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DOI:

[10.1016/j.ensm.2018.08.016](https://doi.org/10.1016/j.ensm.2018.08.016)

Document Version

Accepted author manuscript

[Link to publication record in Manchester Research Explorer](#)

Citation for published version (APA):

Li, H., Ma, S., Cai, H., Zhou, H., Huang, Z., Hou, Z., Wu, J., Yang, W., Yi, H., Fu, C., & Kuang, Y. (2019). Ultra-thin Fe₃C nanosheets promote the adsorption and conversion of polysulfides in lithium-sulfur batteries. *Energy Storage Materials*, 18, 338-348. <https://doi.org/10.1016/j.ensm.2018.08.016>

Published in:

Energy Storage Materials

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www.elsevier.com/locate/ensm

PII: S2405-8297(18)30729-3
DOI: <https://doi.org/10.1016/j.ensm.2018.08.016>
Reference: ENSM483

To appear in: *Energy Storage Materials*

Received date: 8 June 2018
Revised date: 19 August 2018
Accepted date: 19 August 2018

Cite this article as: Huanxin Li, Shuai Ma, Houqin Cai, Haihui Zhou, Zhongyuan Huang, Zhaohui Hou, Jiajing Wu, Wenji Yang, Haibo Yi, Chaopeng Fu and Yafei Kuang, Ultra-thin Fe_3C Nanosheets Promote the Adsorption and Conversion of Polysulfides in Lithium-Sulfur Batteries, *Energy Storage Materials*, <https://doi.org/10.1016/j.ensm.2018.08.016>

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Huanxin Li,^{a,b} Shuai Ma,^{a,b} Houqin Cai,^{a,b} Haihui Zhou,^{a,b*} Zhongyuan Huang,^{a,b}
Zhaohui Hou,^{c,*} Jiajing Wu,^d Wenji Yang,^e Haibo Yi,^{a,b,*} Chaopeng Fu,^{a,b} Yafei
Kuang^{a,b*}

^a State Key Laboratory for Chemo/Biosensing and Chemometrics, Hunan University, Changsha, 410082, China

^b College of Chemistry and Chemical Engineering, Hunan University, Changsha, 410082, China

^c School of Chemistry and Chemical Engineering, Hunan Institute of Science and Technology, Yueyang, 414006, China

^d Hefei National Laboratory for Physical Sciences at the Microscale, CAS Center for Excellence in Nanoscience, and CAS Key Laboratory of Mechanical Behavior and Design of Materials, University of Science and Technology of China, Hefei, Anhui, 230026, China

^e School of Materials, The University of Manchester, Oxford Road, Manchester, M13 9PL, United Kingdom

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ABSTRACT: Rational design of hierarchical porous materials with comprehensive properties, e.g. good conductivity, fine dispersibility for sulfur, strong adsorption and catalytic abilities to polysulfides (LiPSs), is urgently needed for the practical application of lithium-sulfur batteries (Li-S batteries). Here, based on density functional theory (DFT) computational results and the design concept of efficient, low-cost and environmental friendliness, we report an ultra-thin (~1 nm) Fe₃C nanosheets growing on mesoporous carbon (Fe₃C-MC) with large specific surface area of 686.9 m² g⁻¹ and pore volume of 6.52 cm³ g⁻¹. Meanwhile, the formation mechanism of two-dimensional Fe₃C is revealed according to DFT results. In the Fe₃C-MC composite, the mesoporous carbon constructs a conductive network for dispersion of sulfur species, while Fe₃C nanosheets play a key role in electronic transmission, LiPSs adsorption and conversion in Li-S batteries. As a result, the Fe₃C-MC composite delivers a high initial capacity of 1530 mA h g⁻¹ at 0.1C, and a capacity of 699 mA h g⁻¹ after 100 cycles at 0.5C at a super-high sulfur loading of 9.0 mg cm⁻², meaning a specific area capacity of 6.291 mA h cm⁻². Such sulfur host is expected to accelerate the practical applications of Li-S batteries benefiting from the low-cost and large-scale process.

KEYWORDS: Biomass source, heat treatment, Fe₃C@mesoporous carbon, multifunctional sulfur host, Li-S batteries

Lithium-sulfur batteries have attracted considerable attention as one of the most promising next generation energy storage systems due to the high theoretical specific capacity (1675 mAh g^{-1}) and high energy density (2600 Wh kg^{-1}).¹⁻³ However, the commercialization of Li-S batteries is hindered by the poor cycle stability and inadequate capacity⁴⁻⁶ resulting from poor electrical conductivity of sulfur, the “shuttle effect” and slow redox reaction of soluble lithium polysulfides.

Many efforts have been made in order to solve these problems. As for the poor conductivity of sulfur, dispersing sulfur into highly conductive materials is an efficient way. Up to now, carbon material is the mainstreamed conductive material being used as sulfur host, which is widely reported.^{4, 7, 8} The sulfur/carbon cathode composite materials display promising initial capacity for Li-S batteries owing to the high conductivity of carbon materials. However, the simple mixing strategy is not enough to address the “shuttle effect” which often leads to rapid decay of the capacity for Li-S batteries. Furthermore, structure-designed carbon materials like carbon nanocages,⁹ carbon nanotubes¹⁰ and mesoporous carbon¹¹ are prepared to physically shield the LiPS shuttling. In this strategy, sulfur species are generally trapped in a relatively enclosed space to prevent the LiPSs from shuttling. However, the physical shield effect of cage-type structure inevitably separate the electrolytes from contacting active sulfur as well, resulting in poor rate capacities.

The “shuttle effect” is a key issue that needs to be solved urgently. The dissolution of LiPSs in the electrolyte and the transmission between electrodes cause serious loss of capacity and unsatisfied cycle stability. The compounds with strong adsorption ability are often used to capture the LiPSs and prevent them from shuttling. Chemical adsorption is an efficient strategy used to block LiPSs shuttling. Among all

the functional carbon composites, materials with more open structure like wrinkled nanosheets (doped graphene,^{12, 13} black phosphorus,¹⁴ C₃N₄ etc.^{3, 15}) ensure the infiltration of electrolyte and display more promising rate capacity. Meanwhile, chemical adsorption has a stronger adsorption force and thereby a more efficient fixation effect on LiPSs. Previously, our group prepared an N-doped CNTs@mesoporous carbon composite by fully using the trace iron source in biomass waste and additional nitrogen precursor, which demonstrated a cathodic sulfur host with strong chemical adsorption to LiPSs and thereby displayed promising performance for Li-S batteries.⁷ However, the limited adsorption sites, cannot meet the need for adsorption of large amount of LiPSs. Further, chemical adsorption can be a more efficient solution when combined with LiPSs fast conversion into an insoluble sulfide.

Another strategy to block the “shuttle effect” is to accelerate the conversion of soluble LiPSs to shorten the existence time of LiPSs and thereby reduce the possibility of their shuttling. This strategy requires the sulfur host possess not only adsorption ability but also excellent electrochemical catalytic ability to LiPSs. Recently, various transition metal compounds (Co₄N,¹⁶ TiN/TiO₂^{17, 18} and Co-N-GC¹⁹) have been reported to possess promising catalytic performance for LiPSs' fast conversion. Dong et al.²⁰ revealed that the Co-N synergistically enhanced Li-S performance, as Co helps to transform long-chain LiPSs to short-chain ones and doped-nitrogen is apt to facilitate the oxidation of LiPSs to S₈. Furthermore, Dong et al.¹⁶ also designed a Co₄N mesoporous sphere with superior performance for Li-S batteries even at ultra-high sulfur content (~95%). Yang et al.¹⁷ reported a twinborn TiO₂-TiN heterostructure to realize the trapping-diffusion-conversion of LiPSs for ultra-long life Li-S batteries. These report revealed the important role of polar

transition metal compounds as sulfur host for Li-S batteries, i.e. efficient capture and rapid conversion of LiPSs. Nevertheless, the polar transition metal compounds often possess relative low specific surface area. To sum up, the sulfur host with excellent performances should possess the comprehensive properties: 1. High conductivity; 2. Larger specific surface area for sulfur dispersion; 3. Strong adsorption to LiPSs; 4. Excellent catalytic ability for LiPSs conversion, as well as 5. Low-cost and environmental friendliness.

As we know, iron (Fe) is a common transition metal element, which has been widely used in many fields because of its abundant reserve, low cost, non-toxicity, good biocompatibility and natural catalytic activity. Meanwhile, biomass waste is also a kind of low-cost renewable carbon source which can be easily obtained in a large scale. According to the required properties for sulfur host as well as the considerations above, we conducted DFT calculations to predict the possible structure, conductivity, adsorption and catalytic abilities to LiPSs of Fe_3C . The DFT results indicate that Fe_3C tends to form a two-dimensional structure in high temperature deposition process, and it might possess a strong adsorption and catalytic ability to LiPSs as most of transition metal compounds do. The adsorption to LiPSs inhibits the migration of LiPSs while the catalytic effects accelerate the conversion, both of which can restrict the “shuttle effect”. Therefore, we aim at designing and synthesizing a two-dimensional Fe_3C /mesoporous carbon composite with high conductivity, large specific surface area, strong adsorption ability and excellent catalytic activity using iron compound and biomass as precursors to LiPSs to realize high-performance sulfur host for Li-S batteries with excellent stability. In our designing strategy, the mesoporous carbon can be obtained through annealing biomass waste and the polar conductive Fe_3C also can be formed by adding Fe sources into biomass at annealing process. The Fe_3C can

provide sufficient active sites for the adsorption and conversion of LiPSs. Thus, the designed Fe₃C/mesoporous carbon composite should address the major issues mentioned above effectively.

Herein, the Fe₃C-MC composite was prepared by the specific process as follows: biomass waste corncob, used as carbon source, was pretreated by concentrated sulfuric acid and then mixed with Fe precursor ferrous sulfate. Finally, the mixture was annealed at 800 °C under nitrogen atmosphere and Fe₃C-MC composite was obtained. The resultant composite (Fe₃C-MC) displays a hierarchical structure with ultra-thin two-dimensional Fe₃C nanosheets growing on mesoporous carbon (MC) material. The formation mechanism of the two-dimensional Fe₃C nanosheets is investigated based on DFT calculations. Meanwhile, DFT results also indicate that Fe₃C is a conductive polar compound with strong adsorption ability and excellent activation ability to LiPSs, which might promote the capture and transformation of LiPSs. When the three-dimensional hierarchical conductive Fe₃C-MC composite is used as sulfur host for Li-S batteries, it facilitates the electronic/ionic transportation, captures LiPSs to retard “shuttle effect” and enhances the reaction kinetics simultaneously. The Fe₃C-MC cathode delivers a high capacity and superior long-term stability for Li-S batteries even at high sulfur content and high sulfur loading. Such a sulfur host is expected to promote the practical use of Li-S batteries because of the low cost of raw sources and simple process. The approach for the sulfur host preparation also suggests a new way to produce multifunctional sulfur host to improve the performance of energy storage device in a large scale.

RESULTS AND DISCUSSION

The expected Fe_3C -MC composite was synthesized by a facile pyrolysis method, as presented in **Figure 1a**. Firstly, the cleaned corncobs were firstly ball milled into fine powders with a diameter of about 1 mm (**Figure S4**). Then the corncob powders were pretreated with concentrated sulfuric acid to activate the radicals and remove excess hydrogen and oxygen on corncobs. In previous researches, the biomass source is directly calcined or pre-activated by ZnCl_2 , KOH , K_2CO_3 , etc. to generate mesoporous structure.³¹⁻³⁵ Pretreatment by concentrated sulfuric acid is different from the processes previously reported, in which the C-H and C-O bonds would break before C-C bonds due to strong dehydration of concentrated sulfuric acid to preserve the carbon source, and the structure and composition of biomass significantly change (**Figure S5**).⁷ After thoroughly washed, the pretreated corncob powders were homogeneously mixed with FeSO_4 . Finally, the mixture was heat treated at 800 °C for 2 hours and the Fe_3C -MC composite was obtained (**Figure S3**). For comparison, MC was also prepared by carbonizing the pretreated corncob directly without FeSO_4 addition. As demonstrated in **Figure 1b**, the pretreated biomass displayed a loose structure of cross-linked fiber chains. Then, the added FeSO_4 was adsorbed on the fiber chains and stored in the pores. During heat treatment, part of the biomass decomposed into small gaseous molecules and the concentration of Fe in carbon matrix increased. As a result, the Fe atoms crystallized out while C atoms permeated into the crystals, forming Fe_3C nanosheets. To better understand the formation mechanism of the two-dimensional Fe_3C , we calculated the surface energies of three mutually perpendicular planes on Fe_3C (**Figure 1c**). It is well known that the crystals tend to grow on planes with larger surface energies to minimize the energy of whole system, especially at high temperature. The surface energies of (0 0 2) and (-2 2 0) planes are 15.74 and 9.02 eV, respectively, while that of (2 2 0) plane is 4.85 eV.

Therefore, the Fe and C atoms are more likely to be deposited on (0 0 2) and (-2 2 0) planes while the deposition on (2 2 0) plane is prohibited at annealing process, forming two-dimensional Fe_3C nanosheets. In the end, the (0 0 2) and (-2 2 0) planes disappeared while the (2 2 0) plane exposed in the final Fe_3C nanosheets.

Figure 1. (a) The schematic diagram for synthesis of MC and Fe_3C -MC; (b) Structural schematic diagram for the formation of Fe_3C nanosheets; (c) Formation mechanism of Fe_3C nanosheets

Then, DFT calculation was performed to predict the possible trapping and conversion ability of Fe_3C for LiPSs. The Li_2S_6 was selected as a representative prototype molecule for modelling. The optimized free Li_2S_6 molecule displays a structure of deformation crown.²⁶ **Figure 2a** demonstrates the optimized geometric structure and bonding state when Li_2S_6 is adsorbed on the Fe_3C surface. The favorable binding sites are the two S atoms at the bottom, with each S atom being strongly

bonded with three Fe atoms. The Li atoms are away from the Fe_3C surface to reduce the electrostatic repulsion of iron atoms. The calculated adsorption energy of Li_2S_6 on Fe_3C surface is -3.85 eV (energies of E_{ads} , E_{tot} , E_{LS} and E_{sur} are illustrated in **Table S1**), indicating that Fe_3C possesses excellent adsorption ability for LiPSs.²⁷ The representative reported adsorption energy results are illustrated in **Table S3**, revealing the superior adsorption ability of Fe_3C compared with the other adsorbents.^{28, 29} The bond length of Li_2S_6 before and after adsorption was also calculated by DFT. **Figure S2** shows the length of all the bonds, in the optimized free Li_2S_6 molecule, all the S-S bonds are 2.059-2.104 Å while Li-S bonds are 2.344-2.411 Å. However, after adsorption, two S-S bonds have changed obviously (Bond 1 and Bond 2 as pointed out). The states of the two S-S bonds before and after adsorption on Fe_3C are shown in **Figure 2b**. In bond 1, the initial length of S-S bond is 2.059 Å. After adsorption on Fe_3C , the S-S bond 1 is activated (almost broken) as the distance between the two S atoms has changed to 3.348 Å. In another S-S bond (bond 2), the length is 2.014 and 2.486 Å before and after adsorption, respectively, also indicating activation by Fe_3C . The increase of the length of S-S bonds demonstrates the bond energies are reduced, which means the Li_2S_6 molecule is in an activated state and more prone to reaction.²⁹ The DFT calculation suggests that the Fe_3C might possess not only superior adsorption ability to LiPSs, but also excellent catalytic effect for LiPSs fast transformation.³⁰

Figure 2. (a) Optimized geometries (top view, front view and side view) of Li_2S_6 on orthogonal Fe_3C and (b) the geometric deformation and bond length (bond 1 and bond 2) of Li_2S_6 before and after adsorption

Then the influence factors for forming Fe_3C nanosheets were investigated. Variety of samples was annealed at different temperatures with addition of different FeSO_4 concentration. The SEM images of samples with and without FeSO_4 addition are shown in **Figure S6**. The samples annealed with FeSO_4 addition exhibit ordered ultra-thin squamae-like nanosheets on the surface (**Figure S6a-c**). The directly annealed sample without FeSO_4 addition displays typical loose mesoporous carbon morphology with plenty of folds on the surface (**Figure S6d-f**). Further, the XRD results of the products obtained under different conditions are illustrated in **Figure**

S7a. It can be deduced that when the annealing temperature is lower than 750 °C or the Fe concentration is below 0.06 wt. %, the Fe source tends to combine with the small amount of oxygen contained in biomass and generates Fe₂O₃/C composite. But when the annealing temperature is higher than 950°C or the Fe concentration is above 3.3 %, the Fe source is more likely to be reduced and form elementary substance of Fe. The most appropriate condition for the generation of Fe₃C is annealing at 750-950 °C with Fe concentration of 0.1-0.3 wt. % (**Figure S7b**).

To reveal the detail structure and composition of the composites, especially for the nanosheets, further analyses on Fe₃C-MC composite are shown in **Figure 3**. The SEM image of the composite in **Figure 3a** shows that squamae-like Fe₃C nanosheets are well-wrinkled and ultra-thin, and possess large specific surface area (**Figure S8**). TEM images in **Figure 3b** showed the squamae-like Fe₃C nanosheets and mesoporous carbon actually interspersed together with good connection (**Figure S9**). **Figure 3c** shows the HRTEM image of the nanosheets, revealing clear lattice fringes and the characteristic spacing of 0.203 nm, corresponding to the (220) planes of Fe₃C (more details see **Figure S10**).³⁹ The AFM image of Fe₃C nanosheets reveals a lamellar structure (**Figure 3d**) and the thickness of the nanosheets is ~1.0 nm, indicating that the Fe₃C nanosheets are ultra-thin with only ~10 atomic layers. The EDS analysis on the ultra-thin nanosheet area, as demonstrated in **Figure 3e**, reveals the Fe to C atomic ratio of approximately 3:1, again indicating that the nanosheets are composed of Fe₃C.⁴⁰ The typical TEM image and corresponding elemental mapping of the Fe₃C-MC are shown in **Figure 3f**, revealing that C, Fe and N elements are uniformly dispersed in the composite. The N might come from the biomass precursors. In **Figure 3g**, a broad peak of carbon at 2θ=20-30° is observed from the product without FeSO₄ addition, indicating that carbon is mainly amorphous.⁷ For the

product with FeSO_4 addition, in addition to the broad carbon peak, sharp peaks at $2\theta=29.51^\circ$, 34.21° , 40.63° , 43.74° , 44.57° , 48.40° and 64.81° are observed, corresponding to the (111), (200), (201), (220), (022), (202) and (321) planes of Fe_3C (PDF#35-0772).³⁶ Moreover, the surface composition and chemistry of the products prepared with and without FeSO_4 addition were analyzed by XPS. For the product without FeSO_4 addition, two peaks at 284.6 eV and 401.0 eV corresponding to C 1s and N 1s were observed, with atomic ratio of 95.42 at.% and 4.58 at.% respectively. For the other one with FeSO_4 addition, predominant peaks for C 1s, N 1s and Fe 2p at 284.6 eV, 401.0 eV and 707.9 eV were detected with atomic ratio of 89.54 at.%, 4.01 at.% and 6.45 at.%, indicating the presence of additional Fe element (**Figure S11**). The nitrogen element might be introduced from the biomass precursor. The high resolution spectrum of Fe 2p (**Figure 3h**) is resolved into two distinguishable peaks at 707.9 eV and 722.6 eV, corresponding to the Fe-C bondings (Fe 2p_{3/2} and Fe 2p_{1/2}) of Fe_3C .^{37, 38} Thus, the composite is confirmed to be composed of mesoporous carbon and Fe_3C as expected. The content of Fe_3C in the composite is determined to be ~23.25 wt.% according to the TGA test and XRD analysis of the residue after TGA (**Figure S12**).

Figure 3. (a) SEM image of Fe₃C-MC; (b) TEM and (c) HRTEM images of Fe₃C-MC; (d) AFM image and corresponding thickness analysis of Fe₃C-MC; (e) EDS analysis of Fe₃C nanosheets in composite; (f) TEM image of Fe₃C-MC and corresponding EDS mapping images of C, N and Fe; (g) XRD patterns of MC, Fe₃C-MC-5, Fe₃C-MC-10, Fe₃C-MC-15; (h) Fe XRS high resolution peaks in Fe₃C-MC; (i) Nitrogen adsorption-desorption isotherms and pore size distributions of Fe₃C-MC

Further, Brunauer-Emmett-Teller (BET) analysis of Fe₃C-MC is illustrated in **Figure 3i**, demonstrating the isotherms of Fe₃C-MC displays closed hysteresis loop.⁴¹

The Fe₃C-MC-10 possesses a largest specific surface area of 686.9 m² g⁻¹ with pore volume of 6.52 cm³ g⁻¹. The detail isotherms of Fe₃C-MC with different ratios are presented in **Figure S13a**, and the pore size distribution curve of the Fe₃C-MC are shown in **Figure S13b**, demonstrating fine pores with diameters of ~10 nm and large pores from 30 to 80 nm. The huge specific surface area facilitates the dispersion of sulfur and the formation of electrochemical reaction interface with the electrolyte to increase the electrochemical capacity of the sulfur cathode. The hierarchical porous structure is very conducive to mitigating the problem of volume expansion during electrochemical redox. To investigate the performance of Li-S battery with the Fe₃C-MC as sulfur host, firstly the Fe₃C-MC was mixed with 80 wt. % sulfur through a typical molten method to prepare Fe₃C-MC/S composite. The SEM and TEM images of Fe₃C-MC/S composite are illustrated in **Figure 4**. In the SEM image, the squamae-like nanosheet structure of Fe₃C still can be seen (**Figure 4a**) although sulfur was mixed into the composite, indicating that sulfur was uniformly dispersed in the composite. In **Figure 4b**, it is more obvious that the fine sulfur particles are uniformly distributed on the squamae-like Fe₃C nanosheets. Thus, the mesoporous in Fe₃C-MC composite provided large space while the squamae-like nanosheets offered plenty of adsorption sites for sulfur species. Further, the typical TEM image of Fe₃C-MC/S and corresponding mapping images of C, N, Fe and S are illustrated in **Figure 4c** showing that all the elements were evenly distributed in the composite. The intensities of light elements C and N are a little weaker while the intensities of Fe and S are stronger. Especially, the strong S intensity indicated the sulfur is rich and uniformly dispersed in the composite. Generally, polar metal compounds (MO_x, MS_y etc., M=metal element) possess limited conductivity although they exhibit strong adsorption for LiPSs.^{24, 42-52} However, the ultra-high electrical conductivity is the primary condition

that must be satisfied for sulfur host for Li-S batteries. Recently, high-conductivity polar compounds (TiN,⁵³ Co₄N etc.¹⁶) as sulfur host with excellent performances have been reported. To assess the conductivity of the sulfur host prepared in the present study, firstly the electrical conductivity of MC and Fe₃C-MC were measured, as illustrated in **Table S6 (See Support Information)**. The MC displayed good conductivity of 0.223 S cm⁻¹. Remarkably, the Fe₃C-MC showed even better conductivity of 1.067 S cm⁻¹, indicating that the interconnected conductive network constructed by Fe₃C nanosheets is more conductive than MC. Further, the Nyquist plots of batteries with Fe₃C-MC and MC as sulfur hosts are obtained. The diameter of the semicircle at high frequencies reflects the charge transfer resistance (R_{CT}).⁷ Before cycling, the values of R_{CT} are estimated to be ~32 Ω and ~60 Ω for Fe₃C-MC and MC respectively, as shown in **Figure 4e**, indicating faster charge transfer capability of Fe₃C-MC than MC. The charge transfer resistances decreased to ~12 Ω , and ~32 Ω for Fe₃C-MC and MC respectively after 1000 cycles, as shown in **Figure 4f**, suggesting that the electrode materials are not fully infiltrated by electrolyte at the beginning. The battery with Fe₃C-MC as sulfur host exhibits smaller resistance values both before and after cycling owing to the extremely high electrical conductivity.

Except for the conductivity, strong adsorption ability to LiPSs is also important for sulfur host to block the “shuttle effect” of Li-S batteries. DFT calculation has predicted the strong adsorption ability of Fe₃C towards LiPSs.²⁹ To intuitively reveal the adsorption effects of sulfur host samples to LiPSs, Li₂S₆ was selected as the representative LiPSs.² The MC and Fe₃C-MC were added to the solution of Li₂S₆ in dioxolane (DOL)/dimethoxyethane (DME) solvent, as shown in **Figure 4d**. The original solution of Li₂S₆ was yellow, and the color of Li₂S₆ solution with MC became a little lighter but still is yellow, showing a limited adsorption capacity of MC. For the

Li_2S_6 solution with $\text{Fe}_3\text{C-MC}$, the excellent adsorption ability of the composite is obvious since the yellow Li_2S_6 solution turned into completely colorless. For the $\text{Fe}_3\text{C-MC}$ composite, by penetrating small radius element with low stoichiometric ratio into metal element, high-conductivity and strong-polarity were realized simultaneously. The C atoms filled in the spacing of Fe altered the local density of the electronic cloud of Fe and thereby enhanced the polarity, but did not block the electron conduction since the radius of C atom is small enough. According to the Raman analyses of Li_2S_6 solution and the blank one (**Figure 4g**), the Li_2S_6 solution displays two additional peaks at 218 and 478 cm^{-1} , corresponding to the characteristic peaks of Li_2S_6 . In the Raman spectrum of Li_2S_6 solution with MC addition, the two peaks at 218 and 478 cm^{-1} are weaker but still existed, indicating the limited adsorption ability of MC towards Li_2S_6 . With $\text{Fe}_3\text{C-MC}$ adding into Li_2S_6 solution, the characteristic peaks of Li_2S_6 in the Raman spectrum completely disappeared, suggesting that the $\text{Fe}_3\text{C-MC}$ composite possesses superior adsorption ability and capacity for Li_2S_6 and thereby no Li_2S_6 species remained in the solution.¹⁶ The optical images of the original electrodes and separators and those in MC/S and $\text{Fe}_3\text{C-MC/S}$ batteries after cycling are shown in **Figure 4h**. Compared to the original electrodes and separators, in the MC/S battery, both electrode and separator adsorbed residual yellow LiPSs. However, in the $\text{Fe}_3\text{C-MC/S}$ battery, no obvious yellow LiPSs can be observed, indicating the fast conversion of LiPSs on $\text{Fe}_3\text{C-MC}$ composite.

Figure 4. (a) SEM image of $\text{Fe}_3\text{C-MC/S}$; (b) TEM image of $\text{Fe}_3\text{C-MC/S}$; (c) Typical TEM image of $\text{Fe}_3\text{C-MC/S}$ and corresponding mapping images of C, N, Fe and S; (d) Optical photos of different samples immersed in a $\text{Li}_2\text{S}_6/\text{DOL}/\text{DME}$ solution after 12 h; (e) Nyquist plots of batteries with MC and $\text{Fe}_3\text{C-MC}$ as sulfur hosts before cycling; (f) Nyquist plots of batteries with MC and $\text{Fe}_3\text{C-MC}$ as sulfur hosts after 1000 cycles; (g) Raman spectra of a blank solution without Li_2S_6 , Li_2S_6 solution, Li_2S_6 solution with MC and $\text{Fe}_3\text{C-MC}$, respectively; (h) Optical photos of original electrodes and separators and those in MC/S and $\text{Fe}_3\text{C-MC/S}$ batteries after cycling

Further, the electrochemical performances of the batteries were investigated in detail. CV curves of the batteries using MC and $\text{Fe}_3\text{C-MC}$ as sulfur hosts are shown in **Figure 5a**. Two obvious CV curves can be seen in all the batteries, corresponding to the reduction of S_8 to high-order LiPSs (Li_2S_x , $4 \leq x < 8$) and then to low-order

Li₂S₂/Li₂S. Meanwhile, the anodic peaks indicate the oxidation of Li₂S₂/Li₂S to S₈. The working potentials of MC and Fe₃C-MC batteries are 2.082 and 2.106 V while the charging potentials are 2.287 and 2.208 V, respectively. Compared with MC battery, the cathodic peaks of Fe₃C-MC battery shift to a higher potential while the anode peak shift to a lower potential, indicating a lower over-potential of the Fe₃C-MC battery. Under a current density of 0.5 A g⁻¹, the over-potentials of MC and Fe₃C-MC batteries are 267 and 165 mV respectively, revealing the redox reaction kinetics and the reversibility of Fe₃C-MC batteries are significantly improved.⁵⁴ Moreover, the charge/discharge curves of MC and Fe₃C-MC batteries at 0.1 C and 0.5 C in **Figure S14** also show that the over-potential of Fe₃C-MC battery is much lower, indicating a faster redox reaction during the charge/discharge processes. The enhanced redox reaction kinetics contributes to fast transformation of LiPSs, which is ascribed to the activation of Fe₃C to S-S bonds according to the DFT calculation and the N doping in the composite.⁵⁵⁻⁵⁷ The CV curves of Fe₃C-MC battery show almost overlapped shapes within 5 cycles, as shown in **Figure 5b**, demonstrating excellent cycling stability.

The capacity and stability of MC, Fe₃C and Fe₃C-MC as sulfur hosts for Li-S batteries were investigated. Firstly, the rate capacities were evaluated as shown in **Figure 5c**. The battery with Fe₃C-MC as sulfur host exhibit a high initial capacity of 1530 mA h g⁻¹ and superior reversible rate capacities of 1423, 1268, 1130, 1034, 916 and 727 mA h g⁻¹ at current densities of 0.1C, 0.2C, 0.5C, 1C, 2C and 5C respectively, significantly better than that for the battery with MC as sulfur host (1241, 1089, 867, 658, 441 and 282 mA h g⁻¹ at current densities of 0.1C, 0.2C, 0.5C, 1C, 2C and 5C respectively). **Figure 5d** shows the charge/discharge curves of the battery with Fe₃C-MC host at different current densities, showing two well-defined plateaus and high coulombic efficiency. **Figure 5e** shows the cycling stability of the

batteries at a current density of 0.5C. It is evident that the battery with Fe₃C-MC host displays much better cycling stability than that with MC and Fe₃C hosts. The battery with MC host exhibits a capacity of 1215 mA h g⁻¹ at the first cycle and remains only 468 mA h g⁻¹ after 600 cycles, and the one with Fe₃C host exhibits a capacity of 1478 mA h g⁻¹ at the first cycle and remains 642 mA h g⁻¹ after 800 cycles. Remarkably, the battery with Fe₃C-MC host displays an initial capacity of 1465 mA h g⁻¹ and preserves 920 mA h g⁻¹ after 1000 cycles at 0.5C, showing only 0.037% decay for per cycle (performances for different ratios of Fe₃C-MC see **Figure S21**). The superior performance of Fe₃C-MC host for Li-S battery is one of the best among all the reported batteries as far as we know (**See Support Information Table S7**). The coulombic efficiency of Fe₃C-MC battery is also close to 100%. The superior performance is ascribed to the excellent conductivity, strong adsorption to LiPSs and superior catalytic activity of Fe₃C nanosheets, which facilitate the anchoring and fast conversion of LiPSs.

Figure 5. (a) CV curves of MC and Fe₃C-MC batteries; (b) CV curves of Fe₃C-MC battery from 1st to 5th cycle; (c) Rate performances at current densities of 0.1C, 0.2C, 0.5C, 1C, 2C and 5C with MC and Fe₃C-MC as sulfur hosts; (d) Charge/discharge curves of the battery with Fe₃C-MC as sulfur host at different rates within a potential window of 1.7-2.8 V vs. Li⁺/Li; (e) Cycling stability of MC, Fe₃C and Fe₃C-MC batteries at 0.5 C for 1000 cycles

In addition, the performances of Fe₃C-MC batteries with different sulfur contents (sulfur content: 80, 90 and 95 wt.%) were investigated. **Figure S15-16** present the optical images of Fe₃C-MC, sulfur and the mixture (Fe₃C-MC/S), indicating the

presence of much mesoporous structure in the Fe₃C-MC composite for sulfur loading. TGA analysis in **Figure S18** shows that almost all of the sulfur is retained in the Fe₃C-MC/S samples after melting diffusion treatment. The cycling stability of the batteries with Fe₃C-MC/80S, Fe₃C-MC/90S and Fe₃C-MC/95S were tested, as shown in **Figure S19**, which remained 1120, 864 and 721 mA h g⁻¹ after 200 cycles at 1C, respectively. The excellent performance indicates that the ultra-thin conductive and polar Fe₃C nanosheets are able to immobilize the LiPSs and to improve redox reaction rate even at ultra-high sulfur content. Moreover, the long-term stability of Fe₃C-MC batteries with different sulfur loading were investigated, as shown in **Figure 9**. At current density of 0.5C, capacities of 1224, 1102, 989, 906, 814 and 699 mA h g⁻¹ can be retained with sulfur loading of 1.5, 3.0, 4.5, 6.0, 7.5 and 9.0 mg cm⁻² after 100 cycles, which means specific area capacities of 1.836, 3.306, 4.451, 5.436, 6.105 and 6.291 mAh cm⁻², respectively. In addition, the cross-sectional SEM images of the electrodes with different sulfur loading and the electrodes after 200 cycles are shown in **Figure S22** and **Figure S23**, which show that the thickness of electrodes after cycling were only slightly increased, indicating porous structure effectively alleviate the volume expansion of S during charge-discharge process. The results indicates that the cost-effective production of Fe₃C-MC composite from biomass waste exhibits excellent performance as a sulfur host for Li-S battery not only at high sulfur content but also at high sulfur loading conditions, which provides a promising and novel strategy for commercial applications of Li-S batteries.

Figure 6. (a) Cycling stability of Fe₃C-MC battery at 0.5C with sulfur loading of 1.5, 3.0, 4.5, 6.0, 7.5 and 9.0 mg cm⁻²; (b) Specific capacities and (c) specific area capacities of Fe₃C-MC host battery after 100 cycles with sulfur loading of 1.5, 3.0, 4.5, 6.0, 7.5 and 9.0 mg cm⁻²

CONCLUSIONS

In summary, based on DFT calculation, we designed and synthesized a Fe₃C-MC composite which is composed of mesoporous carbon and ultra-thin conductive squamae-like Fe₃C nanosheets, using biomass waste corncobs as basic carbon source and ferrous sulfate as iron source. The composite possesses large specific surface area of 686.9 m² g⁻¹ with pore volume of 6.52 cm³ g⁻¹ and high electrical conductivity of 1.067 S cm⁻¹. The squamae-like Fe₃C nanosheets were grown on the surface of mesoporous carbon with a thickness of only ~1 nm, on which strong adsorption and rapid conversion for LiPSs were realized simultaneously. The capturing-conversion of

LiPSs occurred on the active sites of Fe₃C simultaneously, which effectively prevented the outflow of LiPSs, leading to a low over-potential and a high reversible capacity for Li-S battery. By using this Fe₃C-MC composite as a sulfur host, the issues related to Li-S batteries like poor electrical conductivity, LiPSs shuttling and slow redox reaction are addressed almost simultaneously. As a result, the Fe₃C-MC cathode delivered a high initial capacity of 1530 mA h g⁻¹ under the current density of 0.1C, and also, superior reversible capacities of 1423, 1268, 1130, 1034, 916 and 727 mA h g⁻¹ at current densities of 0.1C, 0.2C, 0.5C, 1C, 2C and 5C, respectively. After 1000 cycles at 0.5C, a capacity of 920 mA h g⁻¹ was still retained at a high sulfur content of 80 wt.% (1465 mA h g⁻¹ at the first cycle), resulting in a very low capacity decay of 0.037% per cycle. Moreover, at a super high sulfur loading of 9.0 mg cm⁻², a capacity of 699 mA h g⁻¹ is still preserved after 100 cycles at 0.5C, which means a specific area capacity of 6.291 mA h cm⁻². Such a sulfur host is expected to promote the practical use of Li-S batteries because of the low cost of sources, large-scale process and promising performances. The preparation approach of the sulfur host also suggests a new way to produce multifunctional sulfur host to improve the performance of energy storage device.

EXPERIMENTAL SECTION

DFT calculation for the LiPSs adsorption: Calculations were performed using DFT implemented in the Vienna Ab initio Simulation Package (VASP).²¹ The projected augmented wave potential²² and generalized functional²³ were used to describe the electron-ion interaction and exchange-correlation energy, respectively. The plane-wave cutoff energy was set to be 300 eV. The periodically repeated unit cells were 13.50 Å×13.62 Å with 5 atomic layers. The k-point used in sampling for

orthogonal Fe_3C (220), (-220) and (002) planes were $8 \times 8 \times 1$ grids. A vacuum distance larger than $10 \text{ \AA}$ was used to remove the interaction between successive slabs. In structural optimization, the lower half of the slabs were fixed to their bulk truncated positions allowing all other atoms to fully relax until the force converged to $0.01 \text{ eV/\AA}$.²⁴ The adsorption energy (E_{ads}) for Li_2S_6 on the Fe_3C surface was defined as $E_{\text{ads}} = E_{\text{tot}} - E_{\text{LS}} - E_{\text{sur}}$, where E_{tot} is the total energy of the adsorbed system, E_{LS} is the energy of Li_2S_6 in vacuum and E_{sur} is the energy of the optimized clean Fe_3C surface slab.²⁵ The specific surface energies are calculated with the formula: $E_{\text{sur}} = (E_{\text{slab}} - n E_{\text{bulk}})/2A$, where E_{slab} is the energy of the slab, E_{bulk} is the energy of a unit cell, n is the number of unit cells and A is the area of the surface.

Synthesis of Fe_3C -MC: Firstly, biomass waste, corncob, was pretreated using the method reported previously.⁷ Typically, corncob was ball-milled to fine powders, and then pretreated with concentrated sulfuric acid at $60 \text{ }^\circ\text{C}$ for 2 hours until yellow powders turned into black. After being thoroughly washed and dried, the pretreated corncob was mixed with ferrous sulfate homogeneously. Finally, the mixture was annealed at $800 \text{ }^\circ\text{C}$ for 2 hours in a quartz tube furnace under N_2 atmosphere and then Fe_3C -MC composite was obtained. The resultant Fe_3C -MC composites with different ferrous sulfate mass ratios (Fe_3C -MC- x , x is the mass ratios of ferrous sulfate) were illustrated in **Support Information** (BET: **Figure S10**; ICP-AES and EDS: **Table S5**). For comparison, mesoporous carbon (MC) was also prepared by annealing the pretreated corncob without addition of ferrous sulfate.

Materials characterization: The prepared carbon materials were examined using scanning electron microscopy (SEM, Hitachi S-4800, Japan) and high resolution transmission electron microscopy (HRTEM, JEM-2100F, Japan) equipped with energy-dispersive X-ray spectrometer (EDS). High-angle annular dark-field

scanning transmission electron microscopy (HAADF-STEM) was also used to investigate the element distribution. X-ray diffraction (XRD) patterns were obtained using the X-ray diffractometer (Philips PC-APD) with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) operating at 40 kV, 60 mA. X-ray photoelectron spectroscopy (XPS) analysis was performed on the ESCALAB250 XPS spectrometer with a Mg K α X-ray source (1350 eV). Fourier transform infrared spectroscopy (FTIR) analysis was carried out using a Fourier transform infrared spectrometer (FTIR-5300). Brunauer Emmett Teller (BET) specific surface areas were calculated based on the nitrogen physical adsorption (Beckman Coulter SA-3100, USA). Atomic force microscopy (AFM) analysis was conducted using a NT-MDT Ntegra Solaris instrument. The content of Fe in the composite was measured by inductively coupled plasma atomic emission spectrometry (ICP-AES). The electrical conductivity of the electrodes was measured by a standard four point probe resistivity measurement system (RTS-9, Guangzhou, China). Thermogravimetric analysis (TGA) was conducted on a simultaneous DSC-TGA analyzer (NETZSCH-409PC) from 20 °C to 900 °C in air atmosphere to determine the content of Fe₃C in the composite, while performed from 20 °C to 500 °C with a heating rate of 5 °C min⁻¹ in the N₂ atmosphere to evaluate the sulfur content of each electrode.

Electrochemical measurements of lithium sulfur batteries: Electrochemical experiments were performed using 2025 type coin cells. The working electrode was prepared by adding sulfur cathode material into the MC or Fe₃C-MC active material film to form MC/S or Fe₃C-MC/S electrode. The electrolyte was 0.5 M lithium bis-trifluoromethanesulfonylimide (LiTFSI) dissolved in a mixed solvent of 1, 3-dioxolane and 1, 2-dimethoxyethane (DOL/DME, 1:1, v/v). The sulfur loading are range from 1.5 to 9.0 mg cm⁻², and the amount of the electrolyte used in assembling

each cell was $\sim 6 \mu\text{L}/\text{mgS}$. Galvanostatic charge-discharge measurements were performed at room temperature in a potential range of 1.7-2.8 V (vs. Li^+/Li) at 0.1 C, 0.2 C, 0.5 C, 1 C, 2 C, and 5 C (1 C = 1672 mA g^{-1}) with a battery tester (LAND CT-2001A, China). Cyclic voltammetry (CV) was performed with an electrochemical workstation (CHI 660C) between 1.7 and 2.8 V at a scan rate of 0.1 mV s^{-1} . Electrochemical impedance spectroscopy (EIS) analysis was conducted using the same equipment from 10^5 Hz to 10^{-2} Hz .

ASSOCIATED CONTENT

Notes

The authors declare no competing financial interest.

ACKNOWLEDGEMENTS

This work is supported by National Natural Science Foundation of China (Grant No. 51672075, 51704106, 51772092). National Supercomputing Center in CHANGSHA is acknowledged for allowing the use of computational resources including TIANHE-1. Professor Xiaorong Zhou from The University of Manchester, UK is appreciated for polishing the language during the preparation of this manuscript.

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TOC GRAPHIC:

Ultra-thin Fe_3C nanosheets@mesoporous carbon ($\text{Fe}_3\text{C-MC}$) composite is prepared for lithium sulfur batteries based on biomass waste. The $\text{Fe}_3\text{C-MC}$ composite possesses high conductivity, large specific surface area ($686.9 \text{ m}^2 \text{ g}^{-1}$), strong adsorption ability and excellent catalytic activity to lithium polysulfides, which addresses the major issues of lithium sulfur batteries in a low-cost and large-scale way.