Polar and Conductive Iron Carbide@N-doped Porous Carbon Nanosheets as a Sulfur Host for High Performance Lithium Sulfur Batteries

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ABSTRACT.

The practical application of Li-S battery is inherently limited by the low conductivity of sulphur and the dissolution of polysulfides. The enhancement of conductivity and introduction of polarity to sulphur host is an effective strategy to overcome this long-standing challenges. In this work, a facile one-step carbonizing process is used to synthesize a unique porous and conductive nanocomposite where Fe_3C nanoparticles is embedded in nitrogen-doped porous carbon sheets ($\text{Fe}_3\text{C}@NPCS$). As demonstrated in Li_2S_4 adsorption experiments and confirmed by density functional theory calculations, Fe_3C nanoparticles are able to strongly adsorb polysulfides via strong Fe-S chemical bonds. Due to the remarkable conductivity, Fe_3C nanoparticles can also accelerate the electrochemical reactions of the polysulfides through fast electron transportation. The carbon sheets prevent the aggregation of Fe_3C nanoparticles in the synthesis, and accommodate sulfur and its volume expansion during charge/discharge. With these features, the resultant sulfur cathodes ($\text{Fe}_3\text{C}@NPCS\text{-S}$) deliver an excellent cycling performance with a capacity decay of 0.036% per cycle, and high rate performance of ca. 1127, 1020, 907, 802, 731 and 647 mAh g^{-1} under the current density of 0.3, 0.5, 1, 2, 3 and 5 C-rate, respectively.

Introduction

With increasing demand for renewable energy facilities, electric vehicles and portable devices, next-generation energy storage technologies with high capacity and long life have been attracting intensive research interest.[1-3] Lithium sulfur batteries are considered a promising option because of their high theoretical capacity of ca. 1600 mAh g⁻¹ and high theoretical energy density of ca. 2500 Wh·kg⁻¹ [4]. However, the commercialization of lithium sulfur batteries faces several key challenges including low sulfur utilization, poor coulombic efficiency and rapid capacity fading [5, 6].

To overcome these challenges, various sulfur hosts have been proposed to confine the soluble intermediate lithium polysulfide species (Li_2S_x , $6 < x < 8$) and facilitate the electrochemical redox reactions during charge/discharge processes. Intensive research on a wide spectrum of porous carbon hosts has established that the carbonaceous pores can encapsulate the sulfur and accommodate the electrochemical transformation between sulfur and lithium polysulfide.[7-13] However, the carbon materials lack strong interfacial interactions with the lithium polysulfide species because the carbon materials are commonly non-polar while polysulfides are polar [14-19]. Another strategy is to improve the polarity of the carbon materials by heteroatom doping and using polar material as adsorption materials, such as metal oxide. In this regard, various metal oxides have been trialed to suppress the shuttle effect and prolong the lifetime of Li-S batteries, including TiO_2 , SiO_2 , Al_2O_3 , MnO_2 , and Co_3O_4 [20-24]. These oxide materials can inhibit the migration of polysulfides by the chemical adsorption of the polysulfides. Unfortunately, most metal oxides are not good electronic conductors. The subsequent electrochemical conversion reaction on the metal oxides is impeded due to slow electron transfer, leading to low sulfur utilization [25-29].

The ideal sulfur host offers dual functions to resolve these inherent problems, i.e. strong chemical adsorption ability to suppress the migrating polysulfides and high conductivity to collect current from the accelerated electrochemical conversion reactions. Carbonaceous materials can be polarized by N doping and embedding polar nanoparticles, enhancing the chemical interactions with the lithium polysulfide species [30-32]. Iron carbide (Fe_3C) is a robust material that has attracted increasing attention because of its abundance and low cost, and more importantly, its inherent characteristics of high electronic conductivity due to it being a metal-like material [33, 34]. Furthermore, Fe_3C could be an effective polysulfide adsorbent if strong Fe-S bonds can be formed between Fe_3C and polysulfides [35, 36]. Herein, a facile one-step carbonizing process is used to synthesize a porous and conductive nanocomposite where Fe_3C nanoparticles are embedded onto nitrogen-doped porous carbon sheets (i.e. $\text{Fe}_3\text{C}@NPCS$). The carbon sheets allow even distribution of the Fe_3C nanoparticles and facilitate excellent conductivity as a bulk, which is beneficial to sulfur hosts (Fig. 1). The polysulfide species can be chemically adsorbed onto the Fe_3C nanoparticles due to the strong chemical interaction between Fe and S as proven in density functional theory (DFT) calculations. In other words, the $\text{Fe}_3\text{C}@NPCS$ offers dual functions i.e. suppress the shuttle effect to accelerate electron transfer of the electrochemical reactions, resulting in improved charge/discharge capacity in high current density and prolonged Li-S battery lifetimes.

Experimental Section

Material synthesis

The $\text{Fe}_3\text{C}@NPCS$ was synthesized by a facile approach, in which urea (10 g), glucose (0.5 g), iron (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) (0.1 g), and DI water (100 mL) were stirred at 90 °C until the precursors have been deposited. The co-deposited precursors were placed into a crucible and then heated to 800 °C at a rate of 5 °C min⁻¹ for 2 h in N_2 atmosphere. For comparison, preparation

of nitrogen-doped porous carbon sheets (NPCS) were synthesized via the same method without the addition of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$.

The $\text{Fe}_3\text{C@NPCS-S}$ composite was first prepared by mixing the $\text{Fe}_3\text{C@NPCS}$ and pure sulfur (weight ratio of $\text{Fe}_3\text{C@NPCS}$: S was 1:3) in CS_2 solution. Then, the mixture was gradually evaporated by ultrasonic dispersion. Second, the dried mixture was pressed into a cylindrical shape with a 5-mm diameter by a mold. Finally, the products were heat-treated in Ar atmosphere at 130 °C for 4 h to obtain $\text{Fe}_3\text{C@NPCS-S}$ composites. The NPCS-S composites were synthesized via the same method by using NPCS.

Structure Characterization

Structural analyses were performed using (i) high-resolution X-ray diffractometer (XRD) with $\text{Cu-K}\alpha$ radiations on a PANalytical X'Pert³; (ii) scanning electron microscope (SEM) on JEOL JSM-7001F; (iii) transmission electron microscopy (TEM) and energy dispersive spectrum (EDS) mapping using a FEI Tecnai F30 TEM (operating at 300 kV); and (iv) X-ray photoelectron spectroscopy (XPS) on Axis Ultra imaging photoelectron spectrometer with the monochromatic Al $\text{K}\alpha$ line (Al $\text{K}\alpha$, $h\nu = 1486.7$ eV). All the collected spectra were calibrated with C 1s peak at 284.8 eV, and analysed using CasaXPS software. The thermal stability of the samples was monitored using a thermogravimetric analysis (SDT Q600, TA instruments) from 30 to 600 °C under nitrogen with a heating rate of 10 °C/min. Nitrogen sorption isotherms were measured utilizing the Quantachrome Autosorb-IQ instrument at 77 K.

Electrode Fabrication and Electrochemical Characterization

The positive electrode consists of 80 wt. % as-prepared compounds, 10 wt. % carbon black and 10 wt. % polyvinylidene fluoride (PVDF) as a binder. These materials were dispersed in N-methyl-

2-pyrrolidinone (NMP), and the resultant slurry was coated onto an aluminium foil, which was used as the cathode electrode (c.a. 1.5 mg cm^{-2} sulfur loading) during the electrochemical measurements. The electrode was cut into circular discs with a diameter of 12.9 mm and compact density of 1.2 g cm^{-3} . The electrolyte was 1 M $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ (LiTFSI) dissolved in a mixture of 1,3-dioxolane (DOL) and dimethoxymethane (DME) (1:1 by volume) with 0.1 M LiNO_3 additives used as electrolyte. All the simulated coin-type cells (CR2032) were assembled with lithium metal as the negative electrode in an argon-filled M-Braun box. The cyclic voltammogram (CV) measurements were carried out at room temperature on a 660e electrochemical station (CHI China). The electrochemical tests were carried out by a fully automatic program test instrument (LAND, China), with constant current and voltage ranging from 2.8 to 1.8 V (vs. Li/Li^+).

Density functional theory calculations

The first principle calculations were evaluated through spin-polarized density functional theory as implemented in the Vienna Ab initio Simulation Package (VASP) with the projected augmented wave (PAW) approach and generalized gradient approximation by Perdew-Burke-Ernzerhof with a Hubbard U correction. The plane-wave energy cut-off was set as 520 eV. A $15.1 \text{ \AA} \times 13.4 \text{ \AA}$ supercell of (001) surface of Fe_3C with 8 atom layers and a Γ -centred Monkhorst-Pack $3 \times 3 \times 1$ grids in k-point sampling were used. The vacuum distance larger than $13 \text{ \AA}$ was applied in calculations to remove the interaction between successive slabs. In structural optimization, the lower six atomic layers of the slabs were fixed while allowing other atoms to fully relax until the force was converged to $0.01 \text{ eV/\AA}$.

Results and discussion

The $\text{Fe}_3\text{C@NPCS}$ was prepared by a carbonization process, where the glucose and urea were pyrolyzed to the nitrogen-doped porous carbon sheets. Meanwhile, the Fe_3C nanoparticles were obtained *via* the reduction and carbonization of FeCl_3 at high temperature. As shown in the scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images, the flexible carbon sheets display a fluffy and corrugated morphology and Fe_3C nanoparticles (c.a. 10-60 nm as shown in Fig. S1 the size distribution histograms) are uniformly embedded in the carbon sheets (Fig. 2 a and b). In addition, the weight ratio of Fe_3C is c.a. 66.5% on $\text{Fe}_3\text{C@NPCS}$ according to the TG analysis (Fig. S2). Without introduction of the FeCl_3 into the precursors, the NPCS illustrates a similar layered nanosheet morphology (see the SEM and TEM image in Fig. S3) obtained by the same high temperature pyrolysis process. The elemental composition of the $\text{Fe}_3\text{C@NPCS}$ is illustrated by energy dispersive X-ray spectroscopy (EDS) mapping (Fig. 2c). A uniform distribution of Fe and N elements on the carbon sheet is clearly observed due to the dispersed Fe_3C nanoparticles and doped N atoms. A distinguishable lattice spacing of 0.22 nm (see Fig. 2b insert) corresponds to the (211) plane of Fe_3C phase. This is in line with observation of X-ray diffraction (XRD) patterns where the diffraction peaks are characteristic of the crystalline planes of Fe_3C phase (JCPDS, No. 65-2411). In addition, the rest diffraction peak at 26.1° suggests the formation of graphitic carbon at high temperature. The NPCS illustrates a high Brunauer-Emmett-Teller (BET) specific area of $556.3 \text{ m}^2 \text{ g}^{-1}$ as shown in Fig. S4. In contrast, the specific area of $\text{Fe}_3\text{C@NPCS}$ decreases to $359.3 \text{ m}^2 \text{ g}^{-1}$ due to the high density of Fe. The pore size distribution in $\text{Fe}_3\text{C@NPCS}$ and NPCS show a broad distribution of micro- and mesopores, with sizes ranging from 0-50 nm. This porous structure is mainly presented by the carbon matrix, which could accommodate and confine the lithium polysulfide species.

The chemical structure of the $\text{Fe}_3\text{C}@NPCS$ nanocomposite is further investigated by the x-ray photoelectron spectroscopy (XPS) as shown in Figure 2e. The survey spectra clearly indicate the presence of iron (Fe), carbon (C), nitrogen (N), and oxygen (O) without any other element. The results of the elemental analysis (see Table S1) reveal that the atomic concentration of N decreases in the presence of Fe_3C nanoparticles. This is attributed to the fact that Fe metal can drastically eliminate nitrogen in the carbonization process at high temperature[37]. There are four types of C illustrated in the C 1s spectra (see Fig. S5), where the major carbon composition is graphitic C with a binding energy of 284.6 eV. The other types of carbon are identified as sp^3 C bonding with N or O (at 285.6 eV), aromatic C bonding with N or O (at 287.1 eV) and carboxyl C ($\text{O}-\text{C}=\text{O}$ at 289.4 eV). In the high-resolution analysis of N 1s, four types of doped elemental N are identified corresponding to pyridinic N at 398.4 eV, pyrrolic N at 399.8 eV, graphitic N at 400.9 eV, and absorbed N species at 402.1 eV as shown in the N spectrum (Fig. 2f) [30]. The atomic concentrations of different N dopants are qualified based on the peak integration and summarized in Table S2. In comparison with the NPCS, the $\text{Fe}_3\text{C}@NPCS$ has a higher ratio of pyridinic N to graphitic N, as Fe_3C nanoparticles could produce more edge sites in the carbon nanosheets which can accommodate pyridinic-type atoms. It has been reported that pyridinic-type N doping can improve adsorption of the polysulfide species for carbon-based materials [38, 39].

The adsorption ability of the sulfur host to polysulfide is important for the suppression of capacity fading. To identify the contribution of Fe_3C and NPCS to polysulfide adsorption, the adsorption ability of the $\text{Fe}_3\text{C}@NPCS$ and NPCS powder was tested in an ex-situ adsorption experiment using an ultraviolet-visible (UV-vis) spectrometer. An equivalent amount of $\text{Fe}_3\text{C}@NPCS$ and NPCS were separately added to a lithium polysulfide (Li_2S_4) solution (1 M in DME). As shown in Figure 3a, the peak of the UV-vis spectra is identified as Li_2S_4 [40]. When exposed to the

Fe₃C@NPCS nanocomposite, the absorbance peak of the Li₂S₄ solution drops rapidly, suggesting decreasing Li₂S₄ concentration. After 30 min, the UV-vis spectra indicate that the Li₂S₄ was completely eliminated. This is in line with the observation of a clear solution in the digital photograph. In contrast, the Li₂S₄ solution with NPCS remained light yellow as illustrated in Figure 3b. Therefore, the adsorption results strongly suggest the Fe₃C nanoparticles can effectively trap lithium polysulfide species, while the NPCS illustrated a neglectable adsorption ability on lithium polysulfide. Also, the Fe₃C@NPCS also have an effective adsorption ability to Li₂S₈ (see Fig. S6a), suggesting that it could trap all kinds of polysulfide anionic species during the lithium sulfur charge and discharge. This strong adsorption ability of Fe₃C nanoparticles was further investigated by density functional theory calculations on the interaction between lithium polysulfides and Fe₃C. As shown in Figure 3c, the (100) surface of Fe₃C was chosen to study the adsorption behavior of lithium polysulfide species (Li₂S and Li₂S₂). The binding energy (E_b) is defined by:

$$E_b = E_{Fe_3C} + E_{LiS_x} - E_{total}$$

Where E_{Fe_3C} is the energy of the clean Fe₃C (100) surface, E_{LiS_x} is the energy of the lithium sulfide species and E_{total} is the total energy of the surface of Fe₃C bonded with different sulfide species. The calculated binding energy of the Li₂S and Li₂S₂ to the Fe₃C (100) surface are 4.87 eV and 6.37 eV, respectively. These binding energies are much larger than the adsorption binding energies for Li-S composites on graphene (< 1 eV) [41-43]. In addition, after the adsorption of lithium sulfide species, the Fe-S bonding peak at 706.0 eV can be found in the Fe 2p_{3/2} XPS spectra (see Fig. S6b), confirming the DFT result of strong Fe-S interactions. This strong adsorption ability of Fe₃C@NPCS could efficiently suppress the shuttle effect for Li-S batteries as a sulfur host.

$\text{Fe}_3\text{C}@NPCS\text{-S}$ and $NPCS\text{-S}$ composites were fabricated by a melt diffusion method as cathode materials for lithium sulfur batteries. The sulfur content is c.a. 74.5 wt.% in these hybrids as shown in the thermogravimetry results (see Fig. S7). The scanning transmission electrons microscopy (STEM) image (Fig. 4a) clearly reveals the morphology of $\text{Fe}_3\text{C}@NPCS\text{-S}$. After sulfur loading, the layered and ridged morphology is retained, where sulfur is uniformly deposited on the $\text{Fe}_3\text{C}@NPCS$ composite. The elemental mappings in Figure 4b indicate that the C, N and Fe mappings are totally in accordance with the morphology of the $\text{Fe}_3\text{C}@NPCS$ nanocomposite and the uniform distributions of sulfur. In addition, the XRD pattern (Fig. 4c) also corresponds to the incorporation of sulfur for Fe_3C nanoparticles.

$\text{Fe}_3\text{C}@NPCS\text{-S}$ and $NPCS\text{-S}$ were used to fabricate Li-S batteries as cathode materials using an identical assembly process of coin cells and their electrochemical properties investigated. The electrochemical performance of the $\text{Fe}_3\text{C}@NPCS\text{-S}$ and $NPCS\text{-S}$ electrodes was first investigated by cyclic voltammogram (CV) measurements as illustrated in Figure 5 a and b. In the first cycle, two reductive peaks were observed at c.a. 2.31 V and 2.02 V. The first reduction peak is generated by the conversion of sulfur into a series of intermediate long-chain lithium polysulfides ($\text{S}_8 \rightarrow \text{S}_8^{2-} \rightarrow \text{S}_6^{2-} \rightarrow \text{S}_4^{2-}$) with lithiation and charge transfer. The peak at 2.02 V resulted from the formation of short-chain sulfide species ($\text{S}_4^{2-} \rightarrow \text{S}_2^{2-} \rightarrow \text{S}^{2-}$) by further lithiation. In the following cathodic process, an oxidation peak at 2.45 V corresponded to the oxidation process from S^{2-} to S [44]. In the following cycles, the reductive peaks positively shifted to a higher position, resulting in a decreased potential separation of redox waves.

This suggests a reduced polarization after the first activation cycle. It is worth noting that the overlapping of subsequent CV profiles indicated good reversibility. In contrast, as shown in Figure 5b, the CV profiles of $NPCS\text{-S}$ illustrate an additional peak shoulder at anodic current between 2.5

to 3 V implying the occurrence of a serious shuttle effect, and much broader redox peaks and larger voltage hysteresis (see Fig. S8) due to its high polarization and poor reversibility. In accordance with the CV profiles, the two plateaus in the galvanostatic charge and discharge profile are related to the transformation from the long-chain polysulfide to the short-chain polysulfide species. It is noted that the $\text{Fe}_3\text{C}@\text{NPCS-S}$ has a lower overpotential and a longer voltage plateau than NPCS-S. These results reveal that the Fe_3C nanoparticles play an important role in simultaneously facilitating the electrochemical reaction and stabilizing the soluble polysulfides within the carbon matrix simultaneously.

The rate performance is determined by the charge/discharge measurement at constant current density ranging from 0.2 to 5 C over the voltage range of 3.0-1.5 V (see Fig. 5c). The $\text{Fe}_3\text{C}@\text{NPCS-S}$ electrodes delivered a discharge capacity of c.a. 1251 mAh g⁻¹ at 0.2 C. The capacity of the $\text{Fe}_3\text{C}@\text{NPCS-S}$ electrode remained ca. 1127, 1020, 907, 802, 731 and 647 mAh g⁻¹ under the current densities of 0.3, 0.5, 1, 2, 3 and 5 C, respectively. In contrast, the NPCS-S electrode illustrates a lower specific capacity and a larger overpotential at different current densities (see Fig. S9). This indicates that the introduction of conductive Fe_3C nanoparticles enhances the electrochemical reaction kinetics through a catalytic effect on decomposition lithium disulfide. The cycling rate performance of the $\text{Fe}_3\text{C}@\text{NPCS-S}$ and NPCS-S electrodes was compared as shown in Figure 5d. The rate performance of $\text{Fe}_3\text{C}@\text{NPCS-S}$ electrode was superior to the NPCS-S electrode from 0.2 to 5 C. When the current rate goes back to 0.5 C, the capacity has fully recovered to 964 mAh g⁻¹. The rate capability is commonly associated with the electrochemical kinetics, internal resistance and charge transfer [45]. Electrochemical impedance spectra (EIS) were generated to further investigate the electrochemical resistance of the $\text{Fe}_3\text{C}@\text{NPCS-S}$ and NPCS-S electrodes (see Fig. S10 and Table S3). The $\text{Fe}_3\text{C}@\text{NPCS-S}$

electrode illustrates a much lower charge-transfer resistance than NPCS-S, suggesting improved electrochemical kinetics and therefore, high rate capacities.

The cycling capacity and corresponding coulombic efficiency of the cells with $\text{Fe}_3\text{C@NPCS-S}$ and NPCS-S electrodes were determined for 300 cycles at 0.5 C. As shown in Figure 6a, the $\text{Fe}_3\text{C@NPCS-S}$ delivered an initial discharge capacity of c.a. 1150 mAh g⁻¹. The corresponding initial coulombic efficiency of $\text{Fe}_3\text{C@NPCS-S}$ was 92.38%. The initial irreversible capacity could be attributed to the decomposition of electrolyte to form the SEI layer and the loss of sulfur due to the shuttle effect [46]. The coulombic efficiency of $\text{Fe}_3\text{C@NPCS-S}$ returned to 99.5% and remained above 99% during the 300 cycles. In contrast, the initial coulombic efficiency of NPCS-S only reached c.a. 70.13%, and kept decreasing from 98.9% to 96.6% in the following cycles. In addition, the discharge capacity of NPCS-S rapidly declined from c.a. 988 mAh g⁻¹ to c.a. 299 mAh g⁻¹ with a capacity decay of 0.232% per cycle. This rapid capacity fading is not only due to the serious shuttle effect, but also slow electrochemical reactions [47, 48]. The discharge capacity of $\text{Fe}_3\text{C@NPCS-S}$ gradually declined to c.a. 676 mAh g⁻¹ with the capacity decay of 0.135% per cycle. The charge/discharge current density was increased to up to 2 C to further investigate the long-term and high-rate cycling performance (up to 1500 cycles and under 2 C) of the $\text{Fe}_3\text{C@NPCS-S}$ and NPCS-S electrodes (see Fig. 6b). After the initial five cycles, the cycling capacity reached a maximum value of c.a. 828 mAh g⁻¹ and 627 mAh g⁻¹ for the $\text{Fe}_3\text{C@NPCS-S}$ and NPCS-S electrodes, respectively. The $\text{Fe}_3\text{C@NPCS-S}$ illustrates a better cycling performance with a capacity decay of 0.036% per cycle compared with the NPCS-S (0.055% per cycle). To investigate the structural evolution after charge/discharge cycling, the morphological characterizations of $\text{Fe}_3\text{C@NPCS-S}$ electrode after 100 cycles at 1C were carried out by using the SEM (Fig. S11). After 100 charge/discharge cycles, there is no morphology change on

$\text{Fe}_3\text{C}@\text{NPCS}$ -S electrode, suggesting the good structural stability. Such a remarkable performance can be attributed to the Fe_3C effectively suppressing the shuttle effect to deal with capacity fading, due to its strong adsorption of polysulfide species.

Conclusion

A sulfur host, $\text{Fe}_3\text{C}@\text{NPCS}$ nanocomposite was prepared by a one-step carbonization method. The Li_2S_4 adsorption experiment and DFT calculations suggest that polar Fe_3C nanoparticles facilitate strong adsorption to polysulfides. The improved conductivity of the conductive Fe_3C nanoparticles accelerates the electrochemical reaction kinetics of Li-S batteries. As a result, the $\text{Fe}_3\text{C}@\text{NPCS}$ nanocomposite could suppress the shuttle effect and deliver remarkable electrochemical performance. Both the rate performance and cycling stability of lithium sulfur batteries are significantly improved with the $\text{Fe}_3\text{C}@\text{NPCS}$ sulfur host. Our results demonstrate that the enhancement of polarity and conductivity of the sulfur host is an effective strategy in the design and fabrication of sulfur host materials for high performance lithium sulfur batteries.

Figure 1 Schematic illustration of roles of the proposed $\text{Fe}_3\text{C}@NPCS$ composite cathode during the charge/discharge processes: improved polarity retains sulfur and polysulfides and enhanced conductivity accelerates the electrochemical reactions in the cathodic chamber.

Figure 2 The SEM (a) and TEM images (b) of the Fe₃C@NPCS at low magnification, inset: high magnification TEM image of the Fe₃C nanoparticles; the SEM and EDS mapping images of Fe₃C@NPCS including the C, Fe and N elements (c); the XRD patterns of Fe₃C@NPCS and Fe₃C standard reference (d); the survey (e) and high resolution N1s (f) XPS spectra of Fe₃C@NPCS and NPCS.

Figure 3 UV-vis spectra and visual images (insert) of the polysulfide solution after exposure to $\text{Fe}_3\text{C}@\text{NPCS}$ (a) and NPCS (b) in a time lapse; (c) the first-principle calculations suggest the adsorption configuration of Li_2S and Li_2S_2 on the Fe_3C surface (the E_b represents binding energy between Fe_3C (100) surface and lithium polysulfide species).

Figure 4 The High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image (a) and EDX elemental mapping image (b) of Fe₃C@NPCS-S; (c) the XRD pattern of Fe₃C@NPCS-S.

Figure 5 Cyclic voltammogram (CV) of the electrodes made with (a) Fe₃C@NPCS-S and (b) NPCS-S for the first six cycles at a scan rate of 0.1 mV s⁻¹; (c) charge and discharge curves and (d) rate cycling performance with corresponding Coulombic efficiency of the Fe₃C@NPCS-S and NPCS-S electrodes at constant current of 0.2, 0.3, 0.5, 1, 2, 3, 5 C.

Figure 6 Cycling capacity and corresponding Coulombic efficiency of the $\text{Fe}_3\text{C@NPCS-S}$ and NPCS-S electrodes at the current density of (a) 0.5 C and (b) 2 C.

Supporting Information.

SEM and TEM images of the NPCS sample, N₂ adsorption/desorption isotherm with the corresponding pore size distribution, High resolution C 1s XPS spectra, thermogravimetry (TG) curves, the cyclic voltammograms, charge and discharge curves and rate cycling performance of NPCS-S cathode at constant current of 0.2, 0.3, 0.5, 1, 2, 3, 5 C-rates, the Nyquist plots and proposed equivalent circuit.

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