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From Double-Helix Structured Seaweed to S-Doped Carbon Aerogel with Ultra-high Surface Area for Energy Storage

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ABSTRACT: A sustainable biomass conversion and green strategy, using red algae derived carrageenan-Fe hydrogel as precursor, is developed to fabricate the 3D hierarchical macro-meso-microporous sulfur-doped carbon aerogel (HPSCA) with tunable nanopores and ultra-high surface area up to $4037.0 \text{ m}^2 \text{ g}^{-1}$. The molecular-level dispersions of Fe^{3+} ions in carrageenan contribute to the ultra-high surface area of HPSCA after carbonization, acid washing and activation process. The attracting structure features make it an applicable candidate material in lithium-sulfur (Li-S) batteries and double-layer supercapacitors (SCs). The highly developed porous structure of HPSCA can accommodate more sulfur (up to 80 wt%) to produce high-energy composite cathode with high specific capacity, cycle stability and long cycle life (400 cycles) in Li-S batteries. Meanwhile, HPSCA can present high specific capacitance of 335 and 217 F g^{-1} (1 A g^{-1}) in the aqueous and organic electrolyte. Superior rate performance also can be obtained, and high capacitance of 204 F g^{-1} at 100 A g^{-1} and 173 F g^{-1} at 50 A g^{-1} in aqueous and organic electrolytes, respectively, is retained.

Graphical abstract

A sustainable biomass conversion strategy is developed to fabricate hierarchical porous sulfur-doped carbon aerogel with ultra-high surface area up to $4037.0 \text{ m}^2 \text{ g}^{-1}$ for energy storage applications.

Keywords: Ultra-high surface area; Carbon aerogel; Biomass; Lithium-sulfur battery; Supercapacitor.

1. Introduction

Exploration of novel electrochemical storage/conversion devices has been driven by the demand of electric transportation and grid storage, leading to materials and system design innovations. For next-generation energy storage systems, supercapacitors (SCs), featuring high power density

and excellent cycle stability, has drawn extensive attention, while it also show some fatal drawbacks (e.g. low energy density most less than 6 Wh kg⁻¹) that hinder industrial applications [1,2]. In contrast, lithium-sulfur (Li-S) battery presents dominating advantages on energy density, up to 2567 Wh kg⁻¹, but demonstrates a poor cycle and power capability due to the well-known shuttle problems, in addition to the insulating nature of element sulfur and the substantial volume expansion (up to 80%) of sulfur cathode [3]. Building nanoporous carbon materials with high surface area is a conventional strategy to address all above problems both in Li-S batteries and SCs [4,5]. The surface area of carbon materials not only defines the charge storage performance at the electrode/electrolyte interface for SCs, but also decides the capability in accommodating sulfur for Li-S batteries. Meanwhile, producing hierarchical macro-meso-microporous structure is another major prerequisite to achieve high electrochemical performance both in Li-S batteries and SCs, for which the macropore can minimize the diffusing distance of electrolyte into nanopores, while mesopore and large micropore are expected to produce high capacitive energy storage or strongly prohibit the dissolution of polysulfide [6-9]. Therefore, seeking exceptionally high surface area with hierarchical nanopores has been a long-pursued goal of functional carbon materials for energy storage application.

Many strategies have been reported to fabricate porous carbons with high surface area, such as chemical activation, templating method and carbonization of various precursors including conjugated microporous polymers, crosslinked or conjugated polymers and metal-organic frameworks, while it is still technically difficult and there are rare reports to synthesis ultrahigh-surface-area carbon materials, for example above 3500 m² g⁻¹, even after chemical activation (KOH) [10-15]. Meanwhile, there are still cost and materials consistency (large-scale synthesis) concerns for the widely applications of nanoporous carbon materials in Li-S batteries and SCs

because of their complicated synthesis procedure involving templates, toxic and extensive chemicals and so on [10,11,15]. For practical use, the facile strategy for mass production of carbon materials with ultrahigh surface area, hierarchical porous structure and fast electron transport is thus highly desired.

The abundant and non-toxic biomass resources have been widely investigated as precursor to produce nanoporous biochar as a green and low-cost strategy [16-20]. Recently, various biomass, such as bamboo, alginate, D-glucosamine, natural silk, and gelatin, has been used to fabricate porous carbon materials for Li-S batteries and SCs [21-24]. In general, the carbonation and following chemical activation is the most used technique to synthesize porous biochar. Nevertheless, the structure features of biochar is mostly depended on the kind of biomass, and generated nanopores is basically disordered. Most importantly, the surface area reported so far is much low (typically below $2000 \text{ m}^2 \text{ g}^{-1}$) for energy storage applications.

Herein, we propose a new approach, using carrageenan-Fe hydrogel as precursor, to fabricate 3D hierarchical inter-connective macro-meso-microporous S-doped carbon aerogel (HPSCA) with ultrahigh surface area. The organic and inorganic component in carrageenan-Fe hydrogel play different roles in the fabrication of HPSCA, for which the carrageenan can produce conductive carbon framework, while the binding Fe^{3+} act as pore forming agents to generate hierarchical pores. Moreover, pyrolyzing the sulfate group riched carrageenan can easily introduce the sulfur (S) heteroatoms into the carbon lattice, which can enhanced the capacitive effect on the surface of carbon materials. The unique structure features in HPSCA, including ultra-high surface area (up to $4037.0 \text{ m}^2 \text{ g}^{-1}$) and S-doping are beneficial for their applications in Li-S batteries and SCs. The HPSCA as matrix materials for sulfur, high specific capacity, high sulfur-loading (up to 80%), excellent cycle stability and long cycle life (up to 400 cycles) are

presented in Li-S batteries. Meanwhile as electrode materials for SCs, it represents superior capacitive behavior of 335 and 217 F g⁻¹ at 1 A g⁻¹ in the aqueous and organic electrolyte, respectively, and superior rate performance (204 F g⁻¹ at 100 A g⁻¹ and 173 F g⁻¹ at 50 A g⁻¹ in aqueous and organic electrolytes, respectively).

2. Experimental section

2.1 Preparation of three-dimensional hierarchical porous sulfur-doped carbon aerogel (HPSCA).

The 2 wt% ι-carrageenan solution was prepared at 80 °C for 1 h, and then, this solution was dropped in a 0.1 M FeCl₃·6H₂O aqueous solution at room temperature and stirred forming carrageenan-Fe hydrogel. The carrageenan-Fe hydrogel was washed and freeze-dried, and then, the freeze-dried hydrogel was dehydrated through the freeze-drying process to obtain carrageenan-Fe aerogel. The aerogel was pyrolyzed at different temperatures (T=300, 400, 500, and 600 °C) at the heating rate of 5 °C min⁻¹ for 1 h in Ar atmosphere and then the obtained samples (SCA-T) were soaked into a 1 M hydrochloric acid solution for 10 h to remove the iron sulfide nanoparticles and leave the mesopores in the carbon aerogels. The obtained samples were mixed with potassium hydroxide with a weight ratio of KOH to samples at 4:1. The obtained mixtures were heated at 800 °C for 1 h in a Ar atmosphere with a heating rate of 5 °C min⁻¹. The obtained samples were washed in 1 M hydrochloric acid and deionized water to neutral. The obtained samples were HPSCA-300, HPSCA-400, HPSCA-500, and HPSCA-600.

2.2 Characterizations.

The morphologies of the samples were characterized by field emission scanning electron microscopy (FESEM; SU8020) and transmission electron microscopy (TEM) and high-resolution TEM (FEI Tecnai G20). The specific surface area was calculated by the Brunauer-

Emmett-Teller (BET) method from the data in a relative pressure (P/P_0) range between 0.05 and 0.25, pore structures were characterized using N_2 adsorption desorption at 77 K (3Flex). The chemical composition was investigated by X-ray photoelectron spectroscopy (XPS) using an ESCALab250 electron spectrometer (Thermo Scientific Corporation) with mono-chromatic 150 W Al $K\alpha$ radiation. The phase structures were characterized with X-ray diffraction (XRD, DX2700, China) operating with Cu $K\alpha$ radiation ($\lambda=1.5418 \text{ \AA}$) at a scan rate (2θ) of 1° min^{-1} with the accelerating voltage of 40 kV. Thermogravimetric analysis (TGA) measurement was carried out on an EXSTAR TG/DTA 6300 instrument (Seiko Instruments, Japan) in air. Raman spectroscopy were obtained on a Renishaw 1000 Raman spectrometer with the 514.5 nm excitation line of an Ar ion laser.

2.3 Electrochemical Measurements.

The S/HPSCA-T composite with 70 wt% and 80 wt% sulfur loading were prepared by firstly grinding sulfur with the obtained HPSCA-T, and then the homogenous mixture was transferred into a stainless autoclave and sealed with a swagelok structured cover. The autoclave was treated at 155°C for 10 h. The S/HPSCA-T composite was mixed with carbon black and PVDF in a weight ratio of 7:2:1 in NMP as a dispersant. The slurry was casted on the Al foil and dried for 10 h at 55°C under vacuum. 2016 type coin cells were assembled in an Ar-filled glove box. Lithium metal was used as the reference electrode and counter electrode and the separator was monolayer polypropylene (PP) Celgard 2500. The electrolyte was composed of lithium bis(trifluoromethanesulfonyl)imide (1 M, LiTFSI) salt solution in dimethoxyethane (DME) and 1,3-dioxolane (DOL) (1:1, v/v) with lithium nitrate (0.25 M, LiNO_3) as an electrolyte additive. The electrochemical performances were tested in a voltage window of 1.7–2.8 V vs Li^+/Li using

a cell testing instrument (LAND CT2001A). The specific capacity was calculated on the basis of the sulfur mass.

Two-electrode symmetric supercapacitor systems were used to measure the performance of all the samples as SCs electrodes with 6.0 M KOH solution and 1 M TEA BF₄/AN as the electrolyte. The two-electrode symmetric supercapacitor systems used 1 M TEA BF₄/AN as the electrolyte were assembled in an Ar-filled glove box. The electrodes were prepared by mixing 85 wt% active material (HPSCA-T), 10 wt% carbon black, and 5 wt% PVDF and dried at 80 °C for 5 h under vacuum. The CVs were carried out on a CHI 760 E electrochemical workstation at room temperature and the galvanostatic charge-discharge measurements were made using a cell testing instrument (LAND CT2001A) over the potential range from 0 to 1 V in 6.0 M KOH solution and 0 to 2.5 V in 1 M TEA BF₄/AN. The electrochemical impedance spectroscopy (EIS) test was carried out over a frequency range from 0.01 Hz to 10 kHz.

In the two-electrode system, the specific capacitance (C_s) of the single electrode was calculated according to the equation:

$$C_s = \frac{2I \times \Delta t}{m \times \Delta V}$$

in which I (A) is the discharge current, Δt (s) is the discharge time, m (g) is the mass of active materials on one electrode, and ΔV (V) is the potential window.

2.4 Computational Details.

The binding energy (E_{bind}) of TEA⁺ and Li₂S₂ on the carbon substrate is defined as:

$$E_{\text{bind}} = E_{\text{sub}} + E_S - E_{\text{sub+S}}$$

where E_{sub} , E_S and $E_{\text{sub+S}}$ represent the ground-state energies of the carbon substrate, Li₂S₂ and carbon- Li₂S₂ composites. TEA⁺ is similarly to Li₂S₂.

3. Results and discussion

3.1 Synthesis of hierarchical porous S-doped carbon aerogel.

Scheme 1. The synthesis process of HPSCA.

Carrageenan, extracted from red algae (seaweed) and composed of alternating disaccharide repeating units of 3-linked β -D-galactopyranose and 4-linked α -D-galactopyranose or 4-linked 3,6-anhydro- α -D-galactopyranose, is environment friendly and low-cost [25-26]. Upon cooling and following the addition of metal ions, it can produce a double helix structure hydrogel with molecular-level dispersed metal ions (Scheme 1) [27-29]. The Fe^{3+} promote the formation of “double helix” structures to produce carrageenan-Fe hydrogel, and the weight percentage of Fe^{3+} in carrageenan-Fe aerogel can reach up to 18.7% (Fig. S1), which is high enough to produce massive nanopores. The Fe^{3+} ions are capable of forming intra-molecular bridges with sulfate groups of ι -carrageenan. Through freeze drying and pyrolyzed at different temperatures ($T=300$, 400, 500, and 600 $^{\circ}\text{C}$), the Fe^{3+} -sulfate group structures ions are converted to iron sulfides NPs at approximate 400 $^{\circ}\text{C}$ (Fig. S2) and stably anchored in a highly dispersed state, which can act as

templates for generating mesopores. It should be noted no iron or iron oxides are detected in the XRD patterns, indicating that the iron ions are preferentially converted into sulfides in Ar atmosphere [19,30]. The sulfate group of carrageenan can give rise to the S-doping in the carbon framework [31]. The obtained samples were S-doped carbon aerogel contained with iron sulfides (SCA-T). After acid washing, the iron sulfides NPs can be removed to generate mesopores in the aerogels. Finally, the potassium hydroxide activating process was carried out at 800 °C in Ar atmosphere to produce HPSCA-T.

3.2 Characterizations of HPSCA-T.

Fig. 1. (a-c) SEM image HPSCA-400 and the corresponding EDS mappings for C, O, S elements. TEM images of (d) SCA-400 and (e) HPSCA-400. (f) HRTEM image of HPSCA-400.

The scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were first used to characterize the morphology of the samples (Fig. 1). The HPSCA-400 exhibits a large amount of honeycomb-like macropores with the cores diameter of about 2-5 μm and thin walls less than 100 nm (Fig. 1a). By zooming into inside wall of macropores, highly developed mesopores with interconnected worm-like structure can be observed (Fig. 1b), which can act as

electrolyte reservoirs to shorten the diffusion distances of ions. The SEM-energy dispersive X-ray spectroscopy (EDS) elemental mappings used to analyze the elemental compositions of HPSCA-400, indicates that the C, O, and S elements are homogeneously distributed in the HPSCA-400 (Fig. 1c).

The hierarchical nanoporous structure can be more clearly revealed by the TEM images. As shown in Fig. 1 and Fig. S3, no iron sulfide NPs (Fig. S4a) are generated for SCA-300, while large amounts of iron sulfide NPs can be observed for SCA-400, SCA-500, and SCA-600, for which the size and content of iron sulfide NPs increase with enhanced annealing temperature (Fig. 1d and S4b,c), in consistent with the results of XRD patterns in Fig. S2. After washing by acid and chemical activation to completely remove the Fe-based salts, developed porous structure is obtained for the HPSCA samples, and the size of mesopores is highly depended on the particle size of NPs (Fig. 1e and S4d,e). For HPSCA-400, the high-resolution TEM (HRTEM) image are also given, and the existence of abundant micropores and amorphous carbon structure can be observed, endowing more electrochemical activity sites for energy storage (Fig. 1f and S4f).

The specific surface areas and detailed pore size distributions of HPSCA-T were measured through the Bru-nauer-Emmett-Teller (BET) method and Barret-Joyner-Halenda (BJH) model. The N₂ adsorption-desorption isotherms of HPSCA-400, HPSCA-500, and HPSCA-600 show the typical type IV adsorption isotherm, while the HPSCA-300 shows an isotherm of type-I, confirming that mesopores in HPSCA are mainly generated from the removing of iron sulfide NPs (Fig. 2a) [32]. The BET specific surface area (S_{BET}) of HPSCA-300, HPSCA-400, HPSCA-500, and HPSCA-600 are 3058.8, 4037.0, 3578.9, and 2988.4 m² g⁻¹, and the corresponding total pore volume are 1.51, 2.62, 2.40, and 1.75 cm³ g⁻¹, respectively. The corresponding pore size

distributions of HPSCA-T calculated from the desorption branch are given in Fig. 2b. As presented, hierarchical macro-meso-micro porous structure is obtained for HPSCA samples. In contrast to microporous HPSCA-300, HPSCA-400 shows a predominant pore size distribution between 1.0-4.0 nm. Moreover, the HPSCA-400, 500 and 600 contain large mesopores with sizes between 5-20 nm. The microporous structure of HPSCA-300 can be attributed to the excluding of Fe-based of salts, while Fe-based salts can be transformed to iron sulfide to produce larger mesopores after removing in HPSCA-400, 500 and 600.

Fig. 2. (a) Nitrogen adsorption–desorption isotherm and (b) the corresponding pore size distribution curve for HPSCA-T. XPS spectra of HPSCA-400, (c) full survey scan spectrum, (d) S 2p spectrum.

The details of the pore structures of HPSCA-T are shown in Table 1. It is clear that the different surface area of HPSCA-T is mainly result from the micropores. For HPSCA-400, there are still massive iron ions that are not transformed into iron sulfides, and during acid washing

and activation process, the molecular-level dispersed Fe-based salts can help to produce massive micropores. In contrast, more and larger iron sulfides nanoparticles can be generated under higher pretreated temperature of 500 and 600 °C, supporting by the TEM images in Fig. S4. Accordingly, such high specific surface area may have contributions from the synergistic effect of following: 1) the removing of highly dispersed metal sulfides NPs and other Fe-based salts, 2) the synergistic effect of the activation from the potassium hydroxide, 3) carrageenan macromolecule with abundant oxygen- and sulfur-containing groups (–OH, –COOH, and –SO₄H) can generate H₂O, CO, and SO₂ during thermal decomposition to generate porous structure, and this can be confirmed by the massive weight loss in Fig. S3 [30].

Table 1. Characteristics of specific surface area (m² g^{−1}) and pore volume (cm³ g^{−1}) for HPSCA-T.

Item	S _{BET} [§]	S _{mi} [§]	S _{ex} [§]	Pore volume
HPSCA-300	3058.8	2293	764	1.51
HPSCA-400	4037.0	2422	1615	2.62
HPSCA-500	3578.9	2075	1503	2.40
HPSCA-600	2988.4	1195	1793	1.75

[§]SBET is the BET surface area, S_{mi} is the micropore surface area, S_{ex} is the external surface area.

The X-ray photoelectron spectroscopy (XPS) measurements were performed to investigate the chemical environments of the S, C, and O atoms in the HPSCA-400. The XPS survey spectrum show the peaks at 163.6, 284.5, and 532.8 eV corresponding to the characteristic peaks of S 2p, C 1s, and O 1s, respectively (Fig. 2c). For the S 2p spectrum in Fig. 2d, two peaks located at 163.6 and 164.7 eV are assigned to the C–S bond, and the peaks located at 167.8 and 169 eV indicate the presence of oxidized sulfur species SO_x [33,34]. The S doping content for HPSCA-

400 is determined to be about 0.83 at% by XPS. The C 1s and O 1s spectrum indicate the presence of residual oxygen-containing groups bonded with C atoms in the sample (Fig. S5). The synthesized HPSCA-T show disordered structure and low graphitization degree through the X-ray diffraction (XRD) pattern (Fig. S6), which has been illustrated by the HRTEM above. Moreover, the increased intensity ratios (peak height ratios) of D-band to G-band from 0.768 to 0.845 in Raman spectroscopy (Fig. S7) indicates that the activation used KOH generates extrinsic defective structure on the carbon framework, which may help to enhance the capacitive effect [35,36].

3.3 Energy storage application of HPSCA-T.

Fig. 3. (a) The CV curves of S/HPSCA-400 at a scan rate of 0.1 mV s⁻¹ in the voltage range of 1.7–2.8 V versus Li⁺/Li. (b) The galvanostatic voltage profiles of S/HPSCA-400 electrode at various rates. (c) The charge specific capacities of S/HPSCA-T at various rates. (d) The cyclic performance and Coulombic efficiency of S/HPSCA-T at 1 C rate. (e) Nyquist plot of S/HPSCA-T as Li-S batteries cathodes.

The HPSCA-T present hierarchical macro-meso-microporous structure with ultrahigh surface area, making it also an ideal matrix materials for sulfur cathode in Li-S batteries. The macropores can ensure the smooth transport of electrolyte ions throughout the whole materials, the mesopores can accommodate more sulfur, and the micropores can strongly adsorb polysulfides to prohibit their dissolution from the cathodes [37]. S/HPSCA-T cathodes materials were prepared via the conventional melt-diffusion method, and no characteristic peaks of sulfur can be detected in the composite even at a high sulfur content of 70 wt% (Fig. S8 and S9), indicating the well dispersion of sulfur in the carbon materials. To evaluate the electrochemical performance, the cyclic voltammetry (CV) curves of the S/HPSCA-400 at the scan rate of 0.1 mV s^{-1} are first given in Fig. 3a. In the cathodic scans, two reduction peaks appear at about 2.30 and 2.05 V, which correspond to the reduction of S_8 ring to high-order polysulfides and further to Li_2S_2 and/or Li_2S . In the following anodic scan, two oxidative peaks at about 2.34 and 2.38 V correspond to the conversion from Li_2S_2 and/or Li_2S to Li_2S_x ($4 \leq x < 8$) and then from Li_2S_x ($4 \leq x < 8$) to S_8 [38]. The peak current density and integrated area intensity of the initial three CV curves show no obvious change, indicating good reversibility of the S/HPSCA-400 cathode.

Fig. 3b shows the galvanostatic voltage profiles of S/HPSCA-400 electrode ($1\text{C}=1675 \text{ mA g}^{-1}$, mass is based on the sulfur). At 0.2 C, the galvanostatic discharge curve exhibits two typical potential plateau at approximately 2.35 and 2.1 V with initial discharge capacity of 1178 mAh g^{-1} , in consistent with the results of CV, and the potential plateau is well-retained even with increasing rate to 2C, suggesting its good kinetic process. It should be emphasized that the S/HPSCA-400 demonstrate a high initial coulombic efficiency of 94.2%, which is one of the deciding parameters for their practical applications. As shown in Fig. S10, through the melting method, element sulfur will diffuse into the mesopores, while it hardly can access into the

micropores of HPSCA. During the discharge process, the massive unoccupied micropores not only can strongly adsorb the generated polysulfide, but also can well accommodate the volume expansion to decrease the dissolution of sulfur species at the opening of nanopores, thus producing an ultra-high initial coulombic efficiency.

The excellent rate performance and cycle stability can be better illustrated by the cycle curves with variation of current rates in Fig. 3c. The charge specific capacities of S/HPSCA-400 are 1110, 950, 870, and 670 mAhg⁻¹ at 0.2, 0.5, 1, and 2 C, respectively. When the rate returns back to 0.2 C after 40 cycles, the discharge specific capacity is recovered to 1024 mAhg⁻¹. Similar to their applications in SCs, the S/HPSCA-400 shows more excellent rate performance and higher capacity than that of S/HPSCA-300, S/HPSCA-500 and S/HPSCA-600 due to the ultra-high surface area of HPSCA-400. The long cycle performance was also evaluated. As shown in Fig. 3d, a high reversible discharge capacity of 798 mAh g⁻¹ after 200 cycles can be obtained for S/HPSCA-400, showing obvious advantages over other samples, for which the specific capacities of S/HPSCA-300, S/HPSCA-500 and S/HPSCA-600 are 700, 695 and 605 mAh g⁻¹, respectively. To illustrate the mechanism of the excellent electrochemical performance of S/HPSCA-400, electrochemical impedance spectra (EIS) tests were conducted and the results are demonstrated in Fig. 3e (the fitted same equivalent circuit shown in Figure S11). All the samples consisted of one depressed semicircle at high frequencies and a straight line at low frequencies. The diameter of high frequencies semicircle refers to the charge transfer resistance of the interface between electrodes and electrolyte (R_{ct}), while the straight line is attributed to Warburg element (W), associated to the Li-ion diffusion in the electrodes [39]. The R_{ct} values of S/HPSCA-300, S/HPSCA-400, S/HPSCA-500, and S/HPSCA-600 electrodes are determined to be 348.1, 168.7, 213.8, and 268.3 Ω , respectively. It is obvious that the

S/HPSCA-400 present a lowest charge-transfer resistance, thus corresponding the best rate and cycle performance.

Fig. 4. The cycling performance and Coulombic efficiency of S/HPSCA-400 with 80 wt% S loading at a 1 C rate, ($1C=1675 \text{ mAh g}^{-1}$).

To further illustrate the advantages of ultra-highly porous HPSCA for its application in Li-S batteries, the S/HPSCA-400 sample with 80 wt% sulfur was also fabricated (Fig. S12). As shown in Fig. 4, stable and long cycle life up to 400 cycles still can be obtained with reversible capacity of 590 mAh g^{-1} , which shows obvious advantages over other carbon aerogel/S composite cathodes and even is among the best results reported for porous carbon/S cathodes at such high sulfur loading (Table S1).

The capacitive performances of HPSCA-T were evaluated using the aqueous (6.0 M KOH solution) and organic (1.0 M TEA BF_4/AN) electrolytes, respectively. The active material loading density of the electrode is about $1.8\text{-}2.1 \text{ mg cm}^{-2}$ and the thickness of the electrode presented by the SEM (Fig. S13) is about $60 \mu\text{m}$. The CV curves of all HPSCA-T electrodes in both electrolytes show uniform rectangular shape, indicating the properties of double layer electrochemical capacitor (Fig. S14 and S15) [40,41]. It is observed that the CV curve area of HPSCA-400 is larger than those of other electrodes at the same scan rate, indicating its higher

specific capacitance (Fig. 5a,b). All the HPSCA-T show symmetric galvanostatic charge-discharge curves in both aqueous and organic electrolytes, and the specific capacitances of HPSCA-400 calculated based the charge times are higher than those of other samples, being in accordance with CV results. (Fig. 5c,d).

Fig. 5. The CV curves of HPSCA-T in the electrolyte of (a) 6.0 M KOH solution, and (b) 1.0 M TEA BF₄/AN at a scan rate of 100 mV s⁻¹. The galvanostatic charge-discharge curves of HPSCA-T in the electrolyte of (c) 6.0 M KOH solution, and (d) 1.0 M TEA BF₄/AN at the current density of 1 A g⁻¹.

The rate performances of HPSCA-T electrodes in aqueous and organic electrolytes are shown in Fig. 6a,b. It is found that in aqueous electrolyte the HPSCA-400 electrode shows specially high capacitances of 335, 307, and 270 F g⁻¹ at 1, 2, and 5 A g⁻¹, respectively, which are much higher than those of other samples. Even at the current density of 100 A g⁻¹, high specific capacitance of 204 F g⁻¹ still can be obtained. It is worth noting that in organic electrolyte, HPSCA-400 also shows high specific capacity of 217 F g⁻¹ at 1 A g⁻¹ and 173 F g⁻¹ at 50 A g⁻¹.

Moreover, HPSCA-400 electrodes show high capacitance retention rates of 93.2% after 10000 cycles in aqueous electrolyte with an ultralow decay rate of 0.00068 % per cycle. Although the cycling stability is not so good in organic electrolyte, a high retention of 89.2 % after 5000 cycles still can be obtained (Fig. 6c,d). The EIS was used to further illustrate the excellent capacitive behaviour of HPSCA-T, which all the samples show small ions and charge transfer resistance in organic electrolyte (Fig. S16). Such excellent double-layer capacitance behavior of HPSCA-400 is among the best results in previously reported various carbon materials tested in two-electrode supercapacitor (Table S2). In addition, it should be emphasized that the 3D interconnected conductive network, enabling the smooth transport of electrolyte ions/molecular into the interior, also contribute to the high capacitance of HPSCA-400 [9,42].

Fig. 6. The specific capacitance of HPSCA-T at various current densities in the electrolyte of (a) 6.0 M KOH solution, and (b) 1.0 M TEA BF₄/AN. Capacitance retention ratio for HPSCA-400 at a charge-discharge current density of 5 A g⁻¹ (c) in 6.0 M KOH solution electrolyte for 10000 cycles, and (d) 1 M TEA BF₄/AN electrolyte for 5000 cycles.

3.4 Theoretical calculation and analysis.

Fig. 7. The S-doping process enhances the electrochemical performance can be demonstrated by DFT using Gaussian 09. Optimized configuration of Li_2S_2 adsorbed on (a) pristine graphene and (b) S-doped graphene. Optimized configuration of TEA^+ adsorbed on (c) pristine graphene and (d) S-doped graphene. Optimized configuration of BF_4^- adsorbed on (e) pristine graphene and (f) S-doped graphene.

For the HPSCA, the homogeneous doping of sulfur cannot be neglected, as which is expected to enhance the electrochemical performance in Li-S batteries and SCs. To investigate the effect of S-doping, the Gaussian 09 program based on hybrid density functional theory (DFT) were performed. All the calculations were carried out using B3LYP/6-31g (d,p) level of theory with all atoms fully relaxed. The single layer graphene or S-doped single layer graphene, and Li_2S_2 , TEA^+ , or BF_4^- molecule were used as the models. The most stable configuration after full

relaxation with Li_2S_2 , TEA^+ , or BF_4^- molecule along with binding energy are shown in Fig. 7. Increasing binding energy can be observed for both electrochemical systems. There is no specific bonding between Li_2S_2 and non-doped graphene, resulting in binding energy of 1.04 eV (Fig. 7a), while obvious increasing binding energy of 1.64 after S-doped graphene can be observed, (Fig. 7b), indicating the strong absorbability on S-doped graphene. Similarly, the increasing binding energy of TEA^+ and BF_4^- on graphene is also obtained after S-doping (Fig. 7c-f), resulting in improved chemisorption between electrolyte ions and active materials. Furthermore, the binding energy of S-O-doped graphene model with Li_2S_2 (1.23 eV) and TEA^+ (5.28 eV) are also higher those of non-doped graphene (Fig. S17). For SCs, the enhanced interactions between S- and S-O-doped carbon surface and electrolyte ions can help to enhance the electric double layer on the active materials surface [43]. Based on all the discussions above, it can be concluded that hierarchical porous HPSCA with ultra-high surface area and homogeneous sulfur doping is a perfect candidate material for energy storage systems, especially in Li-S batteries and SCs.

4. Conclusions

In summary, we develop a nature-inspired carrageenan-Fe hydrogel as ideal carbon precursor to fabricate highly porous carbon materials, for which molecular-level dispersion iron ions can transfer to well-dispersed iron sulfide NPs and other Fe-based salts after carbonation, and thus produce hierarchical macro-meso-microporous structure after removing all the impurities. The fabricated HPSCA-400 demonstrates ultrahigh surface area up to $4037.0 \text{ m}^2 \text{ g}^{-1}$, narrow pore size distribution (1.0-4.0 nm) and interconnected conductive network, and thus greatly enhanced electrochemical performance is obtained for Li-S batteries and SCs. This green and large-scale

strategy opens up a new route to fabricate ultra-highly porous biochar, and can accelerate practical application of high performance Li-S batteries and SCs.

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Appendix A. Supporting information

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

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