640              | 1550                     | 0.65                 | 0.07                     | 0.58                      |
| Hollow ZIF-8 | 710                | 670                      | 0.31                 | 0.06                     | 0.25                      |
| NC           | 750                | 520                      | 0.38                 | 0.17                     | 0.21                      |
| HNC          | 620                | 400                      | 0.54                 | 0.38                     | 0.16                      |
(Zhang et al., 2018d). N-doping leads to the abundant flaws and could effectively improve the electron mobility and electrical conductivity of carbon materials. In addition, the electronegative N atoms can interact with the electrophilic Li⁺ and then immobilize the lithium polysulfides with the strong interaction. The S 2p spectrum of S@HNC could be deconvoluted into two main peaks at 164.1 and 165.2 eV and one weak peak at 168.7 eV (Figure 3F), which are the signals of S 2p3/2, S 2p1/2, and a little sulfate species, resulting from spin-orbit coupling and the oxidation in air (Li and Yin, 2015).

**Electrochemical Performance**

The electrochemical performances of S@HNC and S-NC samples were evaluated by assembling the samples and Li-foil anodes to 2,032 coin cells. The cyclic voltammetry (CV) measurement was first conducted at a sweep rate of 0.1 mV s⁻¹ in the voltage range of 1.7–2.8 V. As shown in Figure 4A, the CV profile of S@HNC cathode exhibits two broad reduction peaks at 2.3 and 1.9 V in the first discharge process, which are ascribed to the formation of long-chain Li₂S₈ and the further transformation of short-chain Li₂Sₓ (x = 6 or 4) and the final generation of insoluble Li₂Sₓ (x = 2 or 1), corresponding to the following equations (Gao et al., 2018; Lin and Liang, 2015).

\[
\text{S}_8 + 2\text{Li}^+ + 2\text{e}^- \rightarrow \text{Li}_2\text{S}_8 \quad \text{(Equation 1)}
\]

\[
3\text{Li}_2\text{S}_8 + 2\text{Li}^+ + 2\text{e}^- \rightarrow 4\text{Li}_2\text{S}_6 \quad \text{(Equation 2)}
\]

\[
\text{Li}_2\text{S}_8 + 2\text{Li}^+ + 2\text{e}^- \rightarrow 2\text{Li}_2\text{S}_4 \quad \text{(Equation 3)}
\]

\[
\text{Li}_2\text{S}_4 + 2\text{Li}^+ + 2\text{e}^- \rightarrow 2\text{Li}_2\text{S}_2 \quad \text{(Equation 4)}
\]

\[
\text{Li}_2\text{S}_2 + 2\text{Li}^+ + 2\text{e}^- \rightarrow 2\text{Li}_2\text{S} \quad \text{(Equation 5)}
\]

In the subsequent oxidation process, the pronounced peaks at 2.3 and 2.4 V are assigned to the reversible conversion of precipitated Li₂Sₓ (x = 1 or 2) to short-chain Li₂Sₓ (x = 4 or 6) and further to long-chain Li₂S₈ and then to S₈ (Zhou et al., 2018). During the following cycles, the reduction peaks are slightly shifted to a higher voltage and the oxidation peaks show a negative shift, implying the increased access of electrolyte to active materials after the first electrochemical reaction process. Meanwhile, the CV profiles are almost coincided and the redox peaks are reproducible after the third cycles, suggesting a good electrochemical reversibility of the S@HNC electrode. The galvanostatic charge/discharge curves of S@HNC are consistent with the CV profiles (Figure 4B). Two defined plateaus at about 2.1 and 2.3 V are well attributed to the reduction and oxidation of active materials in the lithiation and delithiation processes. The initial discharge capacity of S@HNC cathode is 1,103.7 mA g⁻¹ at 0.1 C (1.0 C = 1,675 mA g⁻¹) in the range of 1.7–2.8 V, and the associated charge capacity is 1,025.5 mA g⁻¹ with a Coulombic efficiency of 107.6%. The discharge capacity decreases slowly in the subsequent cycles and gradually stabilizes after the third cycle, which is in perfect agreement with the CV result. Here the higher Coulombic efficiency and premature capacity loss is possibly because of the formation of the stable solid-electrolyte interphase on Li anode. The CV curves of the S-NC electrode show the cathodic and anodic peaks similar to those of S@HNC (Figure 4C), demonstrating the same sulfur conversion reaction processes during cycling. As a comparison, it is noticeable that the peak current of oxidation process has significantly decreased for the S-NC electrode after the first cycle. It is worth noting that all peak currents of the S-NC electrode are lower than that of S@HNC, indicating the faster electrochemical conversion reactions in the S@HNC electrode, which largely benefit from the ink-bottle-like pore structure. Unlike the CV profiles of the S@HNC electrode, the CV profiles of S-NC behave slightly differently from each cycle and cannot reach a steady state. This phenomenon is also observed in the charge/discharge profiles, in which the capacity gradually decreases with cycling (Figure 4D). This could be because the sulfur of S-NC surface transforms into intermediate polysulfides and then enters into the electrolyte, resulting in the irreversible transformation of sulfur species, which is further confirmed by simulating the discharge process in cell battery with a beaker cell experiment. As illustrated in Figure 4E, the electrolyte of the S-NC cell rapidly turns yellow in the first few hours and gradually changes to deep yellow with discharging. This indicates that the generated lithium polysulfides dissolve in the electrolyte and lots
of them cannot return to the cathode and be reduced to sulfur, which causes the massive loss of active materials. In contrast, for the S@HNC cell, only a very small amount of polysulfides dissolve in the electrolyte, leading to the change in electrolyte color from colorless to pale yellow after discharging for about 8 h. This

Figure 4. Electrochemical Characterization and Visualized Experimental Testing of S@HNC and S-NC Electrodes
(A and C) CV curves of S@HNC (A) and S-NC (C) electrodes at 0.1 mV s$^{-1}$ in 1.7–2.8 V.
(B and D) Galvanostatic charge/discharge voltage profiles of S@HNC (B) and S-NC (D) electrodes at 0.1 C.
(E) Digital images of S@HNC (top) and S-NC (bottom) electrodes during the first discharge cycle at 0.1 C (1.0 C = 1,675 mA g$^{-1}$).
suggests that S@HNC has a good confinement and adsorption effect for active sulfur species and can restrict the escape of soluble polysulfides with the outer microporous carbon shell.

A visualized Li₂S₆ adsorption test provides the indirect evidence of polysulfide adsorption capability for NC and HNC host materials (Figure 5A). As predicted, the HNC host exhibits a superior capability of decoloring for Li₂S₆ solution within 10 min by adding a fixed amount of HNC to Li₂S₆ solution, whereas the Li₂S₆ solution does not show significant change after addition of the NC host with the same amount over the same period. This sharp contrast demonstrates that the HNC host has a strong chemical interaction with Li₂S₆, in which Li₂S₆ molecules quickly transfer into the inner cavity through hierarchical pores without any obstacles. The existence of the Li–N chemical interaction was further confirmed by XPS spectra of HNC before and after Li₂S₆ adsorption (Figure S14). It is easy to find that the binding energy of the N 1s peak shifts to a higher position after Li₂S₆ adsorption, which can be assigned to charge transfer from N to Li⁺ (Ghazi et al., 2016). The structural superiority of HNC is also verified by electrochemical impedance spectroscopy test (Figure 5B). It is conspicuous that the Nyquist plot of S@HNC cell battery shows a smaller semicircle at a higher frequency than S-NC, implying the lower charge-transfer resistance in S@HNC.

Figure 5. Electrochemical Performances of S@HNC and S-NC Electrodes
(A) Digital image shows a visualized Li₂S₆ adsorption of HNC and NC samples.
(B) Electrochemical impedance spectroscopy (EIS) profiles of S@HNC and S-NC electrodes.
(C) Rate capabilities of S@HNC and S-NC electrodes at various current rates of 0.1–2.0 C.
(D) Cycle performances and Coulombic efficiency of S@HNC and S-NC electrodes at 0.2 C.
(E) Long-term cycle performances and Coulombic efficiency of S@HNC and S-NC electrodes at 1.0 C for 500 cycles (1.0 C = 1,675 mA g⁻¹).

250 iScience 13, 243–253, March 29, 2019
The rate capabilities of the S@HNC and S-NC cathodes were assessed every ten cycles at various current densities from 0.1 to 2.0 C (Figure 5C). Clearly, the S@HNC cathode has a much higher capacity than S-NC at any charge/discharge current rate. After the 10th cycle at 1.0 and 2.0 C, the specific capacities of S@HNC are 479.7 and 433.4 mA h g$^{-1}$, respectively, and the discharge capacity is very close to the initial value when the current sharply returns to 0.1 C, suggesting the high reversibility and stability of the S@HNC electrode structure. For S-NC, a drastic capacity decay is observed after the first ten cycles at 0.1 C, which mainly results from the irreversible loss of active sulfur. The fast capacity decay also can be seen in the cycling test of S-NC at 0.2 C (Figure 5D). The S-NC electrode delivers a discharge capacity of 716.6 mA h g$^{-1}$ in the first cycle and fades rapidly to 360.6 mA h g$^{-1}$ after 100 cycles, indicating the low sulfur utilization due to the irreversible loss of active sulfur.

In comparison, the S@HNC electrode exhibits an initial discharge capacity of 716.6 mA h g$^{-1}$ in the first cycle and fades rapidly to 360.6 mA h g$^{-1}$ after 100 cycles, indicating the low sulfur utilization due to the irreversible loss of active sulfur. In comparison, the S@HNC electrode delivers a discharge capacity of 716.6 mA h g$^{-1}$ in the first cycle and fades rapidly to 360.6 mA h g$^{-1}$ after 100 cycles, indicating the low sulfur utilization due to the irreversible loss of active sulfur. In comparison, the S@HNC electrode exhibits a discharge capacity of 716.6 mA h g$^{-1}$ in the first cycle and fades rapidly to 360.6 mA h g$^{-1}$ after 100 cycles, indicating the low sulfur utilization due to the irreversible loss of active sulfur. In comparison, the S@HNC electrode exhibits an initial discharge capacity of 716.6 mA h g$^{-1}$ in the first cycle and fades rapidly to 360.6 mA h g$^{-1}$ after 100 cycles, indicating the high reversibility and stability of the S@HNC electrode structure. A comparison of the S@HNC cathode with other reported electrode materials (Jiang et al., 2017; Li and Yin, 2015; Wu et al., 2013; Xu et al., 2013; Yang et al., 2017a; Zhang et al., 2018d) in electrochemical performance is summarized in Table S1. Additionally, it is worth noting that the S@HNC electrode also displays a higher specific capacity and Coulombic efficiency than the S-NC electrode at the sulfur loading of 5 mg cm$^{-2}$ (Figure S15).

The superior electrochemical performance of the S@HNC electrode is mainly owing to its structural superiority by synergistically coupling the chemical interaction and physical confinement (Figure 6). First, the HNC host with ink-bottle-like pores and outer carbon shell enables the sulfur to immerse into the inner cavities of the host, ensuring the effective confinement of sulfur by restricting the polysulfides in the host with small apertures. Furthermore, the high porosity of the host offers the sufficient buffers for volume variation of active materials during lithiation/delithiation processes. The carbon host also contributes to decrease the electrochemical impedance by virtue of the connected carbon framework. More importantly, there are abundant N sites evenly distributed in the carbon host, which undoubtedly strengthen the suppression of polysulfide shuttling and further enhance the sulfur utilization. Therefore, the unique architecture of the host not only inhibits the diffusion of soluble polysulfides but also maintains the stability of the S@HNC electrode structure, thus ensuring the good rate capability and cycling stability.

Conclusion

In summary, a unique S@HNC rhombic dodecahedral architecture has been prepared by a sequential chemical etching, carbonization, and melt-diffusion method. When it is used as the cathode for Li-S battery, the designed S@HNC cathode shows a more superior rate capability and cycling stability in comparison with S-NC. The good electrochemical performance is primarily created by the synergistic effect between chemical interaction and physical confinement, which ensures the efficient entrapment and

Figure 6. Illustration of the Possible Sulfur Loading Process and Confinement Mechanism
confinement of sulfur species with the inner wide bodies and narrow necks. With structural and chemical dual encapsulation, the HNC host enables a super-quick decoloring of polysulfide solution. Then it can be concluded that a host with hierarchical pores is conducive to the polysulfide trapping. Hence this study provides a kind of design principle to produce the sulfur cathodes.

METHODS
All methods can be found in the accompanying Transparent Methods supplemental file.

Limitations of the Study
In this study, the hollow N-doped carbon polyhedrons with hierarchical pores enable high sulfur loading and exhibit fast polysulfide trapping and improved electrochemical performance in lithium-sulfur batteries. However, the relationships between pore structure and electrochemical performance still need more investigation. The metallic material with strong polysulfide affinity can be attempted to integrate with the above-mentioned hollow polyhedrons to further enhance the electrochemical performance.

SUPPLEMENTAL INFORMATION
Supplemental Information can be found online at https://doi.org/10.1016/j.isci.2019.02.019.

ACKNOWLEDGMENTS
The financial support of the National Natural Science Foundation of China (Grant 21574032) is acknowledged.

AUTHOR CONTRIBUTIONS
D.-H.Y. and B.-H.H. designed and conducted the experimental work, H.-Y.Z. and H.L. contributed to the experimental work, D.-H.Y. and B.-H.H. contributed to the preparation and editing of this manuscript.

DECLARATION OF INTERESTS
The authors declare no competing interests.

Received: November 27, 2018
Revised: January 29, 2019
Accepted: February 21, 2019
Published: March 29, 2019

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Supplemental Information

Hollow N-doped Carbon Polyhedrons with Hierarchically Porous Shell for Confinement of Polysulfides in Lithium–Sulfur Batteries

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Supplemental data items

Figure S1. TEM images of NC-2 (A) and NC-5 (b) obtained from partially etching ZIF-8 precursors (core/shell-like structures) by controlling the etching time of 2 and 5 min, related to Figure 1 and Transparent Methods.

Figure S2. N₂ isotherm (A) and corresponding pore size distribution (B) of NC-2 and NC-5 characterized by TriStar II 3020 analyzer, related to Figure 1 and Transparent Methods.
Figure S3. Digital image shows a visualized $\text{Li}_2\text{S}_6$ adsorption of NC-2 and NC-5 samples, related to Figure 1 and Transparent Methods.

Figure S4. XRD patterns of the prepared ZIF-8 and hollow ZIF-8 after chemical etching, related to Figure 1 and Transparent Methods.
Figure S5. XRD patterns of the HNC and NC hosts, related to Figure 1 and Transparent Methods.

Figure S6. TEM image of S@HNC hybrid, related to Figure 2 and Transparent Methods.
Figure S7. Raman spectra of NC and S-NC samples, related to Figure 3.

Figure S8. N$_2$ isotherm (A) and corresponding pore size distribution (B) of ZIF-8 characterized by Micromeritics 3 Flex analyzer, related to Table 1.
Figure S9. N₂ isotherm (A) and corresponding pore size distribution (B) of hollow ZIF-8 characterized by Micromeritics 3 Flex analyzer, related to Table 1.

Figure S10. Pore size distribution of NC and HNC characterized by Micromeritics 3 Flex analyzer, related to Figure 3.
Figure S11. N$_2$ isotherm (A) and corresponding pore size distribution (B) of HNC characterized by TriStar II 3020 analyzer, related to Figure 3.

Figure S12. TGA of S@HNC, related to Figure 3.
Figure S13. High-resolution XPS spectra of C 1s (A), N 1s (B) and S 2p (C) for S-NC, related to Figure 3. The high-resolution spectra of C, N and S for S-NC are very similar to S@HNC, indicating the similar chemical composition and structure. Likewise, three peaks of 284.6, 285.2, and 286.2 eV of C1s spectrum are attributed to C–C, C–O, and C–N–C groups, respectively (Mi et al., 2017). The peaks located at 398.6, 400.4, and 401.4 eV of N 1s spectrum can be attributed to pyridinic N, pyrrolic N, and graphitic N, respectively (Zhang et al., 2018b). Additionally, the peaks at 164.0, 165.1 and 168.8 eV of S 2p spectrum are the signals of S 2p3/2 and S 2p1/2 and a little sulfate species, respectively (Li et al., 2015).
Figure S14. The refined XPS spectra of N 1s for HNC before and after adsorption of Li$_2$S$_6$, related to Figure 5.

Figure S15. Cycling performance of S@HNC and S-NC with a higher sulfur loading at 0.2 C, related to Figure 5.
Figure S16. SEM images of S@HNC cathode before (a, b) and after cycles (c, d), related to Figure 5.
| Cathode materials | Sulfur content (wt%) | Voltage range (V) | High rate/Capacity (mAh g\(^{-1}\)) | Current density | Cycles | Reversible capacity (mAh g\(^{-1}\)) | Reference |
|-------------------|----------------------|-------------------|------------------------------------|----------------|--------|-------------------------------------|-----------|
| HNC               | 72                   | 1.7–2.8           | 2 C/433                            | 1.0 C          | 500    | 433                                 | This work |
| ZIF-8-derived N-doped carbon | 60               | 1.7–2.8           | 0.5 C                              | 400            | 511    | Zhang et al., 2018b                 |
| ZIF-8-derived N-doped carbon | 55               | 1.7–2.8           | 1 C/712                            | 0.5 C          | 400    | 618                                 | Zhang et al., 2018b |
| MOF-5-derived carbon nanoplates | 54               | 1.2–3.0           | 0.5 C                              | 50             | 730    | Xu et al., 2013                     |
| ZIF-8-derived carbon nanosheets | 70               | 1.7–2.8           | 2 C/785                            | 0.5 C          | 300    | 587                                 | Jiang et al., 2017 |
| MOF-derived N-rich carbon | 78               | 1.7–2.8           | 2 C/967                            | 0.5 C          | 1000   | 534                                 | Yang et al., 2017b |
| MOF-derived carbon polyhedrons | 43               | 1.2–3.0           | 0.06 C                             | 100            | 490    | Wu et al., 2013                     |
| MOF-derived N-doped carbon spheres | 37               | 1.0–3.0           | 3 C/251                            | 0.2 C          | 100    | 473                                 | Li et al., 2015 |
Transparent Methods

Materials and Reagents
Zn(CH$_3$COO)$_2$:2H$_2$O (99%) was purchased from Sinopharm chemical reagent Co. Ltd. 2-methylimidazole (99%) was bought from J&K Scientific Ltd. Sigma-Aldrich. Sublimed Sulfur (99.5%) was purchased from Sigma-Aldrich. Tannic acid (98%) was bought from Innochem Co. Ltd. All the chemicals were received as analytical grade and used without further purification.

Synthesis of ZIF-8
ZIF-8 was synthesized according to a previously reported method (Yang et al., 2017a). In a typical process, Zn(CH$_3$COO)$_2$:2H$_2$O (0.30 g, 1.37 mmol) was dissolved in 5 mL of deionized water. The solution was added into 5 mL of aqueous solution containing 1.12 g (13.6 mmol) of 2-methylimidazole under stirring. After a few seconds, the mixed solution was left at room temperature for 24 hr. The ZIF-8 powder was washed several times with methanol and dried at 60 °C.

Synthesis of Hollow ZIF-8
The hollow ZIF-8 was obtained through a chemical etching process with tannic acid as the etching agent (Hu et al., 2016; Zhang et al., 2018a). In a typical method, ZIF-8 (0.30 g) was dispersed in 300 mL of aqueous solution containing 1.50 g of tannic acid. After stirring for 10 min, hollow ZIF-8 was collected by centrifugation and washed with water and ethanol. The partially etching ZIF-8 precursor was prepared by controlling the etching time of 2 or 5 min.

Syntheses of HNC and NC Host Materials
The HNC and NC hosts were prepared by carbonizing hollow ZIF-8 and ZIF-8 in a tubular furnace under a flow of N$_2$ gas at 900 °C for 2 hr with a rate of 5°C min$^{-1}$, respectively. NC-2 and NC-5 were obtained by carbonizing partially etching ZIF-8 under the same condition.

Syntheses of S@HNC and S-NC Hybrids
The HNC or NC host material and the sublimed sulfur powder with a weight ratio of 3:7 were well mixed by grounding for about 30 min. Then, the mixture was thermally treated at 155 °C for 12 hr in a sealed container to fabricate the S@HNC or S-NC composite.

Material Characterization
X-ray diffraction (XRD) patterns were characterized using a Rigaku D/MAX-TTRIII(CBO) diffractometer (Japan) with Cu K$_\alpha$ radiation ($\lambda = 1.54059$ Å). Field emission scanning electron microscopy (FESEM) was taken on a Hitachi S4800 (Japan). Transmission electron microscopy (TEM) was conducted using FEI Tecnai.
G2 20 S-TWIN (USA) and JEOL JEM-2100F (Japan) transmission electron microscopes. Raman spectra were determined by a Renishaw inVia plus spectrometer (UK). X-ray photoelectron spectroscopy (XPS) data were obtained using the Thermo ESCALAB 250Xi analyzer (USA) with Al Kα radiation. N\textsubscript{2} adsorption and desorption analysis was measured using the Micromeritics 3 Flex system (USA) and TriStar II 3020 analyzer (USA) at 77 K. Elemental analysis was carried out by a Flash EA 1112 elemental analyzer (Italy). Thermal gravimetric analysis (TGA) was taken on a Discovery thermoanalyzer (Waters Limited Liability Company, USA) under N\textsubscript{2} at a heating rate of 10°C min\textsuperscript{-1}.

**Electrochemical Characterization**

To prepare the working electrode, the active material, acetylene black, single-walled carbon nanotubes, and polyvinylidene fluoride (PVDF) binder with a weight ratio of 7:1:1:1 were mixed together in N-methyl-2-pyrrolidone (NMP) to form a homogeneous slurry. Then the slurry was uniformly deposited onto an aluminum foil and dried under vacuum at 60 °C for 12 hr. The average mass loading of sulfur was about 1.0 mg cm\textsuperscript{-2} and the higher sulfur loading was about 5.0 mg cm\textsuperscript{-2}. All specific capacity of working electrode was calculated based on sulfur amount. 1.0 M bis(trifluoromethane) sulfonamide lithium salt (LiTFSI) in a mixed solvent of 1,3-dioxolane and 1,2-dimethoxyethane (DOL/DME, 1:1 by volume) with 2 wt% of lithium nitrate (LiNO\textsubscript{3}) was used as the electrolyte. Celgard 2400 film was used as the separator. The ratio of electrolyte to sulfur was about 30 µL electrolyte for per mg sulfur. CR2032 coin cells were assembled by using lithium metal as the counter electrode. Cyclic voltammetry (CV) tests were conducted on a CHI 760E electrochemical workstation (China) in the voltage range of 1.7–2.8 V (vs Li\textsuperscript{+}/Li) at a scan rate of 0.1 mV s\textsuperscript{-1}. Galvanostatic charge/discharge measurements were performed using a LAND CT2001A battery system (China) between 1.7 and 2.8 V. Electrochemical impedance spectroscopy (EIS) was recorded with a Bio-Logic VMP3 Multi-channel potentiostat (France) over the frequency of 100 kHz to 10 mHz.

**Visualization Experiment**

The visualization process of the first discharge cycle was performed in a sealed bottle with S@HNC or S-NC as cathode and lithium foil as anode. Polysulfide adsorption ability of HNC and NC was evaluated by decoloring the Li\textsubscript{2}S\textsubscript{6} solution. First, Li\textsubscript{2}S\textsubscript{6} solution (5 mM) was prepared by dissolving Li\textsubscript{2}S and a stoichiometric amount of sulfur in the electrolyte. Then the adsorption test was performed by dispersing HNC or NC (10 mg) into the above-obtained Li\textsubscript{2}S\textsubscript{6} solution (1.5 mL) for 10 min. For NC-2 and NC-5, the adsorption test was performed by dispersing NC-2 or NC-5 (6.7 mg) into 5 mM Li\textsubscript{2}S\textsubscript{6} solution (1.0 mL) for 12 hr.
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