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Liquid-phase exfoliation of layered biochars into multifunctional heteroatom (Fe, N, S) co-doped graphene-like carbon nanosheets

Weiqian Tian^{a,b}, Qiuming Gao^{a,*}, Armin VahidMohammadi^{c,e}, Jie Dang^d, Zeyu Li^a, Xiao Liang^a, Mahiar M. Hamedi^b, Liming Zhang^{b,*}

^a Key Laboratory of Bio-inspired Smart Interfacial Science and Technology of Ministry of Education, Beijing Advanced Innovation Center for Biomedical Engineering, School of Chemistry, Beihang University, Beijing 100191, China

^b Department of Fibre and Polymer Technology, KTH Royal Institute of Technology, Teknikringen 56, 10044 Stockholm, Sweden

^c Innovation Partnership Building, University of Connecticut, Storrs, CT 06269, United States

^d Chongqing Key Laboratory of Vanadium-Titanium Metallurgy and New Materials, College of Materials Science and Engineering, Chongqing University, Chongqing 400044. China

e A.J. Drexel Nanomaterials Institute and Department of Materials Science and Engineering, Drexel University, Philadelphia, PA 19104, USA

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ABSTRACT

We here report a liquid-phase exfoliation strategy to delaminate multilayered biochars into multi-heteroatom (Fe, N, S) co-doped graphene-like carbon nanosheets, in which the multilayered biochars derived from naturally evolved layer-by-layer precursors. This strategy provides the versatile capability to tailor the textural properties of the as-synthesized carbon nanosheets, such as obtaining a controllable specific surface area of up to 2491 m² g⁻¹. Thanks to the unique integration of graphene-like microstructures with a thickness of 4.3 nm, large specific surface area and hierarchical pores, homogenous co-doping of N, S, and Fe, and high electronic conductivity, the as-synthesized Fe-N-S co-doped carbon nanosheets could act as multifunctional electrodes for electrocatalytic process of oxygen reduction reaction (ORR) and capacitive energy storage. The optimized nanosheets showed a better ORR catalytic performance than commercial Pt/C catalyst, with a more positive onset potential (1.026 V) and half-wave potential (0.829 V), higher long-term stability, and outstanding methanol tolerance in alkaline mediums. Furthermore, the porous carbon nanosheets exhibited excellent super-capacitive performances which delivered a high energy density of 29.1 Wh kg⁻¹ at a high power density of up to 39.5 kW kg⁻¹ in an ionic liquid electrolyte. This liquid-phase exfoliation strategy will offer new inspiration for the synthesis of various biomass-derived graphene-like carbon nanosheets for multifunctional applications.

1. Introduction

Two-dimensional (2D) carbonaceous materials such as graphene and its derivatives [1,2], transition metal carbides (MXene) [3,4], and organic molecules-derived [5,6] or biomass-derived carbon nanosheets (CNSs) [7,8], have shown promising properties for electrochemical energy storage and conversion applications [9,10], as the result of their unique physicochemical properties including high aspect ratio, large specific surface area, high electronic conductivity, and short ionic transport pathways coupled with abundant interfacial active sites [11–13]. With the rapid development of electrochemical energy storage systems over the past decade, a large number of different 2D carbonaceous electrode materials have been developed, but the scalable production of most of these 2D materials relies largely on the expensive precursors and hazardous synthesis procedures.

The fabrication of graphene-like carbon nanosheets from renewable biomass offers a promising green/cost-efficient possibility to develop next-generation 2D carbonaceous materials as advanced electrode materials [14,15]. This is given by homogenously hierarchical architectures of naturally evolved biomass which provide the potential of doping heteroatoms (i.e. O, N, S, P) in carbon matrix to generate atomically dispersed active sites [16–18]. In this direction, some efforts have recently strived toward the fabrication of heteroatoms doped CNSs, such as O-doped CNSs derived from hemp [19], glucose [20], coconut shell [21], and shaddock skin [7], N, O binary-doped CNSs derived from salvia splenden [22], silk [23], shrimp shell [24], mushroom [25],

* Corresponding authors. *E-mail addresses:* qmgao@buaa.edu.cn (Q. Gao), limingzh@kth.se (L. Zhang).

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seaweed [26], cellulose [27], and eucalyptus leaves [28], N, S binarydoped CNSs derived from keratin [29], amino acid [30,31], silk fibroin [32,33], garlic stem [34], ginkgo leave [35], chicken feather [36], and cotton [37], N, P binary-doped CNSs derived from phytic acid [38], bean okara [39], silkworm cocoon [33,40], fish scale [41], and N, S, P trinary-doped CNSs derived from soybeans [42], egg [43], etc. The multiple-doped heteroatoms with different electronegativities can change the charge density and electronic spin distribution of carbon matrix and also can lead to improving the corresponding electrochemical properties of the electrodes for batteries and supercapacitors, or electrocatalysis [44,45]. Among these biomass-derived carbons, multi-heteroatoms co-doping, especially ones with the incorporation of trace amounts of transitional metals [46-50] have shown remarkable multi-functional electrocatalysis properties. Examples of previously reported materials are cocoon silk-derived Fe(Co, Ni)-N-C [51], histidinederived Fe-N-C [48], Porphyra-derived Fe-N-S-C [18], silk-derived Fe-N-S-C [18], bean sprouts-derived Co-N-P-C [45], auricularia auricularjudae-derived Fe-N-C [52], and blue rose-derived Ni-C [53]. These biomass-derived electrocatalysts show comparable catalytic performance to precious metals such as Pt/C while exhibiting better methanol/CO tolerance, ultimate atom efficiency, good durability due to strongly metal-coordinated sites, and also are low-cost. They are thus one of the most promising alternatives to precious metal catalysts for scalable application of next-generation reversible energy conversion and storage devices such as metal-air batteries, fuel cells, and water splitting cells [54,55].

The reported biomass-derived carbon nanosheets are mostly fabricated using the combined strategies of pyrolysis coupled with preconfined ex-situ templates such as montmorillonite clay [56], aminoclay [57], boric acid [58], MgO [37,59], and CaO [60], and/or upon with harsh post-activation using KOH [19], K₂CO₃ [61], NaCl [22], etc. Therefore, developing more efficient and economically viable strategies to fabricate durable multi-heteroatoms co-doped carbon nanosheets with integrated multi-functionalities from hierarchical biomass architectures is still highly desirable but challenging.

We here report a liquid-phase exfoliation strategy to delaminate multilayered biochars into Fe-N-S co-doped carbon nanosheet (Fe-N-S-CNS) from a naturally evolved layer-by-layer (LbL) microstructure. The as-obtained nanosheets have graphene-like microstructures with a thickness of 4.3 nm, high specific surface area and hierarchical pore distribution, high electronic conductivity (7.6 S cm⁻¹), and a

homogeneous multi-heteroatom doped architecture. These combined properties endow that these nanosheets can be used as multifunctional electrodes for energy storage and conversion applications. As proof of concept, we demonstrate that the Fe-N-S co-doped carbon nanosheets have higher catalytic activities for oxygen reduction reaction (ORR) than commercial Pt/C catalysts, and can be used as supercapacitor electrodes with excellent performances both in aqueous and ionic liquid electrolytes.

2. Result and discussion

2.1. Liquid-phase exfoliation of multilayered biochars

The liquid-phase exfoliation strategy for the fabrication of the delaminated carbon nanosheets is schematically illustrated in Fig. 1. In our methodology, we used a lightly mineralized nacre-like architecture as a precursor that is the shells of silkworm chrysalides (SSCs). These silkworm chrysalides, well-known as large-scale silk producers for centuries, are currently discarded as byproducts from the large scale manufacturing of silk threads, after extraction of the silk cocoons [62,63]. The annual production of silk exceeds 200 000 metric tons [63], and our method can thus turn a discarded byproduct at scale into a high-value product. More interestingly, the crustacean shells such as SSCs consist of naturally alternate LbL-stacking of the mineralized aragonite (CaCO₃) layers bonded with the organic macromolecular layers rich in protein and chitin [24], as shown using field emission scanning electron microscopy (SEM) in Fig. S1.

To prepare the Fe-N-S-CNS, we firstly pretreated the SSCs precursor in a concentrated metal ion (such as Fe^{3+}) solution. Thanks to the natural LbL-stacking microstructures of SSCs that offer very large interfaces between the macromolecular layers and the mineralized layers, a large amount of Fe^{3+} ions were concurrently intercalated into the confined interlayer spacing or anchored atomically on the surface of macromolecular layers through strong coordination interaction with dissociative carboxyl and amine groups of protein and chitin [48,64,65]. The pretreated precursors then underwent an in-situ carbonization step at 800 °C under Ar atmosphere. During this step, the organic macromolecular layers were in situ converted into 2D heteroatom-doped biochars containing N, S dopants that originated from the amino and sulfur groups of chitin and/or protein (including asparagine, methionine, glutamate, etc.) [63]. Concurrently, the previously adsorbed Fe^{3+} ions



Fig. 1. Schematic illustration of the synthesis process for the delaminated carbon nanosheets.

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coordinated atomically with amino groups were transformed to Fe-N moieties embedded into carbon nanosheets. While the excess intercalated Fe³⁺ ions in the confined interlayer spacing were first transformed to a 2D carburized intermediate Fe₃C layers, by reacting with adjacent carbon atoms from macromolecular layers at a temperature of 600 °C [7]. As the temperature reached 800 °C, the Fe₃C layers were subsequently converted to α -Fe layers which acted as in-situ templates and graphitizing catalysts to promote the growth of ordered graphene-like nanostructures [21,66,67]. Synchronously, by increasing temperature to 800 °C, the inorganic layers of oriented CaCO3 were completely converted into CaO sheets which also acted as in-situ templates to provide spatially dimensional confinement for the formation of carbon nanosheets [60]. We then used acid leaching to remove the metal-based template layers completely and obtained multilayered biochars, labeled as Fe-N-S-C. Comparison of X-ray diffraction (XRD) patterns of the samples before and after acid leaching (Fig. S2 and Fig. 2i), shows that CaO and crystalline iron species such as metallic, carbides or oxides had been removed in this step.

Atomic force microscope (AFM) images with the corresponding peak-force (Fig. 2a, b) and the SEM image (Fig. S3) both show that Fe-N-S-C has a unique multilayered microstructure. The average thickness of single layers in the stacked multilayers is 4.4 nm \pm 0.2 nm (Fig. 2c) as

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calculated from the statistical average values of 70 measured points. Such unique multilayered microstructure results from the combination of intrinsic LbL-stacked architecture of the precursors and the in situ templated carbonization process assisted by oriented inorganic layers derived from the presence of $CaCO_3$ and Fe^{3+} . After the removal of the templates, the thin carbon layers stacked on top of each other by weak van der Waals forces. To delaminate the stacked multilayers, we used an ultrasonic-assisted liquid-phase exfoliation step in an organic solvent of N-methylpyrrolidone (NMP). This procedure has previously been used to exfoliate carbon nanotube (CNT) [68], graphene from graphite [69], and 2D transition metal dichalcogenides from powders [70]. During this liquid-phase exfoliation step, the van der Waals forces among adjacent nanosheets were balanced by the interaction between solvent NMP and carbon phase, due to NMP possessing matchable surface energy with carbonaceous materials that minimize the energy cost of exfoliation [69]. After liquid-phase exfoliation, we removed remaining aggregates using mild centrifugation and obtained a homogeneous dark dispersion containing the delaminated nanosheets of Fe-N-S-CNS. AFM images (Fig. 2d-f) show that Fe-N-S-CNS consists of individual nanosheets with an average thickness of 4.3 nm \pm 0.3 nm (statistics from 70 measuring points) which is consistent with the thickness of single layers in multilayered Fe-N-S-C. Field emission transmission electron microscopy



Fig. 2. Characterization of the liquid-phase exfoliation process. (a–f) AFM height images, peak-force error images, and height profiles along the crossed lines in the corresponding height images for the sample before liquid-phase exfoliation, Fe-N-S-C (a–c), and the sample after liquid-phase exfoliation, Fe-N-S-CNS (d–f). (g) Nitrogen adsorption-desorption isotherms, (h) corresponding pore size distribution, and (inset h) cumulative pore volume of Fe-N-S-C and Fe-N-S-CNS. (i) XRD patterns of Fe-N-S-C and Fe-N-S-CNS.

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(TEM) analysis (Fig. S4) also shows that Fe-N-S-CNS is comprised by transparent single/few-layered nanosheets consistent with AFM observations, further indicating the successful delamination of multilayered biochars.

We used the nitrogen adsorption/desorption technique to further investigate the liquid-phase exfoliation process. The isotherms at 77 K of Fe-N-S-C (before liquid-phase exfoliation) and Fe-N-S-CNS (after liquidphase exfoliation) both show the hybrid I/IV-type with a hysteresis loop (0.40 < relative pressure $P/P_0 < 0.95$) and two steep uptakes ($P/P_0 <$ 0.01 or > 0.95) (Fig. 2g), indicating the coexistence of hierarchical pore sizes [71]. This was further verified by the calculation from the nonlocal density functional theory (DFT) using the slit model (Fig. 2h). The multilayered Fe-N-S-C shows a specific surface area of 218 m² g⁻¹ based on multipoint Brumauer-Emmett-Teller (BET) (Table S1). After the liquid-phase exfoliation, the produced Fe-N-S-CNS shows a significant increase in its specific surface area up to 1621 m² g⁻¹, seven-fold more than that of multilayered Fe-N-S-C. Fe-N-S-CNS also has a larger total pore volume of 0.71 $\text{cm}^3 \text{g}^{-1}$ especially with a dominating mesopore volume of 0.41 $\text{cm}^3 \text{g}^{-1}$ compared to those of Fe-N-S-C. These are attributed to the liquid-phase exfoliation process that exposed more surface area of nanosheets and generated enormous slit pores. The higher specific surface area as well as the high mesopore volume offer more electrochemically active sites and facilitate mass transport during electrochemical energy storage and electrocatalysis processes [72].

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Additionally, XRD pattern of Fe-N-S-C shows two typically broad diffraction peaks at around 12.9° and 44.1° (Fig. 2i) that are assigned to amorphous pseudo-graphitic structures [7]. The sharp peak at 26.5° is superimposed on the broad peak of amorphous structures, which is ascribed to (002) characteristic peak of ordered graphite domains that suggest the existence of a certain amount of graphite structures embedded in whole carbon skeletons [18,73,74]. The unique graphitic structures were created during the carbonization process, as a result of the catalyzing graphitization effect of the α -Fe phase as discussed above. Comparison with Fe-N-S-C, all of the diffraction peaks in the XRD pattern of Fe-N-S-CNS are dramatically broadened and almost disappeared (Fig. 2i) because of the randomly disordered arrangements of nanosheets after delaminating [56]. A prominent increase in the lowangle region of Fe-N-S-CNS is also noted that is attributed to the high porosity [1], in agreement with the DFT calculation from nitrogen adsorption/desorption isotherm. The results from nitrogen adsorption/ desorption and XRD both further show that the liquid-phase exfoliation/ delamination of multilayered Fe-N-S-C resulted in single/few-layered Fe-N-S-CNS

Raman spectrum of Fe-N-S-CNS (Fig. 3a) shows the D-band at 1345 cm⁻¹ induced by defects or disordered graphitic structures [23], and G-band at 1603 cm⁻¹ ascribed to the ordered sp²-bonded graphene lattices [75,76]. The intensity ratio of G- and D-band (I_G/I_D) that is used to index the degree of graphitic ordering [77], is 1.14 for Fe-N-S-CNS



Fig. 3. Microstructure characterization. (a) Raman spectroscopy of Fe-N-S-CNS and Fe-N-S-aCNS. (b) High-resolution TEM image of Fe-N-S-CNS. (c) EDX-TEM image of Fe-N-S-CNS and (d) corresponding line profile concentration for N, S, and Fe. (e) C 1s, (f) N 1s, (g) S 2p, and (h) Fe 2p spectra of Fe-N-S-CNS.

corresponding to an average width L_a of 5.0 nm (Table S2) for the graphitic domains. These values are higher than reported values for commercial activated carbon Norit ($I_G/I_D = 0.52$, $L_a = 0.5$ nm) [19], nitrogen-doped carbon nanosheets $(I_G/I_D = 1.06, L_a = 4.7 \text{ nm})$ [24], and even reduced graphene oxides ($I_G/I_D = 1.11$, $L_a = 4.9$ nm) [2]. Raman spectrum of Fe-N-S-CNS (Fig. 3a) also exhibits second-order 2D and D + G peaks in the range from 2500 cm^{-1} to 3100 cm^{-1} , which indicates the presence of abundantly ordered graphene-like structure [29,77]. The high-resolution TEM image (Fig. 3b) presents ordered graphene-like lattices at the edge and wrinkles of thin nanosheets in Fe-N-S-CNS, but not any metallic-related crystal structures. The higher values of $I_{\rm G}/I_{\rm D}$ and L_a, and rich graphitic lattices endow a higher electronic conductivity which we measured to 7.6 S $\rm cm^{-1}$ for Fe-N-S-CNS using a four-probed method at a load pressure of 10 MPa. This value is higher than that of commercial available activated carbons such as Supra 50 (4.3 S cm^{-1}) [75].

We used energy-dispersive X-ray (EDX) spectroscopy and X-ray photoelectron spectroscopy (XPS) to gain insight into the heteroatom doping within the nanosheet skeletons of Fe-N-S-CNS. TEM-EDX mappings (Fig. S5) revealed that the heteroatom dopants such as N, S, and Fe are homogeneous distribution throughout the entire nanosheet. We further characterized the co-doping by using EDX concentration profiles of N, S, and Fe (Fig. 3d) along the corresponding lines on the carbon nanosheet (Fig. 3c). The N, S, and Fe profiles correlate tightly with each other, indicating that the heteroatom dopants are not only distributed homogenously but also may form coordination moieties such as Fe-N_x [73]. We further analyzed the surface chemical nature of N, S, and Fe doping using XPS spectra (Fig. S6), which revealed that Fe-N-S-CNS is co-doped by 5.08 atom% N, 2.36 atom% S and 0.26 atom% Fe coupled with primary 85.56 atom% C (Table S2). We investigated the bulk chemical components by using combustion elemental analysis and inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis (Table S2), which further proved the N, S, Fe co-doping within as-prepared carbon nanosheets such as a Fe content of 1.03 wt% (${\sim}0.24$ at%) in Fe-N-S-CNS in agreement with XPS analysis. The high-resolution C 1s spectrum (Fig. 3e) deconvoluted into five peaks at 284.8, 285.6, 283.9, 286.7, and 289.0 eV, which are assigned to sp² C (with the content of 52.6%), C-N (20.1%), C-S (8.2%), C-O (12.4%), and O=C-O (6.7%) (Table S3) [24,78,79]. The predominant sp² C peak evidences the successful construction of a large amount of conjugated graphitic domain. While C-N and C-S peaks suggest the successful doping of N and S heteroatoms through stable covalent bonds [78]. We fitted the high-resolution N 1s spectrum (Fig. 3f) to five peaks at 398.2, 400.1, 401.2, 403.4, and 399.0 eV, ascribed to pyridinic N (N-6, 23.3%), pyrrolic N (N-5, 19.4%), quaternary-N (N-Q; 41.2%), N-oxides (N-O; 5.2%) and Fe-N_x (10.9%) (Table S4) [79-81]. Notably, the positively charged quaternary N accounts for the prime content, which is also named graphitic N and locates at the center and valley position of graphene lattices to enable higher electronic conductivity and four-electron transfer for the electrocatalytic process [48]. The negatively charged pyridinic N and pyrrolic N that have lone electron pairs as electrondonors and situate at the edges and defects of graphene, can offer abundantly accessible active sites for the adsorption of electrolyte ions or oxygen molecules during electrochemical process [24,29]. More importantly pyridinic N enables to anchor positive-charged Fe atomically to form Fe-N_x electrocatalytic sites [48,72]. This structure is further supported by the presence of corresponding Fe-N $_x$ peak in Fig. 3f. The high-resolution S 2p spectrum (Fig. 3g) consists of two main peaks at 163.9 and 165.1 eV, which are related to the thiophene-like structure of S $2p_{3/2}$ (C–S–C, 50.5%) and S $2p_{1/2}$ (C=S, 29.2%) [46], and a small peak at 168.3 eV for sulfur oxides (-SO_x-, 20.3%) (Table S5) [72,76]. The thiophene-like S can change the charge spin density which benefits the electrocatalytic process [29,72]. Notably, the absence of any peak from the coordination between S and Fe atoms suggests that S atoms are unable to anchor Fe, but S atoms with a lower electronegativity of 2.58 enrich the negative charge density of N atoms with higher

electronegativity (3.04) in favor of accelerating the reductive release of intermediates during ORR process [82]. The high-resolution of Fe 2p spectrum (Fig. 3h) exhibits two pairs of peaks of Fe^{2+} at 710.9 eV ($2p_{3/2}$, 22.9%) and 724.4 eV (2p1/2, 26.3%), and Fe³⁺ at 713.6 (2p_{3/2}, 17.1%) and 730.4 eV (2p_{1/2}, 18.4%) (Table S6), which are originated from Fe-N_x. The satellite peak at 717.6 eV (15.3%) further demonstrates directly the formation of Fe-N_x coordination [48,83]. Whereas the absence of the peaks at 707.0 and 720.2 eV originated from metallic iron and iron carbides and oxides [81,84], is consistent with XRD and TEM results. In summary the EDX and XPS results both demonstrate the homogenous doping of N, S, and Fe, which is mainly ascribed to naturally uniform distributions of N, S atoms in the biomass cells. More importantly, the homogenous Fe doping was incorporated in the structure despite the harsh acid leaching in the synthesis, indicating that the doped Fe atoms are stabilized and coordinated atomically with N atoms in the carbon skeletons that originates from the strong chelating between iron cations and dissociative amino groups of precursors [80,85].

Additionally, our synthesis strategy provides the versatile capability to produce porous carbon nanosheets with tailorable textural properties such as specific surface area and pore volume which are highly required for different electrochemical processes. We could synthesize activated carbon nanosheets, labeled as Fe-N-S-aCNS, by adding the activation reagent of ZnCl₂ during pretreatment. The texture characterizations of Fe-N-S-aCNS demonstrated the activation function of ZnCl₂. TEM image (Fig. S7) shows that Fe-N-S-aCNS maintains the typical 2D nanosheet morphology with numerous pores but without any metallic nanoparticle impurities and Zn doping that was further evidenced by the XPS, XRD, and ICP analysis (Figs. S6, S8, and Table S2). The nitrogen adsorption/ desorption isotherm and DFT pore distribution both confirmed the significant increase of micropores/small mesopores and specific surface area (Fig. S9), with a higher total pore volume of 1.70 $\text{cm}^3 \text{ g}^{-1}$ and higher BET specific surface area of 2491 m² g⁻¹ (Table S1), compared to those of non-activated Fe-N-S-CNS (0.71 cm³ g⁻¹, and 1621 m² g⁻¹). The XPS spectra, however, show that Fe-N-S-aCNS has lower heteroatomdoped contents with 4.02 atom% N, 1.97 atom% S, and 0.12 atom% Fe (Table S2), particularly lower sp² C content (50.9%) and quaternary-N (36.4%) than those of Fe-N-S-CNS (Fig. S10, and Tables S3, S4). Such results are attributed to the ZnCl₂ activation process in which Zn ions first interacted strongly with the carbon π -electron structures. As the temperature increases to its boiling point (756 °C) ZnCl₂ then evaporated completely which concurrently etched away some carbon atoms and heteroatom dopants and created enormous nanopores [51]. To investigate the function of Fe catalyzed graphitization in our synthesis strategy, we prepared a control sample of delaminated carbon nanosheet without Fe doping which shows the amorphous structure (Fig. S11) and low electronic conductivity (4.8 S cm⁻¹) compared to Fe-N-S-CNS. Moreover, considering the strong adsorption capability of protein or chitosan with a series of metallic ions of Ni²⁺, Co²⁺, Cu²⁺ [51,85,86], and the variety of crustacean shells with naturally evolved LbL microstructures, our strategy could be extended to synthesize a family of metal-, N-, S- co-doped graphene-like carbon nanosheets, and thus open up more opportunities for biomass-derived carbon nanosheets in multifunctional electrochemical applications such as electrocatalysis and energy storage.

2.2. ORR performance

We evaluated the ORR electrocatalytic activity of as-obtained samples by using a three-electrode system in O₂-saturated 0.1 M KOH electrolyte with the catalyst loading of 0.228 mg cm⁻². Fig. S12 presents a comparison of the linear sweep voltammetry (LSV) curves of different Fe-N-S-CNS catalysts synthesized under different carbonization temperatures (700, 800, 900, and 1000 °C), at a scan rate of 10 mV s⁻¹ with a rotating rate of 1600 rpm. The Fe-N-S-CNS fabricated at 800 °C shows the highest ORR activities with the most positive onset potential ($E_{onset} = 1.026$ V vs RHE) and half-wave potential ($E_{1/2} = 0.829$ V) without iR-

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correction among all catalysts. Notably, all Fe-N-S-CNS mentioned in this work refers to Fe-N-S-CNS fabricated at 800 °C. The ORR activities of Fe-N-S-CNS also outperforms those of commercially available 20 wt% Pt/C ($E_{\text{onset}} = 1.005 \text{ V}$, $E_{1/2} = 0.805 \text{ V}$) (Fig. 4a). Cyclic voltammogram (CV) curve of Fe-N-S-CNS (Fig. 4b) shows a prominent reduction peak at 0.846 V in the O₂-saturated 0.1 M KOH in contrast to the N₂-saturated case that is commensurate with Pt/C, further suggesting its pronounced ORR activity. Fe-N-S-CNS also shows good ORR activity in an acidic electrolyte (Fig. S13). Such high ORR electrocatalytic activity of Fe-N-S-CNS is comparable or superior to the reported biomass-based carbon electrocatalysts (Table S7).

In contrast, the multilayered Fe-N-S-C (before liquid-phase exfoliation) presents rather inferior ORR activities with an $E_{\rm onset}$ of 0.941 V and $E_{1/2}$ of 0.772 V, which are 85 mV and 57 mV more negative than those of Fe-N-S-CNS, and especially with a significantly less diffusion-limited current density ($J_{\rm L}$) of 3.39 mA cm⁻² compared to that of Fe-N-S-CNS ($J_{\rm L} = 6.03$ mA cm⁻²) at a potential of 0.2 V. Such results suggest that the liquid-phase exfoliation process exposed numerous active sites for the ORR, and the high specific surface area and pore volume of delaminated nanosheets altogether boost the mass transfer and O₂ diffusion for ORR process [48,81]. Interestingly, the activated Fe-N-S-aCNS shows an obvious decay for ORR activities ($E_{\rm onset} = 0.971$ V, and $E_{1/2} = 0.786$ V) compared to the Fe-N-S-CNS. This decay is attributed to the activation process which created a higher specific surface area and total pore volume (Table S1) but destructed some graphitic domain and heteroatom-doped active sites such as pyridinic N and

graphitic N moieties (Table S4), and also decreased the Fe content (Table S2). To further identify the role of Fe active sites in ORR process, we conducted the LSV measurements for Fe-N-S-CNS in 0.1 M KOH containing 10 mM KCN (Fig. S14), since it is known that CN^- ions have strong coordination with iron and thus can severely poison Fe-N_x sites for the ORR. With the addition of KCN, the E_{onset} and $E_{1/2}$ showed 75 mV and 47 mV negative shifts, respectively, simultaneously with a 20% decrease in the J_L . The results suggest the Fe-N_x coordination sites contribute significantly to the superior ORR activity of Fe-N-S-CNS. Additionally, Fe-N-S-CNS poisoned by CN^- shows a comparable ORR activity with Pt/C, suggesting that the N and S doped sites such as pyridinic N, graphitic N, and thiophene-like S moieties are also important contributors to ORR activity [29,48].

To further investigate the catalytic kinetics of ORR, we calculated the Tafel plots from the corresponding LSV curves (Fig. 4c). Fe-N-S-CNS shows a Tafel slope of 60.4 mV dec⁻¹ which is smaller than Fe-N-S-aCNS (66.5 mV dec⁻¹) and even Pt/C (65.7 mV dec⁻¹). The smaller Tafel slope that reflects the rate-determining step in the catalytic process [46], implies that Fe-N-S-CNS has the superior kinetic for the ORR process. To investigate the ORR pathway, we calculated the electron-transfer number (n) along with the yield of peroxide (H₂O₂) that is produced by the side reaction of a two-electron process [73], based on rotating ring-disk electrode (RRDE) curves. As shown in Fig. 4d, Fe-N-S-CNS shows an electron transfer number of around 4 and H₂O₂ yield of below 10% that are comparable to those of Pt/C, suggesting a high selectivity for four-electron transfer pathway which is desirable to the



Fig. 4. Electrocatalytic performances. (a) LSV polarization curves of Fe-N-S-CNS, Fe-N-S-CNS after 5000 cycles, Fe-N-S-aCNS, Fe-N-S-C, and commercial Pt/C at a rotating rate of 1600 rpm and a scan rate of 10 mV s⁻¹ in O₂-saturated 0.1 M KOH. (b) CV curves of Fe-N-S-CNS and Pt/C at 5 mV s⁻¹ in O₂- and N₂saturated 0.1 M KOH. (c) Tafel plots of Fe-N-S-CNS, Fe-N-S-aCNS, and Pt/C obtained from the corresponding polarization curves. (d) Electron transfer number and peroxide yield of Fe-N-S-CNS, Fe-N-SaCNS, and Pt/C in O2-saturated 0.1 M KOH. (e) Durability evaluation from chronoamperometric curves of Fe-N-S-CNS and Pt/C at 1600 rpm in O2saturated 0.1 M KOH. (f) Chronoamperometric curves for the methanol-crossover effect of Fe-N-S-CNS and Pt/C after adding 10 mL methanol into the O2-saturated electrochemical cell.

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electrochemical reduction of oxygen to water [82].

We used the accelerated durability test (ADT) to evaluate the durability of the Fe-N-S-CNS catalyst based on cycling at 50 mV s⁻¹ in N₂saturated 0.1 M KOH. After 5000 cycles, we collected the LSV curve at 1600 rpm in O₂-saturated 0.1 M KOH which shows slight negative shifts of 9 mV and 12 mV in E_{onset} and $E_{1/2}$, respectively (Fig. 4a), indicating outstanding long-term stability. We also conducted the chronoamperometric (CA) tests in 0.1 M KOH to further investigate the stability of catalysts. As shown in Fig. 4e, Fe-N-S-CNS exhibits remarkable stability that retains 94.3% of the initial current after 50,000 s, much higher than Pt/C that can only retain 63.2% of its initial value. We also used the chronoamperometric test to evaluate the resistance to methanol crossover of catalysts through injecting methanol into O2-saturated 0.1 M KOH (Fig. 4f). Notably, after injecting methanol, Fe-N-S-CNS showed a negligible change of current density, whereas Pt/C showed a significant jump in its relative current. More importantly, Fe-N-S-CNS has an almost negligible change of ORR activity with or without methanol (Fig. S15), much superior to the Pt/C for which the cathodic peak for ORR disappeared and a typical inverse peak of methanol oxidation appeared after injecting methanol (Fig. S16). Such results indicate that Fe-N-S-CNS is highly tolerable to methanol crossover, which is an essential feature in practical applications such as fuel cells.

The superior ORR activities of the as-obtained heteroatom-doped carbon nanosheets especially Fe-N-S-CNS, results from the combination of porous graphene-like nanosheet microstructures and Fe, N, S co-

doped chemical composition, which we believe have four unique features: (i) The thin thickness of nanosheets (4.3 nm) and large specific surface area (1621 $\text{cm}^2 \text{g}^{-1}$) with hierarchical pores that were created by liquid-phase exfoliation process, not only exposes enormous active sites available at the interfaces between catalysts and reactants but also shorten the diffusion pathway to facilitate mass transfer during ORR process. (ii) The homogeneous Fe, N, S co-doping offers a great number of catalytic active centers along nanosheets, especially such as Fe-N_x, pyridinic N, graphitic N, and thiophene-like S moieties which facilitate O2 adsorption and reduction. (iii) The N, S doping induces uneven charge density in carbon nanosheet and thus endows positive charge on neighboring carbon atoms with strong electronic affinity in favor of oxygen adsorption during ORR process. These are consistent with many experiments and density functional theory (DFT) calculations which have revealed the Fe-Nx coordination sites coupled with the electronic effects from surrounding S doping presenting high ORR electrocatalytic activities and kinetics [18,72,76,82,87]. The electron donation from surrounding N, S dopants can make the Fe catalytic centers with less positive charges, which weaken the binding energy between the Fe centers and adsorbed intermediates (OOH*, O*, and OH*) in a fourelectron ORR pathway, thereby accelerating the production of OH⁻ in alkaline medium [82,87]. (iv) The high electronic conductivity enabled by the Fe catalyzed graphitization and quaternary-nitrogen doping, accelerates electron transfer thereby boosting ORR activity.



Fig. 5. Supercapacitive performances. (a) CV curves at a scan rate of 50 mV s⁻¹ of Fe-N-S-C, Fe-N-S-CNS, and Fe-N-S-aCNS-based symmetrical supercapacitors in 6 M KOH aqueous electrolyte. (b) Charge/ discharge curves at a current density of 1 A g⁻¹ of Fe-N-S-CNS and Fe-N-S-aCNS-based symmetrical supercapacitors in 6 M KOH aqueous electrolyte. (c) CV curves at 100 mV s^{-1} and (d) charge/discharge curves at 1 A g-1 of Fe-N-S-CNS and Fe-N-S-aCNSbased symmetrical supercapacitors in 1 M EMI BF4 ionic liquid electrolyte. (e) Specific capacitance of Fe-N-S-CNS and Fe-N-S-aCNS-based symmetrical supercapacitors at different current densities in different electrolytes of 6 M KOH (above) and 1 M EMI BF4 (below). (f) Rogone plots of Fe-N-S-aCNSbased symmetrical supercapacitors in different electrolytes.

2.3. Supercapacitive performance

To evaluate the supercapacitive performance of the as-fabricated carbon nanosheets, we assembled symmetrical two-electrode supercapacitors in 6 M KOH aqueous electrolyte and 1 M 1-ethyl-3-methylimidazolium tetrafluoroborate (EMI BF₄) ionic liquid electrolyte (Fig. 5). The Fe-N-S-CNS and Fe-N-S-aCNS that were fabricated by the liquidphase exfoliation strategy, both show nearly rectangle-shaped cyclic voltammetry (CV) curves (Fig. 5a and 5c) and almost symmetric triangle-shaped charge-discharge curves (Fig. 5b and 5d), even at high rates in both aqueous and ionic liquid electrolyte systems (Figs. S17 and \$18). Based on the CV curves, it can be seen that both electrodes show ideal capacitive behavior where the dominating capacitance contribution is from double-layer capacitance and only a small a partial capacitance is superimposed from the pseudo-capacitance of the heteroatoms (N, O, S) doping [24,71]. Such Electrochemical behavior is attributed to the initial graphene-like nanosheet microstructure with a unique integration of high specific surface area and rational doping of N, O, S elements. The ideal capacitive behaviors of the electrodes in both electrolytes were also demonstrated by electrochemical impedance spectroscopy (EIS) with small equivalent series resistance (ESR) (Figs. S17e and S18e), such as an ESR of 0.36 Ω for Fe-N-S-CNS, and an ESR of 0.69Ω for Fe-N-S-aCNS in 6 M KOH. In contrast, the multilayered Fe-N-S-C (before liquid-phase exfoliation) shows a significantly lower current response (Fig. 5a), due to its small specific surface area (218 m^2 g^{-1}) without enough electrode/electrolyte interfaces to store charge.

More interestingly, the Fe-N-S-aCNS always shows a larger capacitance response at the same sweep rates in both electrolyte systems compared to the Fe-N-S-CNS (Fig. 5e). In 6 M KOH, Fe-N-S-aCNS shows a higher specific capacitance of 313 F g^{-1} at a current density of 1 A g^{-1} and maintains 68% of its initial capacitance (213 F g^{-1}) at a high current density of 50 A $g^{-1},$ while Fe-N-S-CNS has a capacitance of 227 F g^{-1} at 1 A g $^{-1}$ and 176 F g $^{-1}$ at 50 A g $^{-1}$ giving a 77% rate capability. The higher capacitance values of Fe-N-S-aCNS result from its higher surface area (2491 m² g⁻¹) and larger pore volume (1.70 cm³ g⁻¹) which provides larger accessible electrode/electrolyte interfaces for capacitive charge storage. We could also prove this point using EIS which depicts a smaller charge transfer resistance of 0.16 Ω for Fe-N-S-aCNS than that for Fe-N-S-CNS (0.23 Ω) (Fig. S17e), indicating more efficient charge transfer in Fe-N-S-aCNS [88]. While the slightly better rate capability of Fe-N-S-CNS results from its higher conductivity (7.6 S cm^{-1}) which helps electron transfer at higher rates [89]. In 1 M EMI BF₄ ionic liquid electrolyte, Fe-N-S-aCNS also exhibits a higher capacitance of 173 F g^{-1} at 1 A g^{-1} and 94 F g^{-1} at 50 A g^{-1} , in agreement with the aqueous electrolyte system. The EIS of the Fe-N-S-aCNS in ionic liquid electrolyte also shows a smaller charge transfer resistance (0.68 Ω) compared to Fe-N-S-CNS (1.57 Ω) (Fig. S18e).

We utilized the Ragone plots (Fig. 5f and S19) to present the gravimetric energy density and power density of the Fe-N-S-CNS- and Fe-N-SaCNS-based supercapacitors based on the total electrochemically active electrode weights. In aqueous electrolyte, Fe-N-S-aCNS-based devices achieve the highest energy density of 10.9 Wh kg^{-1} at the power density of 250 W kg⁻¹, and maintain the energy density of 7.4 Wh kg⁻¹ at the highest power density of 12.7 kW kg⁻¹. Notably, in ionic liquid electrolyte, Fe-N-S-aCNS-based devices possess a wider voltage window of 3 V than that of aqueous system, resulting in a significantly high energy density of 54.1 Wh kg⁻¹ and still retaining a high value of 29.1 Wh kg⁻¹ at a high power density up to 39.5 kW kg⁻¹. Whereas Fe-N-S-CNS-based devices show the highest energy density of 7.9 Wh kg^{-1} in aqueous electrolyte and 41.2 Wh kg⁻¹ in the ionic liquid electrolyte. The energypower densities of our devices are comparable or even superior to previously reported supercapacitors using biomass-based carbon nanosheet electrodes (Fig. S20). The energy densities of our devices are superior to the commercially available activated carbon-based supercapacitors (~5 Wh kg^{-1}) and can bridge the performance gap between electrochemical capacitors and Ni-metal batteries [90]. Additionally, the Fe-N-S-aCNS-

based devices display superior cycling stability with 98.6% capacitance retention after 10 000 cycles in 6 M KOH (Fig. S17f) and also exhibit excellent stability with 92.7% retention of initial capacitance after 5 000 cycles in 1 M EMI BF₄ (Fig. S18f).

3. Conclusion

We have demonstrated a versatile strategy for synthesizing heteroatom (Fe, N, S) co-doped graphene-like carbon nanosheets by using liquid-phase exfoliation of multilayered biochars obtained from a naturally evolved layer-by-layer biomass precursor. The as-synthesized carbon nanosheets have five noteworthy features: (i) They possess graphene-like microstructures with a thin thickness (4.3 nm), high specific surface area, and pore volume that can be tailored by the incorporation of different metal salts. (ii) They have homogeneous multi-heteroatom (Fe, N, S) co-doping that is ascribed to the natural nitrogen-, sulfur-rich chemistry of precursor, and more importantly the strong coordination between amino-groups and Fe ions for anchoring Fe-N moieties on carbon nanosheets. (iii) They show a high electronic conductivity (7.6 S m^{-1}) which results from the iron-based catalyzed graphitization and high quaternary-N (41.2%) doping, (iV) They act as the ORR catalysts which exhibit superior electrocatalytic activity with 24 mV more positive of half-wave potential than that of commercial Pt/ C, and outstanding durability and methanol tolerance better than Pt/C. (V) They have unique porous structures that enable them as supercapacitor electrodes to deliver a combination of high energy- and powerdensity (29.1 Wh kg⁻¹ at 39.5 kW kg⁻¹) in ionic liquid electrolytes. The synthesis strategy presented here opens the door to fabricate a family of multifunctional graphene-like carbon nanosheets with non-precious metal, N, S co-doping, from various naturally evolved layer-by-layer biomass precursors, and we will pursue this direction in our future works.

4. Experimental section

4.1. Materials

The ferric trichloride (FeCl₃), zinc chloride (ZnCl₂), hydrochloric acid (HCl), N-methyl-2-pyrrolidone (NMP), potassium hydroxide (KOH), and other reagents were purchased from Beijing Chemical Works. The shells of silkworm chrysalides (*Bombyx mori*) were obtained from Yantai in China.

4.2. Fabrication of carbon nanosheets

We fabricated Fe-N-S-CNS through a liquid-phase exfoliation strategy to delaminate the multilayered biochars. In brief, the precursors, the shells of silkworm chrysalides (SSCs), were alternatingly rinsed several times with distilled water and ethanol and dried at 50 °C in a conventional oven, and then the dried SSCs were milled into powders in a hammer mill. The powders of SCCs were added into 3 M FeCl₃ solution with a mass loading of 5 wt% which is the ratio of SCCs powders to FeCl₃ solution. The mixtures were treated by bath-ultrasonic at 40 Hz for 3 h and were sequentially stirred at 80 °C to evaporate water until drying thoroughly to introduce the Fe^{3+} adequately into the skeleton of precursors as our previous work reported [7]. The pretreated precursors were then carbonized at 800 °C (700, 900, 1000 °C) for 2 h with a heating rate of 2 °C min⁻¹ under argon flow of 150 mL min⁻¹ in a tube furnace. The resulting biochar, labeled as Fe-N-S-C, was washed in an excess amount of 1 M HCl solution for 12 h to remove the impurities thoroughly and then was rinsed by deionized water to a pH value of around 7. To get few/single-layered carbon nanosheets, the obtained multilayered Fe-N-S-C powders underwent a liquid-phase exfoliation step. Briefly, 0.5 g as-prepared carbon powders were redispersed in 100 mL NMP, and the mixtures were deaerated with argon coupled with bath-sonication for 1 h. After liquid-phase exfoliation, the aggregates

were isolated by centrifugation at 500 rpm for 30 min and the homogenous black supernatant was subsequently vacuum-filtered to collect the final samples labeled as Fe-N-S-CNS. We also measured the yield of Fe-N-S-CNS by filtering a certain volume of the dispersion over a porous polypropylene membrane (pore size of 64 nm) and weighing the obtained solid after drying totally at 110 °C, and the yield of Fe-N-S-CNS was obtained to be ~8 wt%. Fe-N-S-aCNS was prepared by similar procedures where the difference was the addition of the activation agent, ZnCl₂, with a 1:2 mass ratio for SCCs to ZnCl₂ when pretreating the precursors. We also prepared the control sample of delaminated carbon nanosheets without Fe doping by using similar procedures of Fe-N-S-CNS, except for the pretreatment of precursors within the 3 M FeCl₃ solution.

4.3. Characterization of materials

We characterized the morphology of samples by using field emission scanning electron microscopy (FESEM, S-3400 N, Hitachi), field emission transmission electron microscopy (FETEM, JEM2100F, JEOL), and atomic force microscope (AFM, Multimode, Bruker). We conducted the nitrogen adsorption/desorption isotherms at 77 K using Micromeritics ASAP 2010, and obtained the specific surface area from the multipoint Brumauer-Emmett-Teller (BET) and pore size distributions from nonlocal density functional theory (DFT) model using silt model. We recorded powder X-ray diffraction (XRD) patterns using a diffractometer (X-6000, Shimadzu) with Cu K α radiation ($\lambda = 0.154$ nm) at 40 kV, and conducted Raman spectra measurements on LabRAM HR800 using a 514 nm laser wavelength. We performed electrical conductivity on a standard four-point probe system (Jandel RM3) with a pin distance of 1 mm. We investigated the surface chemical compositions on an X-ray photoelectron spectroscopy (XPS, Escalab 250, Thermo).

4.4. Electrochemical characterization

ORR tests: We conducted all ORR tests on a Wavedriver 20 electrochemical workstation (Pine instrument) using a three-electrode system consisting of Ag/AgCl (saturated KCl) as the reference electrode, a Pt wire as the counter electrode and a rotating disk electrode (RDE, Pine instrument) and a rotating ring-disk electrode (RRDE, Pine instrument) coated with the catalyst film as the working electrode. To prepare the working electrode, the catalyst inks were first obtained by ultrasonically dispersing 5 mg of catalysts in a mixed solution containing 475 µL of ethanol, 475 μL of deionized water and 50 μL of 5 wt% Nafion solution for 1 h. For comparison, the commercial Pt/C catalyst (20 wt% Pt) ink was prepared by using the same process with the same mass loading. The as-prepared catalyst ink was deposited uniformly on the glassy carbon electrode (GCE) that has been polished by α -Al₂O₃ slurry and then dried at room temperature. The final mass loading for all catalysts in the working electrode was kept the same, *i.e.*, 0.228 mg cm⁻². We used 0.1 M KOH and 0.1 M HClO₄ as electrolytes and conducted all of the experiments at 25 °C. The electrolytes were bubbled by O₂/N₂ for 30 min to saturation in the cell before testing and maintained O2/N2 saturation during the testing. All recorded potentials were converted to the scale of reversible hydrogen electrode (RHE) according to the Nernst equation: $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \text{pH} + E^{\text{o}}_{\text{Ag/AgCl}}$, where $E_{\text{Ag/AgCl}}$ is the experimentally recorded potential, pH value is from the electrolyte that was used, and E^o_{Ag/AgCl} is 0.197 V at 25 °C. Cyclic voltammetry (CV) curves were recorded with a scan rate of 5 mV s^{-1} and linear sweep voltammetry (LSV) measurements were performed at a scan rate of 10 mV $\rm s^{-1}$ with a Pt ring potential holding at 1.5 V vs RHE especially for RRDE. The electron transfer number (n) and H2O2 percentage (H2O2%) released during ORR were calculated by the following equations: $n = 4I_D/(I_D + I_D)$ $I_{\rm R}/N$), and $H_2O_2\% = 200*I_{\rm R}/N/(I_{\rm D} + I_{\rm R}/N)$, where $I_{\rm D}$ is the disk current, $I_{\rm R}$ is the ring current, and N is the current collection efficiency of Pt ring (N = 0.37). Tafel slopes were obtained from the plots of applied potential vs log (kinetic current density, J_k) of LSV curves recorded at 1600 rpm, and the corresponding J_K was calculated from the Koutecky-Levich (K-L) equation of $1/J = 1/J_K + 1/J_L$ where J is the measured current density and J_L is the diffusion-limited current density. The current density was normalized by the geometric area of GCE from an engineering aspect that is especially meaningful for developing practical devices [91]. The accelerated durability test (ADT) was conducted for 5000 cycles with a scan rate of 50 mV s⁻¹ between 0.6 and 1.0 V (vs RHE) in N₂-saturated 0.1 M KOH, based on a US Department of energy ADT protocol [73]. Chronoamperometric (CA) testing was conducted at 0.65 V with a rotating rate of 1600 rpm in O₂-saturated 0.1 M KOH. The methanol-tolerance and the role of iron during the ORR process were performed by LSV curves in O₂-saturated 0.1 M KOH with using 10 mM KCN and 1 M CH₃OH, respectively.

Supercapacitor tests: We evaluated the supercapactive performance of the electrodes by using symmetrical two-electrode configurations in 6 M KOH and 1 M 1-ethyl-3-methylimidazolium tetrafluoroborate (EMI BF₄) in acetonitrile on a CHI660D electrochemical workstation. The working electrodes were prepared by pasting the slurry containing 90 wt% active materials, 5 wt% PTFE binder, and 5 wt% acetylene black that was mixed in the NMP solvent onto conducting carbon substrates as the current collector, drying overnight in a vacuum oven, and pressing at 10 MPa. The two identical electrodes were separated by a porous polypropylene membrane and were assembled into a 2025-type coin cell. Specific gravimetric capacitance, C, was calculated from discharge curves according to the following equation: $C = 2(I \times \Delta t)/(m \times \Delta V)$, where *I* is the discharge current, Δt is the discharge time, *m* is the mass of active material on each electrode, and ΔV is the operating voltage. Gravimetric energy density, E, and power density, P, based on two electrodes, was calculated according to the following equations: E = $C\Delta V^2/(8 \times 3.6)$ and $P = E/\Delta t$. We used electrochemical impedance spectroscopy (EIS) to calculate the equivalent series resistance (ESR) that was obtained from the highest frequency interception of the plots with the real axis [92], and charge transfer resistance (R_{ct}) that was obtained from the diameter of the semicircle in the high- to mediumfrequency region [88].

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

The data that support the findings of this study are available from the corresponding authors upon a reasonable request.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cej.2020.127601.

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