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Nitrified coke wastewater sludge flocs: attractive precursor for N, S dual-doped graphene-like carbon with ultrahigh capacitance and oxygen reduction performance[†]

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Abstract

The handling of a huge amount of sludge produced from industrial wastewater treatment plants is a critical issue. We report a facile and cost-effective pyrolysis approach to transform coke wastewater sludge flocs into valuable carbon materials that show the potential of being used in energy-storage devices and fuel cells. The nitrified sludge flocs are naturally rich in carbon, nitrogen, sulfur, and other inorganic particles and thus are attractive precursors for producing N, S dual-doped carbon with a hierarchical mesoporous graphene-like structure via the simple one-step pyrolysis method without the addition of external N- and/or S-containing organic compounds, chemical activation agents, or graphitization catalyst precursors. Owing to its unique features, the resulting nitrified sludge floc derived carbon (NSFC) exhibits outstanding capacitive performance. The specific capacitance determined in 1 M H₂SO₄ at a current density of 1 A g⁻¹ is 889 F g⁻¹, the highest among reported values for carbon-based materials in inorganic electrolytes, as far as we are aware. The NSFC also shows an excellent cycling stability with only 1.2% loss in capacitance after 10000 cycles at a current density of 20 A g⁻¹. The NSFC also achieves superior activity towards oxygen reduction reaction (ORR) and proves to be a promising metal-free ORR electrocatalyst showing comparable electrocatalytic performance, higher selectivity, and longer durability as compared to the commercial Pt/C benchmark.

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1. Introduction

The design and synthesis of heteroatom-doped carbon materials that are applicable in energy-related devices have been subjects for extensive investigation in recent years. Researchers have reached a consensus that doped carbons exhibit higher surface wettability, catalytic activity, and charge-storage capability compared to pristine carbons.^{1,2} For example, literature provides ample evidence that N-doped carbons are advantageous for use as electrode materials in supercapacitors³⁻⁶ or as electrocatalysts for oxygen-reduction reaction (ORR) in fuel cell cathodes.⁷⁻¹⁰ Further studies have also shown that the dual-doped carbon not only containing N but simultaneously incorporating S atoms offers more beneficial properties than merely N-doped carbon in the field of electrochemical applications.¹¹⁻¹⁴ The commonly adopted approach to synthesizing such heteroatom-doped carbon materials is pyrolysis or chemical vapor deposition of carbon-containing precursors such as organic monomers or polymeric molecules that are rich in N and S elements.¹¹⁻¹³ These precursors are expensive and non-environmentally friendly, and some are even toxic to human beings. The use of alternative materials that are naturally abundant and sustainable is thus desirable. Along this line, many recent attempts have been made to use biomass such as willow catkin,¹⁴ microorganisms,¹⁵ hemp,¹⁶ gelatin,¹⁷ soybean,¹⁸ coconut shell,¹⁹ cornstalk,²⁰ silk,²¹ human hair,²² and egg white⁴ as precursors for carbon materials with superior electrochemical performance.

The pyrolysis of biomass without any additional controls usually leads to the production of activated carbons with a nonporous structure (mainly particulate structure), a low surface area, and a low degree of graphitization (low conductivity), none of which are favorable features with respect to their application in supercapacitors or fuel cells. It has been reported that additional templates,^{17,22} activation chemicals,^{14-16,21} and metal catalysts¹⁹⁻²¹ have been amended and mixed with the precursors before pyrolysis, yielding heteroatom-derived carbon nanosheets with graphene-like morphology, which enable beneficial electrochemical properties. To further reduce the complexity of the preparation process and avoid expensive precursor systems, there is an urgent need to find a biomass precursor that is naturally rich in the aforementioned compounds.

Coke wastewater featured with complex composition is a typical industrial wastewater in China, with about $2.85 \times 10^8 \text{ m}^3$ per year released from coke plants.²³

The treatment of coke wastewater results in an estimate of $1.4 \times 10^5 \text{ m}^3$ of dewatered sludges as by-products, becoming huge hazardous solid wastes requiring further treatment and disposal. The current approaches to sludge management include landfilling and incineration, which suffer from the problems of high capital costs and secondary environmental pollution. Treating sludge as a resource for the recovery of materials or energy has received increasing attention from environmental and material scientists.^{24,25} One viable alternative to environmentally friendly sludge management is to utilize the sludge as a precursor for synthesizing carbon-based material, owing to its abundance of cellular biomass.^{8,26,27} In addition to carbon elements, the coke wastewater sludge (CWS) contains inherently large levels of nitrogen and sulfur atoms, most of which originate from the parent coal. These intrinsic features enable the CWS to be a potential precursor for synthesizing heteroatom-doped carbon materials. Likewise, the CWS contains inorganic nanoparticles to be utilized as templates for porous structure as well as inorganic salts as the activation agent and graphitization catalyst for hierarchical graphene-like morphology.

The aim of this work is to demonstrate that the CWS is an appropriate and attractive precursor for fabricating N, S dual-doped graphene-like carbons with a porous structure, meeting the requirements of sustainable sludge treatment and simultaneous recovery of energy-related carbon materials. To regulate and define the chemical compositions and morphology of the sludge and further the properties of the carbon material, the CWS is subject to acclimation with successive feedings of ammonium, so that nitrified CWS flocs are formed. These newly enriched flocs rich in nitrifying microorganisms are effective in transforming ammonium to nitrate, an important step in removing nitrogen in the wastewater. The graphene-like carbons derived from the nitrified CWS exhibit ultrahigh capacitance and oxygen-reduction performance due to the hierarchical graphene-like structure, appropriate pore size, and heavy N and S doping.

2. Experimental

2.1 Acclimation of nitrified coke wastewater sludge flocs

The initial activated sludge was collected from an aerobic tank in a local coke wastewater treatment plant (Shaoguan Iron & Steel Group Co., Ltd., Guangdong, China). The sludge was cultivated in a wide-mouth glass bottle (5 L) with air

93 bubbling. The medium included 0.1 M phosphate buffer solution (PBS, pH 7.5), 4.4 g
94 L^{-1} NaHCO_3 , 10 ml L^{-1} vitamin solution, and 10 ml L^{-1} mineral solution.²⁸ To obtain
95 mature sludge flocs able to efficiently and stably degrade ammonium, NH_4Cl was
96 successively added in increasing concentrations (i.e., 50, 100, 200, 300, 400 and 500
97 mg L^{-1} $\text{NH}_4^+\text{-N}$) for several cultivation periods. **Fig. S1** in the Supplementary
98 Information shows the variations in the concentration of $\text{NH}_4^+\text{-N}$ as a function of
99 cultivation time. It was revealed that a 480-hour cultivation completely transformed
100 500 mg L^{-1} $\text{NH}_4^+\text{-N}$ within 2.5 days, indicating that the sludge was successfully
101 acclimated with nitrifying microorganisms. Characterization by phase contrast
102 microscopy revealed that the ammonium-acclimated sludge exhibited a flocculent
103 morphology (see **Fig. S2** in the Supplementary Information). The SEM images (see
104 **Fig. S3** in the Supplementary Information) showed that in comparison to the initial
105 sludge, more numbers of microorganisms were available in the nitrified sludge flocs.

106 2.2 Synthesis of carbon from nitrified sludge flocs and physical characterizations

107 The resulting nitrified sludge flocs were dried in an oven at 65 °C, ground into
108 particles by an agate mortar, and sieved to 100 mesh. To synthesize nitrified sludge
109 floc carbon (NSFC), the dry particles were heated at 800 °C for 2 h in a tubular
110 furnace under an N_2 flow. Subsequently, the obtained black powder was washed with
111 HCl (volume ratio = 1:5) to remove inorganic residues. After centrifugation, the
112 powder was subject to a thorough rinse with deionized water until the pH value of the
113 washed water reached 7.0. The NSFC was prepared after the solid samples were dried
114 and sieved to 300 mesh. For comparison, the initial sludge flocs without ammonium
115 acclimation were also used as precursors for synthesizing carbon. The reference SFC
116 (without nitrification treatment) was synthesized according to the same procedures
117 described above.

118 The surface morphologies and structures of the resulting NSFC and SFC were
119 examined by a field emission scanning electron microscope (FESEM; Merlin, Zeiss
120 Co., Germany) and a transmission electron microscope (TEM; JEM-2100F, JEOL Ltd.,
121 Japan). The surface area was measured by the Brunauer-Emmertt-Teller (BET)
122 method, and the pore size was measured by the Barrett-Joyner-Halenda (BJH) method
123 through nitrogen adsorption-desorption isotherms at 77 K by a surface area and pore
124 size analyzer. Raman spectra were recorded on a LabRAM ARAMIS Raman
125 Spectrometer instrument using the Ar ion laser with an excitation wavelength of 514.5
126 nm. The electronic structure of the surface of the powders was examined by X-ray

photoelectron spectroscopy (XPS; ESCALAB 250Xi, Thermo Fisher Scientific Co., USA) with Al K α radiation (1486.6 eV). Elemental composition was determined by energy dispersive spectrometer (EDS; X-MaxN20, Oxford, UK) and XPS. The electrical conductivities of the resulting NSFC and SFC were measured by a standard four-point resistivity probe system (RTS-9, Guangzhou Four-probe Corporation, China).

2.3 Preparation of carbon-modified electrodes and electrochemical tests

The working electrode was a rotating disk electrode (RDE; diameter 3.0 mm) made of glass carbon (GC). Prior to use, the GC-RDE was sequentially polished with 1 μm , 0.3 μm , and 0.05 μm alumina ($\alpha\text{-Al}_2\text{O}_3$) powder, washed with deionized water, and ultrasonicated in ethanol and deionized water (each for 10 minutes). The NSFC or SFC samples of 8 mg amounts were dispersed in a mixed solution containing 200 μL of ethanol, 60 μL of Nafion (5 wt% diluted by water and 1-propanol, Dupont D520, USA) and 740 μL of deionized water. The catalyst ink was obtained upon vibration for 10 seconds and sonication for 15 min. A volume of 3.5 μL of the catalyst ink was dropped onto the clean GC-RDE surface with a microsyringe. When the solvent evaporated at ambient temperature, a thin carbon layer formed, indicating that the carbon-modified electrode was prepared. For comparisons, Pt (20%)/C catalysts were used as benchmarks. The commercial Pt/C (20 wt%, Johnson Matthey, USA) in an amount of 4 mg was dispersed in the same solution, and the Pt/C-modified electrode was prepared according to the same method.

All the electrochemical tests were conducted at ambient temperature with a CHI 660E Electrochemical Workstation (Chenhua Instruments, China). The three-electrode system was adopted for the electrochemical measurements, with the carbon-modified GC electrode, a saturated calomel electrode (SCE), and a Pt foil used as the working electrode, reference electrode, and counter electrode, respectively. The potentials reported throughout this paper refer to those of the SCE if not described otherwise. Cyclic voltammetry (CV) and galvanostatic charge/discharge (GCD) measurements were undertaken to determine the capacitive performance of NSFC or SFC in 1 M H_2SO_4 solution. CV was carried out over the potential range of 0-0.80 V with different scan rates from 10 to 200 mV s^{-1} . GCD was tested at various current densities in a range from 1 to 15 A g^{-1} . The specific capacitance (F g^{-1}) was calculated according to the following equation:

$$C = \frac{I_d \Delta t}{m \Delta V} \quad (1)$$

where I_d/m is the discharge current density normalized to the mass loading of carbon (A g^{-1}); Δt represents the discharge time (s); and ΔV refers to the potential change (V). Electrochemical impedance spectroscopy (EIS) was recorded in the frequency of 0.01 to 100 kHz at the open circuit potential with 5 mV amplitude. The stability of SFC or NSFC was tested by GCD run upon 10,000 cycles at 20 A g^{-1} .

The ORR activity was examined in alkaline media containing O_2 -saturated 0.1 M KOH solution by performing linear sweep voltammetry (LSV) measurements. LSV was carried out from +0.20 to -0.80 V at different rotation rates from 400 to 2500 rpm with a scan rate of 5 mV s^{-1} . To ensure that the environment was either oxygen-saturated or oxygen-free, O_2 or N_2 (99.999%) were aerated in the solution for more than 20 mins. The kinetic parameters such as the number of electrons transferred were calculated based on the Koutecky-Levich equations as shown below,

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

$$B = 0.62nFD^{\frac{2}{3}}\nu^{-\frac{1}{6}}C_{\text{O}} \quad (3)$$

where J , J_k , and J_L denote the measured, kinetic, and diffusion-limited current density (mA cm^{-2}), respectively; ω is the angular velocity of the rotating electrode (rad s^{-1}); n is the number of electrons transferred; F is the Faraday constant ($F = 96485 \text{ C mol}^{-1}$); D is the diffusion coefficient of O_2 in 0.1 M KOH solution ($D = 1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$); ν is the kinetic viscosity of the solution ($\nu = 0.01 \text{ cm}^2 \text{ s}^{-1}$), and C_{O} is the bulk concentration of O_2 ($C_{\text{O}} = 1.20 \times 10^{-3} \text{ mol L}^{-1}$). Comparisons between NSFC and Pt/C with respect to the ORR stability were evaluated by chronoamperometric measurements at a constant potential of -0.35 V at a rotation rate of 900 rpm in O_2 -saturated 0.1 M KOH solution for 8 h. The tolerance toward methanol was also compared by this method for 900 s, except for 3 M methanol injected at a certain moment.

3. Results and discussion

The morphology and microstructure of the resulting sludge floc derived carbon (SFC) and nitrified sludge floc derived carbon (NSFC) were characterized by the use of SEM and transmission electron microscopy TEM. It is observable from the SEM images (**Fig. 1a and b**) that both materials exhibit an interconnected porous network. The NSFC distinctly shows a hierarchical porous graphene-like structure, whereas

192 this morphology is less pronounced in the SFC. A hierarchical porous network is
193 expected to facilitate the adsorption and diffusion of the ions and reactants, thus
194 improving the electrochemical performance of the supercapacitors or the ORR
195 activity.^{12,21,29-31} The TEM images (**Fig. 1c and d**) further reveal that the NSFC is
196 composed of crimped nanosheets, being typical features of graphene. In contrast,
197 stacking structures with the presence of granular particles are seen from the surface of
198 the SFC. Similar graphene-like nanosheets were also obtained from the biomass
199 precursors^{19,21} through the pyrolysis process, in which ZnCl_2 and FeCl_3 were utilized
200 as a chemical activation agent and a graphitization catalyst precursor, respectively. In
201 our case, the inherently abundant iron and other metal ions (see Table S1 in the
202 Supplementary Information) in the coke wastewater sludge flocs should function as
203 the catalyst and activator, promoting the formation of graphene-like carbons. The
204 hierarchical and interconnected structure more distinctly observed from the NSFC
205 should stem from fairly dense and connective biofilms that are formed as a
206 consequence of sludge acclimation with ammonium (see **Fig. S3** in the
207 Supplementary Information).

208 The BET surface area and pore structure of the NSFC and SFC samples were
209 determined using N_2 adsorption-desorption isotherms. **Fig. 1e** shows that both the
210 curves exhibit type IV isotherms, featured with a distinct hysteresis loop at a relative
211 pressure P/P_0 in the range from 0.4 to 1. This clearly indicates the existence of
212 mesopores, as previously noted.^{12,15,21,29} Notably, the NSFC sample has a BET surface
213 area of $549.30 \text{ m}^2 \text{ g}^{-1}$ and a pore volume of $1.681 \text{ cm}^3 \text{ g}^{-1}$, larger than the 363.14 m^2
214 g^{-1} and $0.408 \text{ cm}^3 \text{ g}^{-1}$ related to the SFC sample, respectively. The hierarchical porous
215 NSFC sample exhibits an average pore size of 12.13 nm. It is assumed that the
216 mesoporous structure with a large pore size benefits the diffusion of electrolyte ions
217 and reactants, thus enhancing the high-density energy storage and the catalytic ORR
218 performance.^{12,18,21} **Fig. 1f** shows the Raman spectra of the prepared SFC and NSFC
219 samples. Both the spectra exhibit two distinct peaks, located at 1320 cm^{-1} and 1590
220 cm^{-1} , which are ascribed to the D (defects and disorder) and G (graphitic) bands of
221 carbon materials, respectively; they also show a weak broadened peak located at 2810
222 cm^{-1} , which is assigned to the 2D band characteristic for multilayer graphene
223 structures. The relative D/G band intensity ratio is an indicator of the graphitic degree.
224 The D/G intensity ratio related to the NSFC sample (1.03) is bigger than that (0.85)
225 associated with the SFC sample, which means that more defects are possibly caused

by higher levels of heteroatom doping (such as N and S) in the NSFC. The weak and broad 2D peak observed in the NSFC sample might also suggest a defective structure of graphene due to heteroatom doping.¹²

Fig. 1 The SEM images of the as-resulted SFC (a) and NSFC (b); the TEM images of the as-resulted SFC (c) and NSFC (d); Nitrogen adsorption/desorption isotherms of the SFC and NSFC samples (e); and Raman spectra of the SFC and NSFC samples (f).

The chemical composition of the samples characterized by XPS and EDS (**Fig. 2a** and **Table S1** in the Supplementary Information) confirmed the variations in the contents of C, N, O, and S between the NSFC and the SFC samples. For example, the XPS results suggested that the NSFC sample had a higher surface atomic concentration of N (7.43%) and S (3.42%) in comparison to the SFC sample (3.09% N and 1.71% S). The detection of peaks associated with Si and Ca elements in the

SFC indicated the presence of impurities; however, these elements were not detected from the NSFC. These results provide evidence that coke wastewater sludge acclimated with ammonium is an effective precursor, greatly enhancing the element contents of N and S and significantly removing the inorganic metal impurities in the resultant carbon materials. The SEM images (**Fig. S3** in the Supplementary Information) reveal a greater population of bacteria and lesser amounts of inorganic particles visible from the acclimated sludge flocs, which should explain the rarely detected inorganic impurities. The detection of high-content N and S demonstrates the successful preparation of carbon materials with the dual dopants. The high-resolution N 1s spectra (**Fig. 2b and c**) can be deconvoluted into three peaks located at 398.5, 400.8 and 401.7 eV, attributed to pyridinic (N-6), pyrrolic (N-5), and graphitic (N-Q) nitrogen, respectively.^{10,12-14} The abundance of the sum of N-6 and N-5 in the NSFC is 70.7%, higher than the 66.5% related to the SFC, suggesting that in the NSFC, more N atoms reside at the periphery of the graphene framework. This result is consistent with the Raman result revealing that more defect contents and fewer levels of graphitization are present in the NSFC in comparison to the SFC. The high-resolution S 2p spectra (**Fig. 2d and e**) can be fitted by three peaks located at 164.2 and 165.4 eV corresponding to thiophene-S (C-S-C) 2p_{2/3} and 2p_{1/2}, respectively and at 168.4 eV attributed to sulfoxide groups (-C-SO_x-C, x = 2,3,4).¹¹⁻¹⁴ The thiophene-S atoms account for up to 84.9% of the content in both the SFC and the NSFC samples, showing that S is predominantly bonded with the carbon frameworks. **Fig. 2f** summarizes the relative percentages of different components derived from peak-fitting of XPS, clearly illustrating their discrepancies between the SFC and NSFC samples.

The NSFC has a high electrical conductivity reaching about 280 S cm⁻¹, approximately two times larger than that of the SFC (142 S cm⁻¹). This should be mainly attributed to the pronounced porous graphene-like structure and high N and S contents in the NSFC. The above characterization results demonstrate that the resulting NSFCs achieve favorable features with respect to their application as electrode materials for supercapacitors and ORR. These include a hierarchical porous graphene-like structure, an appropriate pore size, and heavy N and S doping. Compared with previously reported routes that rely on pure chemicals to synthesize N, S dual-doped graphene, the nitrified coke wastewater sludge flocs were used as precursors to yield the desired products. These offer many advantages including (i)

the transformation of solid wastes into useful carbon materials, (ii) the elimination of the need for multiple hazardous organic precursors, (iii) the avoidance of the external addition of chemical activation agents, graphitization catalyst precursors, and templates for porous morphology, and (iv) the ease in scaling up.

Fig. 2 XPS survey spectra of the SFC and NSFC samples (a); the high-resolution N 1s XPS scan of SFC (b) and NSFC (c); the high-resolution S 2p XPS scan of SFC (d) and NSFC (e); and the relative content of different N and S species derived from peak-fitting of XPS.

The capacitive performance of the resulting materials was tested with a three-electrode system using CV and GCD techniques. **Fig. 3a and b** shows the CV curves of the SFC and NSFC electrodes at different scan rates (10, 20, 50, 100 and 200 mV s⁻¹). Both carbon electrodes exhibited good rate ability, evident from increased current density with the increases in the scan rate. The current density of the NSFC was higher than that of the SFC at all measured scan rates, suggesting the greater specific capacitance of the NSFC. It was clear that all the CV curves were composed of two parts: (i) a nearly rectangular shape representing electrochemical double-layer capacitance (EDLC) originating from interaction between the electrode surface and electrolyte ions and (ii) well-broadened peaks representing pseudocapacitance stemming from redox reactions. These Faradic peaks were more pronounced in the CV curves of the NSFC electrode, in good agreement with more

307 content of N and S atoms doped in this sample. It is well documented that the
308 abundance of N and S has an enhancing effect on pseudocapacitive performance,
309 owing to the redox reactions of pyrrolic nitrogen, and thiophenic-like sulfur.^{12,14}

310 All the GCD curves (**Fig. 3c and d**) at various current densities (1, 2, 3, 5, 10, and
311 15 A g⁻¹) were roughly linear and symmetrical, indicative of good capacitive behavior
312 and electrochemical reversibility. The small deviation from linearity further supports
313 the presence of a pseudocapacitive contribution. Consistent with the CV results, the
314 GCD tests demonstrated that the NSFC electrode had a much higher capacitance
315 compared to the SFC electrode, evident from the much longer time required for a
316 charge/discharge cycle at all measured current densities. The mass specific
317 capacitance for all the cases was calculated according to Equation (1). The retention
318 of capacitance as a function of current densities is an important parameter, indicating
319 the quality of an ideal supercapacitor. The plots in **Fig. 3c and d** suggest that both
320 electrodes showed a relatively high capacitance retention ability. The good retention
321 capability reflects the appropriate size distribution of mesopores accessible for ion
322 transport even at a higher current density.^{12,21} It should be stated that the specific
323 capacitance (889 F g⁻¹) of NSFC at 1 A g⁻¹ exceeds the theoretical value (520 F g⁻¹) of
324 EDLC of graphene.¹² This suggests that coke wastewater sludge acclimated with
325 nitrifying bacteria is an excellent precursor for synthesizing heteroatom-doped
326 graphene with ultrahigh capacitive performance. Comparisons of our results with
327 representative published data on N- and/or S-doped carbon materials were performed
328 and are listed in **Table 1**. The resulting specific capacitance of carbon materials is
329 highly sensitive to the precursor material and the preparation method as well as to the
330 doping level. Clearly visible is that our result outperforms most of the existing data. It
331 is comparable to the value in a recent report concerning the ordered mesoporous
332 few-layer carbon synthesized by the template-assisted chemical vapor deposition
333 (CVD) method.³ The ultrahigh capacitance of the NSFC can be explained by the
334 following synergistic effects. (i) The relatively high surface area not only provides
335 sufficient active sites accessed by electrolyte ions but also facilitates charges transfer
336 and charge capacity.^{21,35,36} (ii) The hierarchical mesoporous graphene-like structure
337 with a large pore volume enables facile adsorption and diffusion of electrolyte
338 ions.^{12,21,29} (iii) The richness in dual N and S doping introduces defects on the carbon
339 framework, which is favorable for the enhanced wettability and electrical
340 conductivity.^{12,14} (iv) The pyrrolic N and thiophene-S available in the NSFC can

contribute to the pseudocapacitance due to the fast Faradic reactions of these species.^{12,37,38}

Fig. 3 Capacitive performance determined using a three-electrode cell in 1 M H₂SO₄. CVs of the SFC (a) and NSFC (b) electrodes at different scan rates; GCD curves of the SFC (c) and NSFC (d) electrodes at different current densities and the variations of specific capacitance as a function of cycle number; Nyquist plots of the SFC and NSFC electrodes (e); and Cycle stability of the SFC and NSFC measured at a current density of 20 A g⁻¹ with the inset showing the specific GCD curves obtained from the 1st, 1000th, 5000th and 10000th cycles (f).

The EIS results show that a near-vertical curve is observed in the low-frequency region for both the SFC and NSFC electrodes (**Fig. 3e**), confirming a good capacitive

353 behavior. The diameter of a semi-circle in the high-frequency region represents the
354 charge transfer resistance; it is apparent that the NSFC electrode allows a faster
355 electron transfer as indicated by the smaller diameter. The long-term charge/discharge
356 tests (**Fig. 3f**) also reveal that both the NSFC and SFC electrodes display a good
357 cycling stability. The specific capacitance of the NSFC electrode at 20 A g⁻¹ remains
358 at 548 F g⁻¹, which is 98.9% of the initial value (554 F g⁻¹) after 10000 cycles.

359
360 **Table 1** Comparisons of the specific capacitance between this work with representative published
361 data on N and/or S-doped carbon materials.

Carbon material	Capacitance (F g ⁻¹)	Current density (A g ⁻¹)	Electrolyte	Reference
N-doped ordered mesoporous few-layer carbon	855	1	0.5 M H ₂ SO ₄	3
N-doped mesoporous carbon derived from protein	390	0.25	1 M H ₂ SO ₄	4
N-doped carbon fibers derived from eggshell membrane	284	0.2	1 M H ₂ SO ₄	32
N, S dual-doped graphene synthesized from graphene oxide and L-cysteine	566	0.5	6 M KOH	12
N, S dual-doped porous carbon nanosheets derived from willow catkin	298	0.5	6 M KOH	14
N, S dual-doped carbon flakes derived from human hair	340	1	6 M KOH	2
S-doped graphene obtained from graphite using electrochemical method in the present of sodium thiosulphate	320	3	3 M KOH	33
S-doped porous reduced graphene oxide via annealing of graphite oxide with dibenzyl disulfide	343	1	2 M KOH	34
S-doped mesoporous carbon fibres via carbonization of sucrose with MgSO ₄	150	1	6 M KOH	35
N, S dual-doped graphene-like carbon derived from nitrified coke wastewater sludge flocs	889	1	1 M H ₂ SO ₄	This work

362
363 Previous studies^{11,13,39,40} have shown that N, S dual-doped graphene obtained from
364 pure chemical precursors exhibits pronounced electrocatalytic activity towards ORR,
365 most possibly because the increased content of heteroatoms present in the graphitic
366 framework and the synergistic effects between the two dopants give rise to
367 non-electron-neutral carbon atoms with improved charge sites that favor the
368 molecular adsorption of oxygen and its reduction. The electrocatalytic performance of

the as-prepared SFC and NSFC samples as ORR electrocatalysts was investigated under alkaline conditions at room temperature by LSV and RDE tests.

Fig. 4a illustrates the LSV curves of the SFC, NSFC, and commercial Pt/C electrodes at an electrode rotation rate of 1600 rpm. No apparent electrochemical process was displayed in the N₂-saturated solution; in contrast, distinct ORR behaviors were observed for the SFC and NSFC electrodes in the O₂-saturated solution. The onset potential and the limited current density corresponding to the NSFC electrode were much higher than those of the SFC electrode (-0.04 vs. -0.10 V; 4.40 vs. 2.85 mA cm⁻²) and were comparable to those of the Pt/C electrode (-0.04 vs. -0.01 V; 4.40 vs. 4.42 mA cm⁻²). This observation provides evidence that the NSFC electrode has outstanding ORR electrocatalytic activity. The RDE measurements on the electrodes at a variety of rotation rates from 400 to 2500 rpm were performed to gain further insight into the reaction kinetics. As illustrated in **Fig. 4b**, the limiting current density increased with the increase in the rotation rate owing to the shorter diffusion distance at higher rotation rates. The Koutecky-Levich (K-L) plots resulting from the NSFC electrode at potentials ranging from -0.30 to -0.70 V displayed good linearity (**Figure 4c**). The number of electrons transferred was calculated according to Equations (2) and (3), showing a range from 3.71 to 4.18 (with an average close to 4.01), as shown in **Fig. 4d**. The RDE voltammograms of the Pt/C and SFC electrodes at various rotation speeds and the corresponding K-L plots are illustrated in Fig. S4 in the Supplementary Information, and the average number of electrons transferred according to the K-L equation was estimated to be 4.05 and 3.26 (-0.30 to -0.70 V), respectively (**Fig. 4d**). This demonstrates that the ORR on the NSFC electrode proceeds via a four-electron pathway similar to that on the Pt/C electrode. The direct reduction of oxygen to OH⁻ is highly desirable when the obtained carbon materials are utilized as the electrocatalysts.

395

Fig. 4 ORR performance determined using a three-electrode cell in 0.1 M KOH. (a) LSV curves of the SFC, NSFC and Pt/C electrodes in N_2 -saturated and O_2 -saturated solution at 1600 rpm; (b) RDE voltammograms recorded for the NSFC electrode at different rotation rates; (c) Koutecky - Levich plots of J^{-1} against $\omega^{-1/2}$ for the NSFC electrode at different potentials; (d) Calculated numbers of electron transfer for the SFC, NSFC and Pt/C electrodes; (e) $i-t$ chronoamperometric responses of the NSFC and Pt/C electrodes at 1600 rpm and -0.35 V upon the addition of 3 M methanol; and (f) durability evaluation of the NSFC and Pt/C electrodes at 1600 rpm and -0.35 V for 28800 s.

The chronoamperometric responses for the ORR upon the addition of methanol (3 M) were measured at the NSFC electrode and the Pt/C electrode. It can be seen from **Fig. 4e** that a slight decline was visible in the ORR current at the NSFC electrode; in contrast, an immediate and significant drop in the ORR current was observed at the Pt/C electrode. This indicates that the NSFC electrode is not sensitive to methanol toxicity. The stabilities of the NSFC electrode and the Pt/C electrode were also compared, as illustrated in **Fig. 4f**, showing variations in the ORR current over 28800 s when the electrode was poised at a potential of -0.35 V. The 28800 s-operation resulted in a 13.9% loss of the current at the NSFC electrode, while this value rose to 27.2% at the Pt/C electrode. These results demonstrate that the NSFC electrode is more advantageous than the Pt/C electrode for the ORR in terms of higher stability and selectivity. The outstanding ORR performance of the NSFC can be attributed to the high porosity and surface area of the graphene-like structure, good electrical conductivity and heavy levels of dual N- and S-doping.^{11,13,39} In addition, the high content of pyridinic-N is beneficial to the ORR activity by improving the onset potential, and the high content of graphitic N is favorable for increasing the limited current density and stability.^{7,41,42} Previous studies⁴³⁻⁴⁵ have also shown that the introduction of S to N-doped carbon can result in the increase in the amounts of pyridinic-N, induce the spin/charge density asymmetry and thus lead to the synergistic effect of N and S, which enhances the electrocatalytic activity toward the ORR.

427

4. Conclusion

We have demonstrated that coke wastewater sludge flocs upon acclimation with ammonium are attractive precursors for producing N, S dual-doped carbons with ultrahigh capacitance and oxygen-reduction performance. A facile and cost-effective pyrolysis approach was adopted for the synthesis, without the addition of external N- and/or S-containing organic compounds, chemical activation agents, or graphitization catalyst precursors. The as-obtained NSFC exhibited a unique hierarchical mesoporous graphene-like structure rich in N (7.43%) and S (3.42%) doping, relatively high surface area (549.30 m² g⁻¹) and pore volume of (1.681 cm³ g⁻¹), and high electrical conductivity (280 S cm⁻¹). These favorable characteristics suggest that these NSFCs are promising electrode materials for supercapacitors and are metal-free catalysts for ORR. The NSFC electrode showed a high specific capacitance of

889 F g⁻¹ at the current density of 1 A g⁻¹ and an excellent cycling stability (with less than a 1.2% loss after 10000 cycles) in 1 M H₂SO₄ solution. When tested as the carbon catalyst for ORR in alkaline electrolytes, it exhibited comparable catalytic activity to the commercial Pt/C catalyst in terms of the close onset potential and kinetic-limiting current and four-electron transfer process. High tolerance to methanol toxicity and superior stability were also achieved for the NSFC electrode. Considering that 1.4 × 10⁵ m³ of dewatered sludges are produced from coke wastewater treatment plants per year in China, the current research work provides a new strategy to transform the solid wastes into promising carbon materials that can find applications in supercapacitors, fuel cells, lithium ion batteries, photocatalysis, and wet oxidation for pollutant removal.

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The N, S dual-doped graphene-like carbons synthesized from coke wastewater sludge flocs exhibit ultrahigh capacitance and outstanding oxygen reduction performance.