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Facile Preparation of N-doped Mesocellular Graphene Foam from Sludge Floccs for Highly Efficient Oxygen Reduction Reaction

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Using environmental wastes to produce energy materials is extremely attractive for economic social development. Herein, sludge floccs (SF), a kind of environmental wastes which are difficult to be disposed, were used as carbon and nitrogen source for the preparation of N-doped mesocellular graphene foam (SF-NMGF) via a simple one-step pyrolysis. Originated from the special composition and structure of SF, the obtained SF-NMGF had large Brunauer-Emmett-Teller surface areas, graphitic frameworks surrounded by ultrathin nanosheets, foam-like mesopores with size centered at about 15 nm, and homogeneous nitrogen incorporation with high percentage (40.5 at%) of graphitic nitrogen. Owing to these unique properties, SF-NMGF showed excellent electrocatalytic activity with 4e as a metal-free catalyst for the oxygen reduction reaction (ORR). Specifically, the prepared SF-NMGF catalyst exhibited high diffusion-limited current, superior durability and better immunity towards methanol crossover for ORR in alkaline solution than a commercial 20 wt% Pt/C catalyst. More importantly, the synthesis of SF-NMGF can be scaled up with low cost, which will be beneficial for both the sludge handling and development of ORR materials.

Introduction

Encompassing environment and energy concerns, recycling of environmental wastes to produce energy materials is extremely attractive for economic social development, because it can meet the increasing energy demands based on improving the quality of our environment but without depleting our natural resources^{1,2}. However, owing to lack of effective strategies, very few work has been done to build a solid bridge between the environmental needs and the energy development^{3,4}, which therefore should be considered from both aspects.

For the environment, sludge is a major byproduct produced from wastewater treatment plants worldwide⁵. Its disposal has been recognized as an ecological burden by the society owing to its harmful components of heavy metals and pathogens^{6,7}. Although some traditional routes including ocean discharge, incineration, composting and land application have been developed for the sludge disposal, they are still suffered from either high capital cost or adverse environmental impacts^{8,9}. Hence, the challenge for sludge management has spurred industries to search for more environmentally-benign sustainable techniques for sludge handling.

For the energy, fuel cells are the most promising clean energy generation devices for which electrocatalysts are crucial for the oxygen reduction reaction (ORR)^{10,11}. Unfortunately, traditional Pt-based materials, which have been

regarded as superior ORR electrocatalysts for a long time, are often spurned away for practical applications due to the high cost, limited availability and insufficient durability^{12,13}. Recently, as an alternative to Pt-based catalysts, metal-free nitrogen-doped carbon materials such as graphene¹⁴, carbon nanotubes¹⁵ and mesoporous carbon¹⁶, have become an active field of research for ORR, owing to their low cost, excellent electrocatalytic activity, fuel crossover effect and good durability. However, nitrogen-doped carbon electrocatalysts are usually fabricated using expensive carbon sources and labor-intensive post-doping^{17,18}, which consequently increase the cost and unavoidably cause ununiformed doping or damage to the synthesized carbon structures¹⁹. What's worse, the pyrolysis of common carbon sources usually result in non-porous and low graphitized materials (low surface area/pore volume and low conductivity) due to the absence of template effect and metal catalysis, respectively^{20,21}.

Considered from the above two aspects, the recycling of sludge or its derivatives to produce ORR electrocatalysts will be highly practical and attractive. First, the microorganisms in sludge are potential C and N sources for N-doped carbon materials. Second, sludge contains a few heavy metals, which will act as catalysts for the graphitization of N-doped carbon materials. Third, sludge is rich in inorganic nanoparticles, which will act as the template for porous materials with large surface area. More importantly, sludge or its derivatives, as environmental wastes with difficulty to be disposed, are very cheap and plentiful. The utilization of sludge to produce ORR electrocatalysts will be also a more environmentally-benign sustainable technique for sludge handling.

Therefore, in this work, sludge floccs (SF), a kind of spongy sludge derivative with much more microorganism (Figure S1A-C), were used for the synthesis of N-doped mesocellular graphene foam via the simple one-step pyrolysis at 900 °C under N₂ atmosphere. The SF-derived N-doped mesocellular graphene foam (SF-NMGF) had foam-like mesopores with

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large surface area and graphitic framework with uniformed doping. As an electrocatalyst for ORR, SF-NMGF showed excellent catalytic activity, stability and tolerance to methanol poisoning effects in alkaline media. This work would provide a robust strategy to bridge the environmental needs and the energy development.

Experimental

Reagents and apparatus

Reagents for cultivation such as $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, NaHCO_3 , CaCl_2 , etc., were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). Nafion aqueous was purchased from Sigma-Aldrich (St. Louis, MO, USA). All the chemicals were used without further purification. KOH solution (0.1 M) was used as the electrolyte. Double-distilled water were used for all experiments.

Transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), scanning transmission electron microscopy (STEM), energy dispersive X-ray (EDX) spectroscopy/mapping experiments were performed on JEM-2010 instruments with an acceleration voltage of 200 kV. The samples were dispersed in ethanol and supported on a holey carbon film on a Cu grid for TEM observation. Scanning electron microscopy (SEM) was performed on a Hitachi S-4800 scanning electron microscope operating at 20 kV. X-ray diffraction (XRD) measurements were obtained on a PANalytical X'pert PRO diffractometer with $\text{Cu K}\alpha$ radiation at a scanning rate of $4^\circ/\text{min}$ in the 2θ from 10 to 80° . Raman spectra were performed on a Labram-1B (Dilor, France) confocal microscopy Raman spectrometer with a 632.8-nm wavelength incident laser light. Thermogravimetric analysis (TG) and derivative Thermogravimetry (DTG) were acquired on a Pyris Diamond TG/DTA thermo-gravimetric analyzer (Perkin Elmer Thermal Analysis). N_2 adsorption-desorption isotherms at 77 K and pore size distribution curves were measured using Tristar 3000 systems. The samples were outgassed for more than 5 h at 250°C before the measurements were performed. X-ray photoelectron spectroscopy (XPS) was carried out on a RBD upgraded PHI-5000C ESCA system (Perkin Elmer) with $\text{Al K}\alpha$ radiation ($h\nu = 1486.6$ eV) as the X-ray source for excitation. Optical photographs were taken using a common Canon camera. Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) for the inorganic elements analysis was carried on a Thermo E. IRIS Duo ICP-AES instrument, while some organic elements analysis was performed on Vario EL cube elemental analyzer.

Electrochemical experiments

Electrochemical experiments including linear sweep voltammetry (LSV) and amperometry were carried out on CHI 660E electrochemical workstation (Chenhua, Shanghai, China). All electrochemical experiments used a conventional three-electrode electrochemical system which consisted a working electrode, a Pt foil auxiliary electrode and a saturated calomel electrode. A glassy carbon rotating disc electrode (GCRDE) was

used as the basal working electrode. All experiments were performed in 0.1 M KOH.

Synthesis of SF-NMGF

Sludge flocs (SF) were first prepared from the waste active sludge in the wastewater treatment plants. Typically, SF obtained from the sequencing batch reactor (SBR) used for cultivation of aerobic granules fed with the synthetic wastewater, as shown in Table S2. The procedure of cultivation has been reported in a previous work²². This bioflocs was actually an intermediate product from activated sludge to aerobic granules, largely produced in the initial phase of cultivation, which was frequently washed out from the reactor. Therefore, this abandoned biomass was recycled to prepare the graphene materials in this paper. Raman spectra showed SF didn't contain any graphitic carbon before pyrolysis (Figure S1) due to no peaks. XRD demonstrated that there were some crystallized inorganics since the presence of a few small diffraction peaks (Figure S2), while the results of XPS, ICP-AES and elements analysis revealed that SF was composed of major C, O, H, N, Ca, Na elements and minor P, S, Mg, K, Fe, etc. elements (Figure S3 and Table S3).

For the synthesis of SF-NMGF, the dry SF were placed in a pipe furnace and carbonized for 5 h at 900°C under N_2 atmosphere. The recovered black powders were dispersed and stirred in HCl solution to remove the inorganic nanoparticles and some metal nanoparticles such as Fe. After centrifugation, washing and drying, SF-NMGF were obtained.

Preparation of modified electrodes and electrochemical test

Prior to use, the GCRDE was polished with 0.3 and $0.05\ \mu\text{m}$ $\alpha\text{-Al}_2\text{O}_3$ powder until a mirror-shiny surface was obtained, then ultrasonicated in ethanol and doubly distilled water for 10 min, respectively. Finally, it was dried in the stream of high purity nitrogen for further use. SF-NMGF samples (2 mg) were dispersed in a solution containing 768 μL of double distilled water, 32 μL of 5 wt% Nafion aqueous solution and 200 μL ethanol. A homogenous catalyst ink could be obtained through ultrasonating the above mixture. Then 10 μL of the resulting catalyst ink was dropped onto the cleaned GCRDE surface to prepare SF-NMGF/GCRDE and the modified electrode was allowed to dry under an infrared lamp for 10 min. The obtained modified electrodes were preserved in a refrigerator at 4°C after being washed with doubly distilled water. The same method was used to prepare Pt/C/GCRDE.

Results and discussion

Characterization of SF-NMGF hybrid

The representative TEM image of the SF-NMGF was shown in Figure 1A. SF-NMGF exhibited a vesicle shape, which is similar with the morphology of microorganisms in SF (Figure S4D). Magnified TEM images showed that SF-NMGF was made up of many ultrathin nanosheets (Figure 1B and Figure S5A, B), which was coincided with the graphene. STEM images demonstrated that the nanosheets interleaved each other to

form foam-like mesopores (Figure 1C and Figure S5C), which were also similar to spongy structures composed by numerous microorganisms in SF (Figure S4C,D). HRTEM images further revealed the mesocellular pores in SF-NMGF (Figure 1D). Moreover, the carbon framework of SF-NMGF was graphitized since well-resolved lattice fringes, attributing to (002) planes of graphitic carbon (graphene)²³, was clearly observed in HRTEM images (inset in Figure 1A and Figure S5D). This can be further validated by: (1) X-ray diffraction (XRD) results (Figure S6A), which exhibited two typical (002) and (100) reflections of graphitic carbon at 2 θ values of 24.7° and 43.6°, respectively, similar to the reduced graphene²⁴, (2) Raman spectrum (Figure S6B), which gave obvious signals similar to the symmetry A_{1g} mode and E_{2g} mode of graphitic carbon atoms at 1346 cm⁻¹ (D-band), 1580 cm⁻¹ (G-band), and 2810 cm⁻¹ (2D-band), respectively²⁵, and (3) TG/DTG curves (Figure S6C), which indicated that the air-heated SF-NMGF sample did not rapidly decompose by combustion until the temperature exceeded 450 °C²⁶

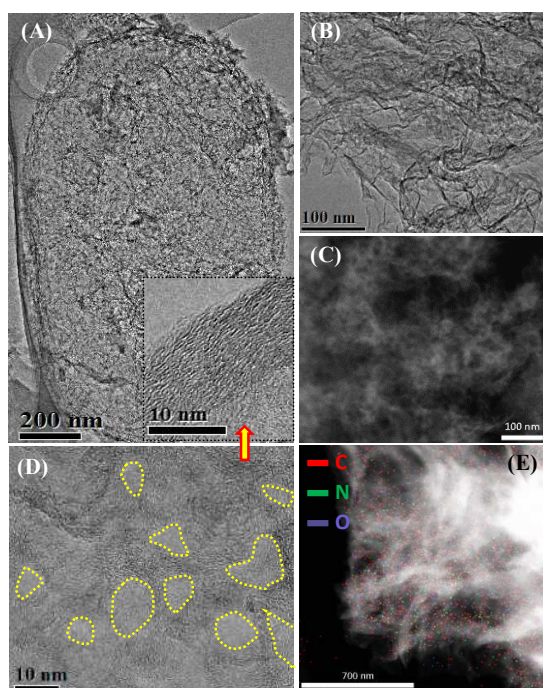


Figure 1. (A, B) TEM images of SF-NMGF with different magnifications. (C) STEM image of SF-NMGF. (D) and the inset in A) HRTEM images of SF-NMGF. (E) EDX mapping of SF-NMGF. More interestingly, from the element mapping (Figure 1E and Figure S7A-D) and the EDX-pattern (Figure S7E), it could be

inferred that SF-NMGF contained carbon, nitrogen and oxygen elements, while nitrogen was homogeneously doped in the carbon network. All these results illuminated that the prepared SF-NMGF was N-doped mesocellular graphene foam with graphitization. And the SF-NMGF had a BET surface area of 370 m²/g, pore volume of 0.69 cm³/g and a major pore diameter centered around 15 nm, as demonstrated by the typical IV N₂ adsorption–desorption isotherm and the pore size distribution curve (Figure 2A).

Based on the above observations, the formation of N-doped mesocellular graphene by using SF can be deduced as shown in scheme 1. As the potential carbon and nitrogen sources, numerous microorganisms (bacteria) in SF were assembled around the inorganic nanoparticles (the inorganic elements and their contents were shown in Table S1), to form spongy aggregates. Notably, as the added nutrition of microorganisms from active sludge to sludge flocs (Table S2)²⁷, the Fe³⁺ ionic would also be adsorbed in microorganisms, which might subsequently transform into the embedded Fe nanoparticles in the microorganisms. After calcination at 900 °C under N₂ atmosphere, the C and N-contained microorganisms, especially their membranes, would transform into N-doped carbon.

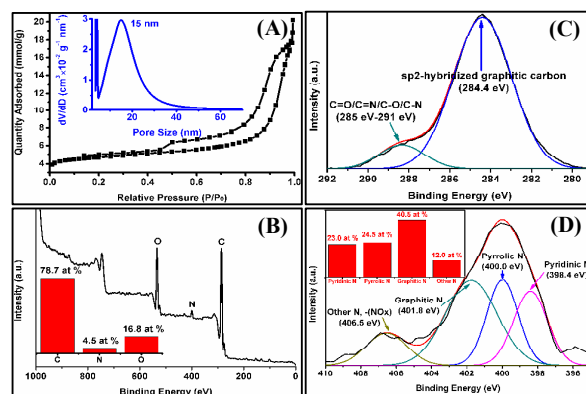
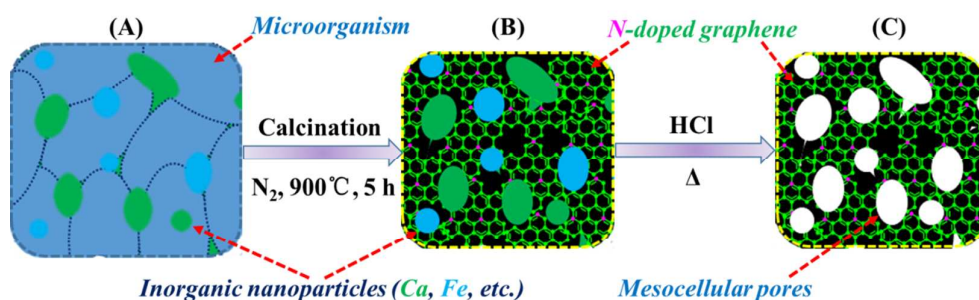


Figure 2. (A) N₂ adsorption-desorption isotherms and corresponding pore size distribution curve (inset in A) of SF-NMGF. A sharp increase of nitrogen absorption at a high relative pressure confirmed the existence of mesocellular pores in SF-NMGF. (B) XPS survey of SF-NMGF, and the inserted chart showed the percentages of carbon, nitrogen and oxygen according to XPS data. (C) High resolution C1s XPS spectra of SF-NMGF. (D) High resolution N1s XPS spectra of SF-NMGF, and the inserted chart showed the content of different types of nitrogen in SF-NMGF.



Scheme 1. Preparation of SF-NMGF by using sludge flocs as precursors. (A), (B) and (C) represented the sludge flocs, inorganic nanoparticles contained SF-NMGF and pure SF-NMGF, respectively.

Meanwhile, the inorganic nanoparticles in SF may act as solid supports to prevent the fusing of carbon, and then result in the formation of nanosheets and mesocellular pores upon being removed in HCl solution (Experimental section). More importantly, metal Fe nanoparticles could also act as the catalyst for the graphitization of carbon nanosheets (graphene)²⁸. Therefore, SF are very appropriate precursors for the N-doped mesocellular graphene foam, and SF-NMGF can be simply prepared in large scale.

Further characterizations of SF-NMGF by X-ray photoelectron spectroscopy (XPS) were shown in Figure 2B-C. The survey spectrum (Figure 2B) showed three typical peaks of C1s, N1s, and O1s, and the corresponding atomic percentages of C (78.7 at%), N (4.5 at%) and O (16.8 at%) could be reached (inset in Figure 2B). The C1s high resolution spectrum was deconvoluted into a dominant peak at 284.4 eV and a small broad peak at 285 - 291 eV (Figure 2C), which could be indexed as the sp^2 -hybridized graphitic carbon and carbon bonded oxygen/nitrogen configurations, respectively^{29, 30}. The N1s high resolution spectrum revealed that SF-NMGF had been doped with four relative nitrogen species of pyridinic (398.4 eV), pyrrolic (400.0 eV), graphitic (401.8 eV) and other nitrogen (406.5 eV)³¹. Their corresponding atomic percentages were 23.0 at%, 24.5 at%, 40.5 at% and 12.0 at%, respectively (Figure 2D). The large amount of graphitic-N in SF-NMGF could be attributed to the effect of Fe iron-coordinated pyrolysis, which would also be able to improve the catalytic activity of ORR^{28, 32}.

Electrocatalytic properties toward ORR

Owing to the unique graphitic and mesocellular porous structure as well as high active N doping, SF-NMGF was expected to be a highly efficient ORR electrocatalyst. Thus, SF-NMGF hybrid modified glassy carbon rotating disk electrode (SF-NMGF/GCRDE) measurement was performed to investigate the ORR activities. For comparison, commercial 20 wt% platinum on carbon black (Pt/C) was also measured. As shown in Figure 3, compared to Pt/C, the ORR onset potential for the SF-NMGF only had a 50 mV deviation from Pt/C, and had a higher diffusion-limited current density than Pt/C.

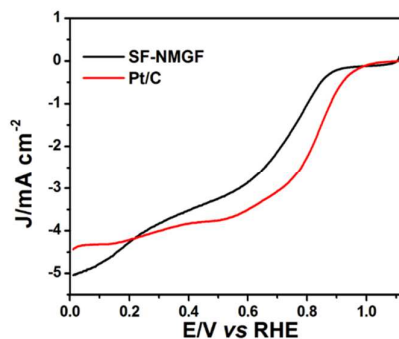


Figure 3. LSVs of different materials in O₂-saturated 0.1 M KOH with a sweep rate of 5 mV/s at a rotation rate of 1600 rpm.

This indicates that the product has a comparable electrocatalytic activity to the commercial Pt/C in the alkaline media. Up to now, some metal-free catalysts for ORR have already been reported^{33, 34}. However, most of the catalysts still exhibit weaker activity than that of commercial 20% Pt/C in alkaline media. The improved catalytic performance observed from the metal-free SF-NMGF produced in the present study might be attributed to the following two reasons: (1) the high percentage of graphitic-N in SF-NMGF, which has been demonstrated beneficial to ORR³⁵, (2) foam-like mesopores with large surface area and graphitic framework with uniformed N-doping, which offer a high probability for the exposure of active sites. All these favorable features might contribute to high rates of oxygen reduction.

Kinetics, stability and selectivity study

To explore ORR in a more quantitative manner, the voltammetric profiles in O₂-saturated 0.1 M KOH as the electrolyte showed that the current density was enhanced by an increase in the rotation rate (from 225 to 2025 rpm, Figure 4A). The transferred electron number per oxygen molecule involved in the ORR process was further determined by the Koutecky-Levich equation, which relates the current density J to the rotation rate of the electrode ω :

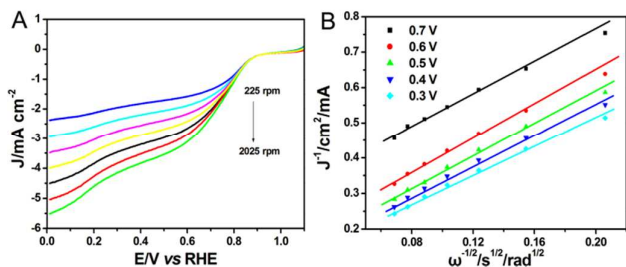


Figure 4. (A) LSVs of SF-NMGF/GCRDE at different rotating rates in 0.1 M KOH solution saturated with O₂. (B) K-L plots of j^{-1} vs. $\omega^{-1/2}$ obtained from the LSV data at different potentials.

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

$$B = 0.62nFC_0D^{2/3} \nu^{-1/6} \quad (2)$$

$$J_K = nFkC_0 \quad (3)$$

where J is the current density, J_K and J_L are the kinetic- and diffusion-limited current densities, ω is the angular velocity of the disk ($\omega = 2\pi N$, N : the rotation frequency), n is the overall number of electrons transferred upon oxygen reduction, F is the Faraday constant ($F = 96485 \text{ C mol}^{-1}$), D is the diffusion coefficient of O₂ in 0.1 M KOH electrolyte ($1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$), C_0 is the bulk concentration of O₂ ($1.2 \times 10^{-3} \text{ mol L}^{-1}$), ν is the kinetic viscosity of the electrolyte ($0.01 \text{ cm}^2 \text{ s}^{-1}$), and k is the electron transfer rate constant. The Koutecky-Levich curves were plotted for different potentials in the Figure 4B. The parallel and straight fitting lines of J^{-1} vs $\omega^{-1/2}$ imply a first-order reaction toward dissolved oxygen. The n value for the SF-NMGF hybrid was derived to be 4.6, 4.3, 4.1, 4 and 4.2 at the potential of 0.3 V, 0.4 V, 0.5 V, 0.6 V and 0.7 V, respectively. These results suggested a four-electron process for ORR on the SF-NMGF hybrid electrode, are similar to ORR catalyzed by a high-quality commercial Pt/C catalyst measured in the same 0.1 M KOH electrolyte. This excellent performance may contribute to the high content of quaternary-N enhanced the catalytic performance by HO• radicals as intermediates.^{36, 37}

The ideal catalyst for ORR should exhibit satisfactory tolerance to the fuel molecule (for example, methanol). Therefore, the catalyst was exposed to fuel molecules for testing possible crossover effects, as shown in Figure 5A.

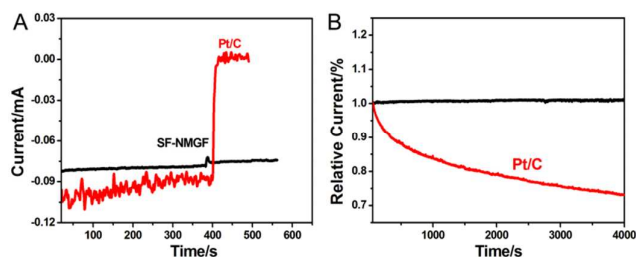


Figure 5. (A) Chronoamperometric responses of SF-NMGF and Pt/C electrodes in O₂-saturated 0.1 M KOH with rapid addition

of 2 M methanol. (B) Chronoamperometric responses (percentage of current retained versus operation time) of SF-NMGF and Pt/C electrodes kept at 0.70 V versus RHE in O₂-saturated 0.1 M KOH.

A sharp decrease in current was observed for the Pt/C electrocatalyst upon addition of 2.0 M methanol. However, the SF-NMGF electrocatalyst did not show obvious change after the addition of methanol. This indicated that the SF-NMGF had higher selectivity toward ORR than the commercial Pt/C.

The stability of SF-NMGF/GCRDE was tested and compared to a reference Pt/C catalyst at a constant voltage of 0.75 V for 4000 s in an O₂-saturated 0.1 M KOH solution (Figure 5B). The activity normalized to the initial activity as a function of time served as a criterion for catalyst stability. Over 4000 s, the ORR activity of SF-NMGF catalysts maintained nearly all of their initial values, which is an exciting result for further applications in alkaline fuel cells. However, the commercial Pt/C catalyst suffered a significant 25% decrease in current density over 4000 s of continuous operation in 0.1 M KOH, exhibiting obvious decay in activity over time. This result suggested that the stability of SF-NMGF catalysts was superior to that of the Pt/C catalyst.

Conclusions

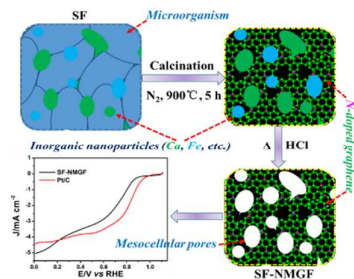
A facile and low cost pyrolysis strategy was used for the high-yield synthesis of N-doped mesocellular graphene foam (SF-NMGF) with high quality. This is an environmental compensation method using waste sludge flocs as the sole starting material without any synthetic chemicals. The obtained SF-NMGF had a high BET surface area, abundant mesocellular pores, graphitic frameworks, homogeneous nitrogen incorporation with high percentage (40.5 at%) of graphitic-N, and exhibited high electrocatalytic activity, operational stability and methanol-tolerance for ORR. This work validated the feasibility using environmental wastes as the starting materials to produce high quality and high performance carbon-based energy materials in large scale and low cost, which therefore might be a potential bridge between the environment needs and the energy development.

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In this work, sludge flocs (SF), a kind of environmental wastes which are difficult to be disposed, were exploited for the preparation of high-quality N-doped mesocellular graphene foam (SF-NMGF) via a simple one-step pyrolysis. The obtained SF-NMGF material exhibited high electrocatalytic activity, operational stability and methanol-tolerance for ORR.