Biomass-Derived N-Doped Porous Carbon as Electrode Materials for Zn-Air Battery Powered Capacitive Deionization

Cuijiao Zhao,^{†,‡} Guoqiang Liu,^{†,‡} Na Sun,^{†,‡} Xian Zhang,^{†,‡} Guozhong Wang,[†] Yunxia Zhang,[†]
Haimin Zhang,^{*,†} and Huijun Zhao^{†,§}

[†] Key Laboratory of Materials Physics, Centre for Environmental and Energy Nanomaterials,
Anhui Key Laboratory of Nanomaterials and Nanotechnology, CAS Center for Excellence in
Nanoscience, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei 230031,
China

[‡] University of Science and Technology of China, Hefei 230026, China

[§] Centre for Clean Environment and Energy, Griffith University, Gold Coast Campus, QLD
4222, Australia

Corresponding Author

*Prof. Haimin Zhang. E-mail: zhanghm@issp.ac.cn

ABSTRACT: Capacitive deionization (CDI) has been a promising technique to obtain fresh water by electrosorption of charged ionic species in seawater/brackish water. Its performance is highly dependent on the physical and chemical properties of CDI electrode materials. Herein, N-doped porous carbon (NPC) with a N content of 1.66 at.% was fabricated using soybean shell as starting material by a facile pyrolysis approach with the assistance of KHCO_3 in N_2 atmosphere. The as-prepared NPC with porous structure and high surface area ($1036.2 \text{ m}^2 \text{ g}^{-1}$) was further functionalized with sulfonic groups in an aryl diazonium salt solution to obtain sulfonyl functionalized NPC (S-NPC) with a surface area of $844.0 \text{ m}^2 \text{ g}^{-1}$. S-NPC as cathode material was assembled into an asymmetric CDI device with aminated activated carbon (A-AC) as anode material, exhibiting superior CDI performance with an adsorption capacity of 15.5 mg g^{-1} and an average adsorption rate of $0.44 \text{ mg g}^{-1} \text{ min}^{-1}$ in 40 mg L^{-1} NaCl solution at an applied voltage of 1.2 V. As a proof of concept study, such configured CDI device was also powered for the first time by a Zn-air battery made from NPC with an open-circuit voltage of 1.28 V owing to N doping in soybean shell derived porous carbon with superior oxygen reduction reaction (ORR) activity, delivering an impressive CDI performance with an adsorption capacity of 15.8 mg g^{-1} and an average adsorption rate of $0.37 \text{ mg g}^{-1} \text{ min}^{-1}$ in 40 mg L^{-1} NaCl solution. This superior CDI performance can be due to S-NPC with high surface area, porous structure and surface rich negative charges resulted from sulfonyl functionalization, favourable for adsorption active sites exposure and mass transport of Na^+ ions.

Keywords: soybean shell derived N-doped porous carbon, sulfonyl functionalization, ORR activity, Zn-air battery, capacitive deionization

1. INTRODUCTION

Owing to the rapid increase of population and serious contamination of water environment, the scarcity of clean freshwater has become a global concerned issue.[1-3] It has been a feasible and effective pathway to obtain freshwater from seawater/brackish water due to their abundant reserves on the earth through some emerging desalination technologies, such as reverse osmosis (RO), thermal processes (TP), electrodialysis (ED) and capacitive deionization (CDI).[4-11] Among them, CDI utilizing the formed electric double layer capacitance (EDLC) at the interfaces of electrodes to adsorb the charged ionic species, has been considered as one of the most promising desalination techniques ascribed to its several advantages of low energy consumption (low applied voltage < 2.0 V), low cost, no secondary pollution, rapid regeneration of electrode and easiness of device.[12] Even so, CDI technique is still on the development way owing to the currently used electrode materials with low capacity to remove salt ions from seawater/brackish water.[13] It has been widely accepted that the electrode materials for high performance CDI should possess the following features: (i) high surface area favourable for the exposure of adsorption active sites to improve electrosorption capacity; (ii) porous structure to improve mass transport; (iii) superior electronic conductivity; (iv) high chemical and electrochemical stability; (v) high salt ions adsorption/desorption rates beneficial for high-efficient salt removal and electrode material regeneration. Many studies have demonstrated that carbon-based materials can meet the requirements of high performance CDI electrodes, such as activated carbon, porous carbon, carbon nanotubes, graphene and their composites with inorganic materials.[14-27] However, almost all carbon-based materials for CDI electrodes reported to date are exclusively synthesized by using petroleum-derived chemicals, undoubtedly enhancing the cost of large-scale production applications. Therefore, seeking low-cost and

abundant carbon sources to fabricate carbon-based materials for high-performance CDI is still highly requested.

Recently, several studies have demonstrated the feasibility of utilizing biomasses (*e.g.*, pomelo peel, watermelon, cotton *etc.*) as starting materials to fabricate porous carbon materials with high surface area by direct pyrolysis or pore former assisted pyrolysis approach for CDI applications.[28-31] Zhang and co-workers reported that N, P co-doped porous carbon with high surface area of $2726 \text{ m}^2 \text{ g}^{-1}$ can be obtained by high temperature pyrolysis of pomelo peel in the presence of $\text{NH}_4\text{H}_2\text{PO}_4$ and KHCO_3 , as electrode material exhibiting good deionization capacity of 20.78 mg g^{-1} at 1.4 V in a 1000 mg L^{-1} NaCl solution.[28] In their work, this high CDI performance can be due to the fabricated carbon material with high surface area, superior micro-/mesoporous structure and N, P co-doping in carbon structure.[32] Zhang's and Wang's groups recently utilized watermelon as starting material to fabricate porous carbon materials with high surface area, directly (or after functionalization) as CDI electrode materials demonstrating great potential for applications in the removal of NaCl or heavy metal ions (*e.g.*, Cu^{2+}) in aqueous solution using low applied voltages.[29] In this respect, Liu *et al.* reported the utilization of cotton as starting material to pyrolytically fabricate porous carbon material with a high surface area of $2680 \text{ m}^2 \text{ g}^{-1}$, directly as free-standing CDI electrode exhibiting an excellent desalination performance with an electrosorption capacity of 16.1 mg g^{-1} in 500 mg L^{-1} NaCl solution.[31] The above reported works have demonstrated that biomass-derived carbon materials are very promising as electrode materials for CDI applications. Besides of the advantages of low cost, abundance, high porosity, large surface area and superior electronic conductivity, biomass-derived carbon materials generally possess the feature of natural N doping in carbon structure resulted from biomass source containing N element.[33-37] This endows biomass-derived N-doped carbon materials with superior electrocatalytic activities of oxygen reduction reaction

(ORR) for potential applications in fuel cells and metal-air batteries.[37-39] As we know, metal-air batteries (*e.g.*, Zn-air, Al-air, Mg-air, Li-air) can generally afford an open-circuit voltage of 1~3 V.[40-43] For instance, Zn-air battery can theoretically provide an open-circuit voltage of ~1.65 V, but actually the obtained open-circuit voltage is ranging from 1 to 1.65 V based on different air cathode electrocatalysts used.[43] Even so, it may be very feasible of utilizing Zn-air battery as power supply to drive CDI device with low applied voltage < 2.0 V for deionization applications from the viewpoint of energy conservation, especially using low-cost and abundant biomass-derived N-doped carbon simultaneously as Zn-air battery electrocatalyst and CDI electrode material. The related study has not been reported in literatures to date.

In this work, biomass-derived N-doped porous carbon was simultaneously used as Zn-air battery electrocatalyst and CDI electrode material for Zn-air battery powered capacitive deionization application. For this, soybean shell was used as starting material to first obtain N-doped porous carbon (NPC) with a high surface area of $1036.2 \text{ m}^2 \text{ g}^{-1}$ by a facile pyrolysis approach with the assistance of KHCO_3 in N_2 atmosphere. The as-prepared NPC was further functionalized with sulfonic groups in an aryl diazonium salt solution to obtain sulfonyl functionalized NPC (S-NPC) with a surface area of $844.0 \text{ m}^2 \text{ g}^{-1}$. The measurement results of CDI assembled with S-NPC demonstrated superior deionization performance with an adsorption capacity of 15.5 mg g^{-1} and an average adsorption rate of $0.44 \text{ mg g}^{-1} \text{ min}^{-1}$ in 40 mg L^{-1} NaCl solution at an applied voltage of 1.2 V. For the first time, we also demonstrated the feasibility of utilizing Zn-air battery made from soybean shell derived NPC with an open-circuit voltage of 1.28 V to drive S-NPC assembled CDI with an electrosorption capacity of 15.8 mg g^{-1} and an average adsorption rate of $0.37 \text{ mg g}^{-1} \text{ min}^{-1}$ in 40 mg L^{-1} NaCl solution. It is believed that high surface area, porous structure and surface sulfonyl functionalization of soybean shell derived NPC contribute high CDI performance.

2. EXPERIMENTAL SECTION

2.1 Materials. Sodium chloride (NaCl), Potassium bicarbonate (KHCO_3), Sulfanilic acid (4-(NH_2) $\text{C}_6\text{H}_4\text{SO}_3\text{H}$), sodium nitrite (NaNO_2), Chloride acid (HCl) and nitric acid (HNO_3) were supplied by Sinopharm Chemical Reagent Co. used without further purification. Commercial activated carbon (AC) and 3-aminopropyltriethoxysilane (APTES) was purchased from Sigma-Aldrich. Carbon paper (HCP030) was used as received from Shanghai Hesen electric co., Ltd. Soybean shell was collected from Hefei (Anhui Province, China) and deionized water was used in all experiments.

2.2 Preparation of N-doped Porous Carbon (NPC) and Sulfonic Functionalized NPC (S-NPC). Soybean shell (powder, 6.0 g) was first mixed with potassium bicarbonate with a mass ratio of 4:1, and then the mixture was transferred to a corundum boat and heated to 800 °C for 3 h with a heating rate of 10 °C min⁻¹ in N₂ atmosphere in a tube furnace. After that, black solid substance was obtained and further ground into powder form, then transferred into 60 mL of HCl /H₂O mixture (1:1, V/V) under stirring for 8 h at ambient temperature. Finally, the black powder was collected by filtering and washing with deionized water, and then dried at 70 °C in an oven for overnight to obtain N-doped porous carbon (NPC).

Before sulfonic functionalization, the as-prepared NPC was first treated with concentrated nitric acid at 80 °C for 3 h to obtain the partially oxidized NPC with surface rich O-containing functional groups to facilitate surface sulfonation reaction. The aryl diazonium salt solution was prepared through the reaction between 0.23 g sulfanilic acid and 0.90 g sodium nitrite in 50 mL of deionized water and 2.5 mL of 1.0 M HCl solution in an ice bath.[44] Subsequently, 0.10 g pre-treated NPC was dispersed into 50 mL of deionized water, and then 2.0 mL of the prepared aryl diazonium salt solution was slowly dropped into the above NPC dispersed solution under

stirring in an ice bath for 2 h.[45]After washing with deionized water and freeze-drying, the sulfonic functionalized NPC sample was denoted as S-NPC. For comparison, soybean shell was also used as starting material to fabricate N-doped carbon (NC) material as the aforementioned procedure except for without the assistance of potassium bicarbonate, and then NC was further functionalized with sulfonic group as the above process. The obtained sample was denoted as S-NC.

2.3 Characterization. Scanning electron microscopy (SEM) measurements of the samples were performed with a field emission scanning electron microscope (SU 8020) at an acceleration voltage of 5.0 kV. Transmission electron microscopy (TEM) images were recorded on a JEOL-2010 microscope operated at an accelerating voltage of 200 kV. The crystalline structures of the samples were identified by X-ray diffraction (XRD, Philips X'pert PRO) using Ni-filtered monochromatic Cu K α radiation (λ K α 1=1.5418 Å) at 40 kV and 40 mA. Raman spectra of the samples were measured on a Renishaw Micro-Raman Spectroscopy (Renishaw inVia Reflex) using 532 nm laser excitation. Fourier transform infrared (FT-IR) spectra of the samples were recorded on a Perkin-Elmer TGA 7 infrared spectrometer to identify the functional groups on the sample surface. Nitrogen adsorption-desorption isotherms of the samples were measured using an automated gas sorption analyzer (Autosorb-iQ-Cx). X-ray photoelectron spectroscopy (XPS) analysis was performed on an ESCALAB 250 X-ray photoelectron spectrometer (Thermo, America) equipped with Al K α 1, 2 monochromatized radiations at 1486.6 eV X-ray source.

2.4 Electrochemical Measurements. The capacitance and galvanostatic charge/discharge measurements of samples were performed in 6.0 mol L⁻¹ KOH (or 1.0 mol L⁻¹ NaCl) solution on a CHI 660E electrochemical station (CHI 660E, CH Instrument, Inc., shanghai, China), using a three-electrode configuration consisted of a working electrode, an Hg/HgO reference electrode (or

Ag/AgCl reference electrode) and a Pt counter electrode. The cyclic voltammetry (CV) and galvanostatic charge/discharge (GCD) measurements were carried out in the potential range of 0~1.0 V. Electrochemical impedance spectroscopy (EIS) was conducted with an amplitude of 5.0 mV and frequency range from 100 KHz to 0.01 Hz. The specific capacitance (C) was calculated from GCD curves according to the following equation:

$$C = I\Delta t / m\Delta V \quad (1)$$

where I is the discharge current density, Δt is the discharge time, m is the mass of the active material, and ΔV is the discharge voltage difference.

The measurements of oxygen reduction reaction (ORR) were carried out on an electrochemical station (CHI 660E, CH Instrument, Inc., shanghai, China) combined with a PINE rotating disk electrode (RDE) system (Pine Instruments Co. Ltd. USA). A glassy carbon (GC) electrode (5.0 mm in diameter) served as the substrate of electrocatalyst was used as working electrode. Ag/AgCl and Pt wire were used as reference electrode and counter electrode, respectively. A conventional three-electrode electrochemical cell with a flowing gas system was applied for electrochemical measurements. Prior to use, the GC electrode was sequentially polished with a 5.0, 3.0, and 0.05 μm alumina slurry and then washed ultrasonically in water and ethanol. The cleaned electrode was dried with a high-purity nitrogen stream. The NPC catalyst ink was prepared by dispersing the catalyst powder (10 mg) into a mixture containing 100 μL of Nafion solution (0.5 wt.%) and 900 μL of ethanol, followed by a ultrasonic treatment for 2 min. Then, 12 μL of the catalyst ink was cast onto the GC electrode surface and dried at room temperature for further measurement.

The ORR performance of NPC electrocatalyst was measured by linear sweep voltammetry (LSV) in an O_2 -saturated 0.1 M KOH solution. The LSV curves were measured from 0.2 to -0.8

V at a scan rate of 10 mV s^{-1} with different disk rotation rates of 400, 625, 900, 1225, 1600 and 2025 rpm. The electron transfer number (n) *per* oxygen molecule in an ORR process was calculated by the Koutecky-Levich (*K-L*) equations:[46, 47]

$$J^{-1} = J_k^{-1} + (B\omega^{1/2})^{-1} \quad (2)$$

$$B = 0.62nF(D_0)^{2/3}\nu^{-1/6}C_0 \quad (3)$$

$$J_k = nFkC_0 \quad (4)$$

where J is the measured current density during ORR, J_k is the kinetic current density, ω is the electrode rotating angular velocity ($\omega=2\pi N$, where N is the linear rotation speed), B is the slope of the *K-L* plots, F is the Faraday constant ($F=96,485 \text{ C mol}^{-1}$), D_0 is the diffusion coefficient of O_2 in 0.1 M KOH ($1.9\times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$), ν is the kinetic viscosity ($0.01 \text{ cm}^2 \text{ s}^{-1}$), and C_0 is the bulk concentration of O_2 ($1.2\times 10^{-3} \text{ mol L}^{-1}$).

The measurements of the Zn-air batteries were performed using home-built electrochemical cells.[48] All data were collected from the as-fabricated cell with a CHI 760D electrochemical workstation (CH Instruments, Inc., Shanghai, China) at room temperature. Briefly, zinc foil was used as the anode and the catalyst loaded onto the gas diffusion layer (Teflon-coated carbon fiber paper with a geometric area of 1.0 cm^2 , the catalyst loading amount was $\sim 2.0 \text{ mg cm}^{-2}$) was used as the air cathode. The electrolyte was 6.0 M KOH solution.

2.5 Capacitive Deionization (CDI) Measurements. The CDI performance of the electrode was measured in batch mode electrosorption experiment. A short-circuit mode was applied to desorb and recover the concentrated NaCl solution for regeneration of the electrode. The CDI testing apparatus consisted of a pump, a conductivity meter, an electrical power supply, a home-made CDI unit and a feed water reservoir, as shown in Scheme S1 (Supporting Information, SI). For meaningful comparison, the prepared NPC, S-NPC and S-NC were used as cathode materials in

home-made CDI device with the same anode of aminated activated carbon (A-AC). The amino-functionalization of commercial AC was performed in 100 mL of acetone including 0.2 mL of APTES under stirring. During CDI measurements, carbon paper was used as current collector, and silicon spacer with a thickness of 1.0 mm was used for separating the cathode and anode. NaCl solution (40~1000 mg L⁻¹) in a beaker was continuously fed into the CDI unit by a peristaltic pump with a constant flow rate of 15 mL min⁻¹ and the effluent was returned to the NaCl stock solution at a direct voltage of 1.2 V. For the electrode regeneration, a short-circuit mode was applied to desorb and recover the concentrated NaCl solution. The CDI electrodes with a size of 40×40 mm were fabricated by loading a mixture of 80 wt.% of the active component (NPC, S-NPC, S-NC and A-AC), 10 wt.% of acetylene black and 10 wt.% of Nafion in isopropyl alcohol homogeneously. After drying at 60 °C for overnight, the loading total amount of active component (NPC, S-NPC, S-NC and A-AC) on carbon paper is about 48 mg. During the CDI measurements, a conductivity meter (Type DDSJ-308A, Leici Company) was located in NaCl stock solution to monitor the variation of the solution conductivity with operation time. The NaCl solution conductivity was recorded every 20 s in the adsorption and desorption processes. The salt adsorption capacity (SAC) was calculated according to the following equation:

$$\Gamma = (C_0 - C)V / m \quad (5)$$

where Γ is the salt adsorption capacity, C_0 and C are the initial and final salt concentrations, respectively, V is the total volume of NaCl solution, and m represents the total mass of the active components including anode and cathode.

The average salt adsorption rate (ν) of CDI electrode materials was calculated according to the following equation:

$$v = \Gamma / t \quad (6)$$

where v is the average salt adsorption rate, Γ is the salt adsorption capacity and t is the total cycling time including adsorption and desorption.

3. RESULTS AND DISCUSSION

3.1 Structural and Composition Characteristics of Soybean Shell Derived Carbon

Materials. In this work, soybean shell as starting material was pyrolytically converted into N-doped porous carbon (NPC) with the assistance of KHCO_3 at 800 °C in N_2 atmosphere. During high temperature pyrolysis, the introduction of KHCO_3 can effectively create porous structure of carbon materials with high surface area, which has been proven in recently reported works.[28, 30, 49] For improving the electrosorption capability, as-prepared NPC was further functionalized by sulfonic groups to obtain sulfonyl functionalized NPC (denoted as S-NPC). Indeed, soybean shell derived carbon material without the assistance of KHCO_3 during pyrolysis displays bulk morphology without the formation of porous structure, as shown in Figure 1a. Comparatively, soybean shell derived carbon material (NPC) in the presence of KHCO_3 during pyrolysis shows obviously dominant macropore structure (Figure 1b). The detailed structure information of NPC was further obtained by TEM characterization. As shown in Figure 1c, large numbers of macropores can be observed for NPC, consistent with the SEM result. Interestingly, more subtle pore structure can be found on macropore walls of NPC (Figure 1d). The above results demonstrate that the introduction of KHCO_3 during pyrolysis indeed facilitates the formation of porous structure of soybean shell derived carbon, favourable for improving carbon material's surface area and mass transport when used as electrode material.[30, 49] Moreover, the porous property of soybean shell derived carbon can be still preserved after sulfonation, as shown in Figure 1e. Figure 1f shows the XRD patterns of soybean shell derived carbon materials with (NPC), without (NC) the assistance of KHCO_3 during pyrolysis and sulfonyl functionalized NPC

(S-NPC). Typically, two broad peaks appear at $\sim 26^\circ$ and $\sim 43^\circ$ corresponding to the (002) and (100) diffraction modes of the graphitic structure, which is characteristic of graphitic carbon materials [50]. Moreover, similar XRD results can be obtained for NPC, NC and S-NPC samples, indicating ignorable effect of the introduction of KHCO_3 during pyrolysis and functionalization by sulfonic groups on the crystalline structure of soybean shell derived carbon.

Figure 1. (a) SEM images of soybean shell derived N-doped carbon (NC) without the assistance of KHCO_3 during pyrolysis. (b) SEM image of N-doped porous carbon (NPC) with the assistance of KHCO_3 during pyrolysis. (c) TEM image of NPC. (d) Enlarged TEM image of NPC. (e) SEM image of sulfonyl functionalized NPC (S-NPC). (f) XRD patterns of NC, NPC and S-NPC.

Raman spectroscopy has been proven to be an efficient means to investigate the defect extent of carbon materials.[28, 51] Therefore, soybean shell derived NPC, NC and S-NPC samples were characterized by the Raman spectrum technique. The Raman spectra (Figure 2a) of NPC, NC and S-NPC samples display two conspicuous diffraction peaks at near 1580 cm^{-1} of the G band and 1352 cm^{-1} of the D band, corresponding to the $\text{E}_{2\text{g}}$ vibration of the sp^2 -bonded carbon atoms and the disordered graphitic carbon, respectively, which are the characteristics of graphitic carbon materials. The intensity ratio of D-band to G-band was generally used to reveal the defect level of carbon materials.[49] As shown, the $I_{\text{D}}/I_{\text{G}}$ values of NPC, NC and are 1.04, 0.96 and 0.97, respectively, and the defect extent of NPC is slightly higher than that of NC and S-NPC, possibly due to the presence of rich pore structure in NPC, favourable for enhancing the material's electrocatalytic activities.[37] Figure 2b shows the FT-IR spectra of NC, NPC and S-NPC samples. The results demonstrate the presence of the characteristic adsorption band of $\text{S}=\text{O}$ at $1150\text{-}1040\text{ cm}^{-1}$ and $650\text{-}575\text{ cm}^{-1}$ for S-NPC,[52, 53] suggesting the successful functionalization of sulfonic groups on the surface of NPC. Figure 2c shows the N_2 adsorption-desorption isotherms of NC, NPC and S-NPC. For NPC and S-NPC samples, a typical type-IV isotherm with a strip hysteresis loops at a wide relative pressure range (0.5-1.0) can be clearly observed, indicating their rich porous property.[54] However, the isotherm of NC sample is very different with NPC and S-NPC, indicating its poor pore structure, consistent with the SEM

characterization. The above results demonstrate the significant role of KHCO_3 as pore former during soybean shells pyrolysis to fabricate porous structure carbon materials.[28, 30, 49] The pore size distribution curves (Figure 2d) of NC, NPC and S-NPC indicate their dominant mesoporous structure. However, the presence of macropores in NPC (Figure 1a, b) may mean that more mesoporous structure can be utilized in NPC and S-NPC for high performance electrochemical applications. Further, the specific surface areas of NC, NPC and S-NPC calculated by the BET method are about 107.3, 1036.2 and 844.0 $\text{m}^2 \text{g}^{-1}$ with corresponding total pore volumes of 0.054, 0.43 and 0.37 $\text{cm}^3 \text{g}^{-1}$, respectively, indicating the formation of porous structure in NPC resulted from the assistance of KHCO_3 during pyrolysis contributing large surface area. Comparatively, NPC after sulfonyl functionalization shows a decreased surface area compared to pristine NPC, possibly owing to sulfonic groups occupying porous structure internal/external surface. This also further indicates the successful sulfonyl functionalization of NPC. In a word, with the assistance of KHCO_3 during pyrolysis, the obtained NPC and S-NPC exhibit porous structure and high surface area, which are beneficial for the enhancement of electrochemical related mass transport and the exposure of electrocatalysis/electrosorption-related active sites, thus improving the performance of electrochemical applications.[37]

Figure 2. (a) Raman spectra of NC, NPC and S-NPC. (b) FT-IR spectra of NC, NPC and S-NPC. (c) and (d) N₂ adsorption-desorption isotherms and corresponding pore size distribution curves of S-NPC, NPC and NC.

X-ray photoelectron spectroscopy (XPS) measurements were performed to measure the chemical composition of NPC and S-NPC. Figure 3a shows the surface survey XPS spectra of NPC and S-NPC samples. Comparatively, soybean shell derived NPC indicates the presence of C, N and O elements, while additional S element can be detected for NPC after sulfonyl functionalization. Figure 3b shows the high resolution C 1s XPS spectra of NPC and S-NPC. As shown, the high resolution C 1s spectrum can be divided into five peaks at binding energies of 284.7 eV, 284.8 eV, 285.9 eV, 288.1 eV and 290.9 eV corresponding to C-C, C-N, C-O, C=O and O-C=O respectively.[39, 55] The above results demonstrate that soybean shell derived NPC

and S-NPC contain rich O, N surface functional groups, favourable for enhancing the carbon material's surface hydrophilicity and wettability for electrochemical applications in aqueous solution electrolyte.[28] Many studies have verified that intrinsic N doping in biomass-derived carbon materials results in their superior electrocatalysis activities, which is a very important advantage of using biomass as carbon source to fabricate carbon material.[37-39] In this work, intrinsic N doping in NPC and S-NPC can be detected by high resolution N 1s XPS spectra. As shown in Figure 3c, the N 1s XPS spectrum of NPC and S-NPC can be deconvoluted into three peaks at the binding energies of 398.1 eV, 400.1 eV and 401.6 eV, ascribed to pyridinic-N (27.6%), pyrrolic-N (32.6%) and graphitic-N (39.8%), respectively.[39, 55] Theoretical and experimental results have proven that pyridinic-N and graphitic-N are responsible for high oxygen reduction reaction (ORR) performance of N-doped carbon electrocatalysts.[46] Comparatively, no S element can be detected for NPC, while the high resolution S 2p spectrum (Figure 3d) of S-NPC can be divided into three peaks at binding energies of 167.3 eV, 168.5 eV and 169.3 eV, corresponding to S-O, S=O and C-S, respectively,[56] further indicating the successful sulfonyl functionalization. Additionally, an important advantage of sulfonyl functionalization on NPC is that sulfonic groups can effectively terminate the co-ions expulsion effect and increase the charge efficiency, thus improving salt ions removal efficiency for capacitive deionization applications.[57]

Figure 3. (a) Surface survey XPS spectra of S-NPC and NPC. (b) High resolution C1s XPS spectra of S-NPC and NPC. (c) High resolution N1s XPS spectra of S-NPC and NPC. (d) High resolution S2p XPS spectra of S-NPC and NPC.

3.2 Electrochemical Capacitance Performance. To investigate the effect of the porous structure and sulfonic functionalization on soybean shell derived carbon materials' electrochemical performance, the cyclic voltammetry (CV) measurements of S-NPC were performed. For comparison, NPC and NC as electrode materials were also evaluated. It is well known that the integral area of CV curve is directly proportional to the electrochemical capacitance of carbon material. As shown in Figure 4a, the integral area of CV curve of NPC obtained at a scan rate of 100 mV s^{-1} in 6.0 mol L^{-1} KOH solution is obviously larger than that of NC, possibly due to its porous structure and high surface area. After sulfonyl functionalization,

S-NPC displays more large CV curve area in comparison with NPC, indicating its higher electrochemical capacitance. This may be ascribed to the contribution of electrochemical active -SO₃⁻ groups aroused pseudo-capacitance and electrochemical double-layer capacitance resulted from carbon material.[57] Figure 4b shows the CV curves of S-NPC obtained at different scan rates in 6.0 mol L⁻¹ KOH solution. As shown, when the scan rate varied from 2 to 20 mV s⁻¹, the quasi-rectangular shape of CV curves can be essentially remained, implying good electrochemical double-layer capacitance behavior.[58] When increasing the scan rate, the quasi-rectangular shape CV curves of S-NPC become slightly deformed, possibly owing to the contribution of electrochemical active -SO₃⁻ groups aroused pseudo-capacitance to the overall specific capacitance.[57] Figure 4c shows the specific capacitances of S-NPC, NPC and NC samples at different current densities from 0.25 to 2.0 A g⁻¹ derived from their galvanostatic charge/discharge (GCD) curves (Figure S1 in the SI). Apparently, the specific capacitances of S-NPC at different current densities are larger than that of NPC and NC. At a current density of 0.25 A g⁻¹, the specific capacitance of S-NPC reaches 215.3 F g⁻¹, while the specific capacitances of NPC and NC are 165.2 F g⁻¹ and 156.5 F g⁻¹, respectively. The high specific capacitance of S-NPC is very favourable for the electrochemical related applications (*e.g.*, electrosorption). The stability test (Figure 4d) of S-NPC shows that after 1000 cycles at a current density of 0.5 A g⁻¹, the capacitance retention is almost 98%, suggesting its high applicable stability. The electrochemical impedance spectra (EIS) of S-NPC, NPC and NC electrodes were also measured in 6.0 M KOH solution, as shown in Figure S2 (SI). The Nyquist plots are interpreted with an equivalent circuit, as shown in the inset of Figure S2 (SI). The results obtained in high frequency region are corresponds to the charge transfer limiting process ascribed to the double-layer capacitance (C_1) in parallel with the charge transfer resistance (R_2) at the contact interface

between the electrode and electrolyte solution. The R_2 values of S-NPC, NPC and NC are 0.40, 0.39, 0.40, respectively. Almost identical series resistance and semicircle radius in high frequency region for S-NPC, NPC and NC indicate an ignorable influence of sulfonic groups functionalization on the electron transfer of soybean shell derived carbon. This is very important for S-NPC as CDI electrode application. For a practical CDI application to remove NaCl from seawater/brackish, it should be more important that the electrochemical capacitance of soybean shell derived carbon materials was measured in NaCl electrolyte. Figure 5a-c shows the galvanostatic charge/discharge (GCD) curves of S-NPC, NPC and NC samples in 1.0 M NaCl solution at different current densities from 0.25 to 2.0 A g⁻¹, and based on these GCD curves, their specific capacitances at different current densities are shown in Figure 5d. Obviously, S-NPC electrode exhibits larger specific capacitances at different current densities compared to NPC and NC electrodes in NaCl solution, further confirming the significant role of sulfonyl functionalization. At a current density of 0.25 A g⁻¹, the specific capacitance of S-NPC can achieve 174.4 F g⁻¹, and the capacitance retention is 65.6% at a current density of 2 A g⁻¹. Compared to NPC and NC, higher specific capacitance of S-NPC in NaCl solution may endow it larger electrosorption capacity for CDI application. This would be further investigated in following CDI measurements.

Figure 4. Electrochemical performances of S-NPC, NPC and NC in 6.0 mol L⁻¹ KOH solution. (a) CV curves of S-NPC, NPC and NC at a scan rate of 100 mV s⁻¹. (b) CV curves of S-NPC at different scan rates. (c) Specific capacitances of S-NPC, NPC and NC at different current densities. (d) Cycling stability of S-NPC at a current density of 0.5 A g⁻¹.

Figure 5. (a), (b) and (c) GCD curves of S-NPC, NPC and NC electrodes in 1.0 mol L⁻¹ NaCl solution over a potential range from -1.0 to -0.1 V at different current densities. (d) Specific capacitances of S-NPC, NPC and NC at different current densities.

3.3 CDI Measurement by DC Power Supply. Recently, several works have demonstrated that biomass-derived carbon can be used as electrode materials for CDI applications.[28-31] In this work, the CDI performance of S-NPC was therefore evaluated using NaCl solution as model substance. For meaningful comparison, NPC and sulfonyl functionalized NC (S-NC) were also measured under the identical experimental conditions. For all experiments, aminated activated carbon (A-AC) was used as CDI anode material. The commercial activated carbon (AC) and aminated activated carbon (A-AC) all exhibit similar surface carbon structure, indicating an ignorable influence of amination on surface structure of AC (Figure S3a, b, SI). The XRD patterns (Figure S3c, SI) of AC and A-AC all show two broad peaks at ~26° and ~43°,

corresponding to the (002) and (100) diffraction planes of graphitic carbon with characteristic D band at $\sim 1352\text{ cm}^{-1}$ and G band at $\sim 1580\text{ cm}^{-1}$ (Figure S3d, SI). Comparatively, the FT-IR spectra (Figure S4, SI) exhibit the characteristic adsorption peaks of N-H at 3424 cm^{-1} and 1630 cm^{-1} for A-AC, indicating successful amination of AC. The N_2 adsorption-desorption isotherms (Figure S5a, SI) of AC and A-AC indicate that the specific surface area of AC after amination shows a decrease possibly owing to the modified amino groups occupied the mesoporous positions of AC (Figure S5b, SI). Batch mode experiments were carried out in a NaCl aqueous solution with an initial concentration of 40 (or 100, 300, 500, 1000) mg L^{-1} under a flow rate of 15 mL min^{-1} at a direct voltage of 1.2 V provided by DC power supply. The obtained NaCl solution conductivity change curves of these three carbon electrodes are shown in Figure 6a-c. In a 40 mg L^{-1} NaCl solution, the conductivity of S-NPC assembled CDI decreases from the initial 82.3 to $61.4\text{ }\mu\text{S cm}^{-1}$ at an applied voltage of 1.2 V (Figure 6a), while the conductivity of NaCl solution decreases from 82.3 to 60.1 and $67.2\text{ }\mu\text{S cm}^{-1}$ for NPC and S-NC assembled CDI cells (Figure 6b, c), respectively. Obviously, NPC assembled CDI displays higher electrosorption capacity (16.0 mg g^{-1}) toward NaCl compared to S-NPC (15.5 mg g^{-1}) and S-NC (10.4 mg g^{-1}) assembled CDI, primarily owing to its larger surface area ($1036.2\text{ m}^2\text{ g}^{-1}$) as well as porous structure. Even so, sulfonic functionalized NPC and NC electrodes all exhibit much faster adsorption rates of 0.44 and $0.34\text{ mg g}^{-1}\text{ min}^{-1}$ in 40 mg L^{-1} NaCl solution at an applied voltage of 1.2 V than that ($0.26\text{ mg g}^{-1}\text{ min}^{-1}$) of NPC electrode, indicating sulfonic functionalization of carbon material with enhanced salt ions adsorption efficiency.[57] Moreover, the desorption rates of salt ions of S-NPC and S-NC are 0.89 and $0.78\text{ mg g}^{-1}\text{ min}^{-1}$ respectively in each CDI cycle, obviously faster than that ($0.56\text{ mg g}^{-1}\text{ min}^{-1}$) of NPC, which is very important for a practical application of CDI. The above results demonstrate that the functionalized $-\text{SO}_3^-$ groups on soybean shell derived carbon material effectively provide the additional attracting force for

the Na^+ ions, and Cl^- ions can be repelled to the opposite electrode, thus improving the CDI performance.[23, 57] For a practical CDI application, its desalination performance in high-concentration NaCl solution is critically important.[59] As shown in Figure 6d, the S-NPC assembled CDI performance was therefore evaluated in 40, 100, 300, 500 and 1000 mg L^{-1} NaCl solutions, exhibiting the desalination capacities of 15.5, 27.8, 28.4, 36.6 and 43.3 mg g^{-1} , respectively. The above results demonstrate that S-NPC assembled CDI can afford high desalination capacity in high-concentration NaCl solution, and the performance of S-NPC assembled CDI is superior to most recently reported carbon-based CDI devices (Table S1 in the SI). The high salt adsorption capacity of S-NPC in higher concentration (*e.g.*, 1000 mg L^{-1}) of NaCl solution could be due to soybean shell derived N-doped porous carbon material with high surface area and sulfonic functionalization affording high salt adsorption capacity; additionally, higher NaCl concentration (*e.g.*, 1000 mg L^{-1}) is favourable for facilitating the establishment of compacted electrical double layer (EDL), thus improving the salt adsorption capacity of S-NPC electrode.[23, 60] Further, Kim-Yoon plots were produced to evaluate the CDI performance of S-NPC, NPC and S-NC derived from their conductivity *vs.* time curves (Figure S6, SI). As depicted in Figure 7a, S-NPC assembled CDI yields a Kim-Yoon plot shifted towards higher mean electrosorption rates than that resulted from NPC and S-NC, further indicating its high deionization capacity. Figure 7b shows the electrosorption capacity of S-NPC assembled CDI at 1.2 V in NaCl solution with different concentrations. The plot of electrosorption capability *versus* NaCl solution concentration can fit very well with the Freundlich model,[61] which may be due to one portion of contribution of functionalized $-\text{SO}_3^-$ groups on soybean shell derived carbon material effectively providing the additional attracting force. The calculated Freundlich constant (K_f) and the tendency ($1/n$) of the adsorbate to be adsorbed are 0.24 and 0.27, respectively.

Figure 6. (a) CDI cycling performances of S-NPC, (b) NPC and (c) S-NC electrodes in 40 mg L⁻¹ NaCl solution at 1.2V. (d) Electrosorption capacities of S-NPC electrode in NaCl solution with different concentrations.

Figure 7. (a) Kim-Yoon plots of S-NPC, NPC and S-NC. (b) Electrosorption isotherm of S-NPC at an applied voltage of 1.2 V in NaCl solution with different concentrations.

3.4 CDI Measurement Powered by Zn-air Battery. In the past few years, many studies have demonstrated that biomass-derived carbon materials with natural N doping exhibit superior

electrocatalytic activities of oxygen reduction reaction (ORR) and great potential as air cathode materials for metal Zn-air batteries.[48, 62-64] This may provide opportunity for biomass-derived carbon assembled CDI application powered by biomass-derived carbon assembled Zn-air battery owing to the applied voltage of CDI matched with the open-circuit voltage of Zn-air battery. The advantages of using zinc-air battery to drive CDI setup are : (1) as a low-cost energy device, zinc-air battery possesses compact structural configuration and high power density; (2) zinc-air battery with an open-circuit voltage ranging from 1 to 1.65 V can meet the requirements of CDI operation as a power supply; (3) soybean shell derived N-doped porous carbon is capable of simultaneously using as electrode material for zinc-air battery and CDI applications. In this work, soybean shell derived NPC was therefore evaluated for ORR in 0.1 M KOH solution with a PINE rotating disk electrode system. The LSV curves of NPC obtained from an O₂-saturated 0.1 M KOH solution at different rotation rates are shown in Figure S7a (SI). As shown, the investigated electrocatalyst exhibits the onset potential of *ca.* - 0.12 V (vs. Ag/AgCl), and the limiting current density increases with rotation rate. The Koutecky–Levich (*K–L*) plots (Figure S7b, SI) derived from Figure S7a (SI) displays good linear relationship at different potentials, and the calculated the average value of the number of transferred electrons (Figure S7c in the SI) within -0.4 to -0.6 V (vs. Ag/AgCl) is 3.97 for NPC, indicating a near four electron ORR process. The stability test in 0.1 M KOH solution (Figure S7d) shows that NPC possesses high durability with 9.9% decrease in current density after 25000 s of continuous run at a rotation rate of 1600 rpm. In contrast, the commercial Pt/C catalyst displays 23.2% decrease in current density under the same conditions, indicating high applicable stability of NPC. The above results demonstrate that NPC possesses superior catalytic activity of ORR, potential for the application in Zn-air battery.[37, 62] Therefore, a home-made Zn-air battery assembled with NPC as air cathode material and Zn foil as anode was constructed for further investigation. As shown in

Figure 8a, the open circuit voltage of the Zn-air battery is ~ 1.28 V, capable of successfully lightening the LED assembled pattern (CEEN, Centre for Environmental and Energy Nanomaterials, inset in Figure 8a). Figure 8b shows the discharge and power density curves of zinc-air batteries assembled with NPC. In the discharge process, the zinc-air battery made from NPC shows a high current density of 111.1 mA cm^{-2} at 1.0 V. The peak power density of zinc-air battery assembled with NPC is 149.9 mW cm^{-2} reached at 0.6 V. Further, this NPC assembled Zn-air battery with an open-circuit voltage of 1.28 V was used as power supply for CDI application. Figure 8c shows the home-made Zn-air battery powered CDI setup. The experimental results (Figure 8d) demonstrate that the S-NPC assembled CDI possesses high cycling stability powered by NPC assembled Zn-air battery with the average adsorption rate and adsorption capacity of $0.37 \text{ mg g}^{-1} \text{ min}^{-1}$ and 15.8 mg g^{-1} , respectively, in 40 mg L^{-1} NaCl solution. The above results confirm the feasibility of using biomass-derived carbon as electrode materials for Zn-air battery powered CDI application.

Figure 8. (a) Open circuit voltage measurement of NPC assembled Zn-air battery (inset of lightened LED pattern). (b) Discharge curve and corresponding power density plot of NPC assembled Zn-air battery at different current densities. (c) Photograph of home-made Zn-air battery powered CDI setup. (d) Cycling stability of S-NPC assembled CDI setup powered by Zn-air battery.

4. CONCLUSIONS

In summary, N-doped porous carbon derived from soybean shell was successfully fabricated and further functionalized with sulfonic groups by simple KHCO_3 -assisted pyrolysis and solution reaction method. Owing to N doping nature, the resulting soybean shell derived porous carbon (NPC) as electrocatalyst exhibits superior ORR activity and potential application in Zn-air battery with an open-circuit voltage of 1.28 V. After sulfonic functionalization, soybean shell derived porous carbon (S-NPC) as cathode material displays high performance of CDI application at a direct voltage of 1.2 V, delivering significantly improved electrosorption rate of Na^+ ions compared to NPC without sulfonic functionalization. For the first time, high desalination performance of S-NPC assembled CDI was achieved by NPC assembled Zn-air battery as power supply. This high CDI performance can be due to the fabricated S-NPC with high surface area, porous structure and surface rich negative charges aroused from the modified sulfonic groups. The findings in this work demonstrate the feasibility of using biomass-derived carbon as electrode materials for energy-saved CDI application.

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ASSOCIATED CONTENT

Supporting Information

The supporting SEM images, electrochemical performances of samples, and ORR measurements of sample.

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Research Highlights:

1. N-doped porous carbon (NPC) was fabricated by pyrolysis of soybean shells.
2. NPC was further functionalized by sulfonic groups for capacitive desalination.
3. NPC constructed Zn-air battery as power supply drove capacitive desalination.

ACCEPTED MANUSCRIPT

N-doped porous carbon was obtained using soybean shell as precursor, followed by surface functionalization via sulfonic groups, as electrode materials exhibiting high performance of Zn-Air battery powered capacitive deionization.

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Biomass-Derived N-Doped Porous Carbon as Electrode Materials for Zn-Air Battery Powered Capacitive Deionization

Cuijiao Zhao, Guoqiang Liu, Na Sun, Xian Zhang, Guozhong Wang, Yunxia Zhang, Haimin Zhang, Huijun Zhao

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