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Title: Sulfur–nitrogen co-doped three-dimensional carbon foams with hierarchical pore structures as efficient metal-free electrocatalysts for oxygen reduction reactions

Novel 3D sulfur–nitrogen co-doped carbon foams with hierarchical pore structures have been fabricated using a convenient, economical, and scalable method. The 3D S–N–CF exhibits better catalytic activity, longer-term stability and higher methanol tolerance than a commercial Pt/C catalyst.

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See Yang *et al.,* Nanoscale, 2013, **5**, 3283.

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Registered Charity Number 207890

Nanoscale

PAPER

RSCPublishing

View Article Online View Journal | View Issue

Cite this: Nanoscale, 2013, 5, 3283

Received 9th December 2012 Accepted 14th February 2013

DOI: 10.1039/c3nr34003a

www.rsc.org/nanoscale

Introduction

The oxygen reduction reaction (ORR) is one of the most important reactions in energy conversion systems such as fuelcells and metal-air batteries.¹ Platinum-based materials are known to be the most active catalysts for ORRs. The high cost, limited supply, and weak durability of platinum catalysts are the greatest barriers to large-scale industrial applications of fuelcells. Extensive efforts have been devoted to reducing the amounts of Pt-based catalysts used or replacing them.²⁻⁵ In particular, the ongoing search for new non-precious-metal catalysts (NPMCs) with excellent electrocatalytic performances for ORRs has attracted increasing interest.^{4,5} In this regard, metal-free heteroatom-doped carbon materials have been the most popular choice because of their excellent electrocatalytic performances and relatively low costs.⁵⁻¹⁷ Despite the good progress in developing metal-free carbon catalysts, the current

Sulfur-nitrogen co-doped three-dimensional carbon foams with hierarchical pore structures as efficient metal-free electrocatalysts for oxygen reduction reactions†

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Despite the good progress in developing doped carbon catalysts for oxygen-reduction reaction (ORR), the current metal-free carbon catalysts are still far from satisfactory for large-scale applications of fuel cell. Developing new metal free doped carbon materials with abundance active sites as well as excellent electron transfer and reactant transport rate towards ORR may be a potential solution. Herein, we develop a novel three-dimensional (3D) sulfur-nitrogen co-doped carbon foams (S-N-CF) with hierarchical pore structures, using a convenient, economical, and scalable method. The experimental results have demonstrated that the obtained 3D S–N–CF exhibited better catalytic activity, longer-term stability and higher methanol tolerance than a commercial Pt/C catalyst. Such excellent performances may be attributed to the synergistic effect, which includes high catalytic sites for ORR provided by high S-N heteroatom loading, excellent reactant transport caused by hierarchical pore structures and high electron transfer rate provided by 3D continuous networks. Our results not only develop a new type of catalysts with excellent electrocatalytic performance by a commercially valid route, but also provide useful information for further clarification of the relationship between the microstructures of metal-free carbon materials and catalyst properties for ORR. More importantly, the idea to design hierarchical pore structures could be applied to other catalytic materials and serve as a general strategy for improving the activity of various ORR catalysts.

> metal-free carbon catalysts are still far from satisfactory for large-scale practical applications. The development of commercially valid metal-free carbon catalysts with pronounced catalytic activity is still a problem. To address this issue, two strategies, namely "microscopic structure" and "mesoscopic morphology" control of these metal-free carbon materials, have been proposed.12 "Microscopic structure control" mainly involves structural adjustment at the atomic scale of doped carbon materials. In this strategy, improving the heteroatom content, tuning the heteroatom bonding configurations, such as C-N bonds, and introducing other heteroatoms (e.g., B, P, S, Se, and I) into carbon materials have been confirmed to be effective for activity enhancement in ORRs.7-11 Very recently, carbon materials doped with dual or multi heteroatoms have also been developed. The synergistic effect arising from codoping of heteroatoms significantly improves the ORR activity.13-15 This also suggests that dual or multi heteroatom doping may be an ideal pathway to improve ORR activity. Among another strategy involving "mesoscopic morphology control", tuning to give high surface areas and adjusting the pore sizes of metal-free carbon materials are now the most active research topics. Recently, incorporation of C₃N₄ into a

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[†] Electronic supplementary information (ESI) available. See DOI: 10.1039/c3nr34003a

mesoporous (~8 nm) carbon was confirmed to enhance the electron transfer efficiency of C₃N₄ (ref. 16). Some metal-free heteroatom-doped ordered mesoporous carbons also show excellent electrocatalytic performance.^{6,16} More recently, Liang et al. reported that a macroporous structure greatly facilitated reactant transport, and C₃N₄/C catalysts with ordered pores of about 150 nm showed the highest ORR performances.17 According to the previous report, the macropores can serve as a buffering reservoir where the electrolyte can shorten the diffusion distances to the interior surfaces, while the mesopores can provide a large accessible surface area for ion or charge transport.18 These factors also motivate our curiosity to see what happens when the macroporous and mesoporous structures coexist in doped carbon materials. The development of doped carbon materials with hierarchical pore structures for ORR may be of both scientific and practical significance.

Carbon foam is a classical low-density carbon material with a continuous three-dimensional (3D) network and abundant pore structures. Carbon foams have been widely used as electrode materials such as supercapacitors and catalyst supports because of their good electrical conductivity and unique microstructure.^{19,20} Considering the structural characteristics of carbon foam and the advantages of dual heteroatom doping described above, it is believed that developing new co-doped carbon foams with hierarchical pore structures for ORRs may be a potential solution to obtaining NPMCs with suitable properties for fuel-cell applications. Although many investigations involving heteroatom-doped carbon foams with hierarchical pore structures have been reported, research into co-doped carbon foams with hierarchical pore structures as ORR catalysts is still rare.

Herein, we demonstrate the successful fabrication of 3D sulfur-nitrogen co-doped carbon foams (S-N-CF) with hierarchical pore structures, using a convenient, economical, and scalable method. Our work gives a new type of 3D carbon foam as an ORR catalyst with several advantages, as follows. First, the resulted S-N-CF with hierarchical pore structures and 3D networks shows exhibited better catalytic activity, longer-term stability and higher methanol tolerance than a commercial Pt/C catalyst in alkaline media. Second, the S-N-CF shows a relatively high heteroatom loading (N: 6.53%; S: 2.88%) and hierarchical pore structures. The heteroatom loadings and the pore sizes can be easily adjusted by simply changing the synthetic parameters. The high heteroatom loading for S-N-CF can provide larger numbers of active sites. The hierarchical pore structures and 3D networks ensure an excellent electron transfer and reactant transport rate towards ORR. Third, in our experiments, all of the raw materials such as SBA-15, sucrose, and thiourea (TH) are common and cheap. This S-N-CF is suitable for large-scale preparation for industrial applications.

Experimental section

Synthesis of S-N-CF

Conventional ordered mesoporous silica SBA-15 (purity \geq 99.0%) purchased from commercial corporation were used as a hard template. The carbon replica was then prepared as follows: typically, SBA-15 (500 mg), sucrose (200 mg, purity \geq 99.9%)

and thiourea (800 mg, purity \geq 99.0%) were mixed under stirring in H₂O at room temperature for 90 min. After evaporation of solvent, the obtained composites were dried and subsequently annealed at 1000 °C in an argon environment for 120 min. After the removal of silica by HF etching, S-N-CF can be obtained. As a control experiment, other carbon materials obtained under various conditions such as the annealing temperature and the mass ratios of sucrose to TH were synthesized in the same way. The heteroatom loadings in these co-doped carbon materials can be adjusted through varying the mass ratio of sucrose to TH as well as the annealing temperatures. For comparison, the raw materials without any dopants (TH) were treated under the same condition. The resulted materials are denoted CMK3-1000, S-N-CF-1000, S-N-CF-1000-1, S-N-CF-1000-2, and so on. Their physical parameters, electrochemical properties, and corresponding experimental data are listed in Table S1.[†]

Electrode preparation

Glassy carbon (GC) electrodes (3 mm diameter, CH instrument Inc.) were polished with a 0.05 and 0.3 μ m alumina slurry (CH Instrument Inc.) and subsequently rinsed with ultrapure water and ethanol. The electrodes were then sonicated in ultrapure water, rinsed thoroughly with ultrapure water and dried under a gentle nitrogen stream. To prepare the working electrode, all of carbon catalyst (1 mg) was ultrasonically dispersed in ethanol (1 mL) under the same process, 10 μ L of the resulting suspension were dropped onto the GC surface and dried at room temperature for 6 h, then Nafion (0.5%) was dropped on GC and dried at room temperature. For comparison, a commercially available Pt/C catalyst (40 wt% Pt) was prepared in the same way.

Electrochemical measurements

The electrochemical measurements to evaluate ORR activity, including cyclic voltammograms (CV), rotating-disk electrode voltammograms and chronoamperometry, were performed at room temperature in 0.1 M KOH solutions, which were purged with high purity nitrogen or oxygen for at least 30 min prior to each measurement.

Characterizations of physical parameters

X-ray photoelectron spectroscopy (XPS) measurements were carried out with an ultra-high vacuum setup, equipped with a monochromatic Al K α X-ray source and a high resolution Gammadata-Scienta SES 2002 analyzer. SEM images were obtained with a JSM-6700F field-emission scan electron microscope. Transmission electron microscopy (TEM) and High-resolution transmission electron microscopy (HRTEM) images were recorded with a JEOL-3010 instrument. The specific surface area was calculated using the Brunauer–Emmett–Teller (BET) equation. The nitrogen adsorption/desorption data were recorded at the liquid nitrogen temperature (77 K) using a Micromeritics ASAP 2020M apparatus. Before the measurements, the samples were evacuated for 10 h at 300 °C.

Results and discussion

Fig. 1 schematically shows the entire procedure for preparing S-N-CF. Briefly, a mixture of sucrose and TH was first infiltrated into an SBA-15 template at room temperature. The resulting mixture was then pyrolyzed at high temperature in an argon environment, followed by removal of the template using HF to obtain silica-free S-N-CF. The mass ratio of sucrose to TH is a key parameter in controlling the morphologies and structures of the final products. Fig. 2 and S1⁺ show SEM and TEM images of the products obtained using different mass ratios of sucrose to TH (the corresponding experimental data of these samples can be seen in Table S1[†]), these clearly demonstrate the morphological transformation procedure from CMK-3-1000 (5:0) to S-N-CF-1000-2 (3:2), S-N-CF-1000 (1:4), and S-N-CF-1000-4 (1:8). Fig. 2a and b show that ordered carbon materials were formed using only sucrose as the carbon source (CMK-3-1000). A highly ordered uniform pore distribution can be seen from the TEM images in Fig. S1a and b.[†] The surface area is determined to be 1127 m² g⁻¹ by N₂ adsorptiondesorption isotherms (Fig. S2a[†]) and the main pore size is calculated to be about 3.8 nm from analysis of the adsorption branch using the Barrett-Joyner-Halenda (BJH) method. After adding TH, carbon foams with continuous 3D networks and abundant macroporous (~400 nm) structures are present, as shown in Fig. 2d-i. The high-magnification SEM images (Fig. 2e and h) further indicate that the size of the macroporous pores increases with increasing mass of TH. Furthermore, from the measurements of pore size distribution (Fig. S2a⁺), it can be observed that the new mesopores (23 nm) are present in S-N-CF-1000-2 and S-N-CF-1000 (Fig. S2b⁺), and the percentage of small pores (3.8 nm) decreases rapidly. The N₂ adsorptiondesorption isotherms in Fig. S2a⁺ reveal that the Brunauer-Emmett-Teller (BET) surface area decreases gradually from 1127 to 850 to 394 m² g⁻¹ for CMK-3-1000, S-N-CF-1000-2, and S-N-CF-1000, respectively. For the series carbon foam samples obtained after introducing TH, we speculated that the relatively large pore structures (~400 and 23 nm) may be formed during



Fig. 1 Schematic illustration of S–N–CF preparation.



Fig. 2 Typical SEM images and schematic diagrams of the resulting carbon materials obtained under different mass ratios of sucrose to TH: (a–c) 5:0, (d–f) 3:2, (g–i) 1:4, (j–l) 1:8.

the pyrogenation of TH, and then TH pyrogenation incidentally also results in the collapse of small pores. In other words, it be believed that the form of the hierarchical pore structure (~400, 23 and 3.8 nm) in the 3D carbon foams may be due to that TH pyrogenation created the relatively large pore structures (~400 and 23 nm) as well as ordered carbon materials left small pore structures (3.8 nm). When the mass ratio of sucrose to TH is 1 : 8, the 3D continuous network structures disappear (Fig. 2j and k) due to the extensive TH pyrogenation. The TEM images in Fig. S1g and h[†] clearly show that S–N–CF-1000-4 is transparent, with wrinkled and graphene-like features.

Fig. 3a and b shows a typical TEM image of S–N–CF-1000. The 3D continuous crosslinked networks and abundant macroporous structures are easily observable for S–N–CF-1000, and these are important for highly effective ion and electron transfer, as well as reactant transport. Elemental composition analysis based on EDX patterns were performed for S–N–CF-1000. The distributions of S and N are relatively uniform in S–N–CF-1000, which is verified by the STEM and corresponding elemental mapping images (Fig. 3c). The chemical status of these elements is further investigated by XPS. The XPS survey spectrum in Fig. 3d shows a dominant C_{1s} peak (~284.5 eV), an O_{1s} peak (~532.0 eV), a N_{1s} peak (~400.0 eV), and two S peaks (~164.5 eV, ~228.0 eV), which further confirm the presence of elemental S and N in S–N–CF-1000. The contents of N and S elements in the dual-doped S–N–CF-1000 are calculated to be



Fig. 3 Typical TEM (a and b), STEM elemental mapping images (c), XPS spectra (d), adsorption–desorption isotherm and pore size distribution (e) for S–N–CF-1000.

6.53% and 2.88%, respectively, comparable to that of N and S dual-doped graphene.14 Considering that TH precursors can be completely removed at high temperatures, the possibility of physical adsorption of some residual precursors on the surface of the S-N-CF-1000 can be discounted. It is reasonable to believe that N and S atoms have been introduced into the carbon framework via covalent bonds. The high-resolution spectrum of C_{1s} in S-N-CF-1000 (Fig. S3b[†]) can be divided into several single peaks, corresponding to C-C, C-N/C-O/C-S and C=O/C=N.14 In the high-resolution N1s spectra of S-N-CF-1000 (Fig. S3c⁺), mainly three types of N-functional groups, pyridinic-N (\sim 398.2 eV), pyrrolic-N (\sim 399.8 eV) and graphitic-N (\sim 401.0 eV) are present, which are typically observed in the case of Ndoped carbons.⁶ The binding energy of XPS-S_{2p} was also used to analyze the sulfur doping in S-N-CF-1000 (Fig. S3d⁺). The former two peaks are in agreement with the reported S_{2p} 3/2 (~163.9 eV) and $S_{\rm 2p\ 1/2}$ (~165.1 eV) positions of thiophene-S owing to their spin-orbit coupling,²¹ while SO_x groups (~168.5 eV) are not evident. These results further indicate that S and N atoms have been successfully doped into the carbon foams. According to Dai's report, carbon atoms at defect sites or oxygen-containing groups in graphite materials can react with NH₃ to form C-N bonds.²² We believe that the formation of C-N and C-S bonds in S-N-CF-1000 may have a similar mechanism.

To evaluate the electrocatalytic ORR activities of the samples, we carried out cyclic voltammetry (CV) measurements in 0.1 M KOH solution. Fig. 4a clearly shows the ORR peaks for all the samples obtained using different mass ratios of sucrose to TH under O2-saturated conditions. For the CMK-3-1000 electrode, a single cathodic reduction peak is present at -0.20 V (vs. Ag/ AgCl). After adding TH, all the carbon materials doped with S and N show higher peak currents than that of the CMK-3-1000 electrode. From Fig. 4a and Table S1,[†] it can be observed that the order of the ORR peak potentials for these carbon catalysts obtained at 1000 °C is directly related to the heteroatom loading. More precisely, the higher the heteroatom loading, the more positive the ORR peak potentials are. These experimental results indicate that N and S dual doping should be very effective for ORR activity enhancement and creating larger numbers of active sites by improving the heteroatom loading in carbon materials could be an effective way of reducing overpotentials toward ORRs. Furthermore, from Fig. 4a, it can also be seen that S-N-CF-1000 shows the highest peak current of all the samples. To gain further insights into the ORR performances of these samples, linear sweep voltammetry (LSV) measurements were performed on a rotating-disk electrode (RDE) at a scan rate of 10 mV $\rm s^{-1}$ and a rotation rate of 1600 rpm, and the results were compared with those carried out on a commercial Pt/C catalyst (40 wt%). From Fig. 4b, it can be seen that all the S and N codoped carbon foams (S-N-CF-1000-2, S-N-CF-1000, and S-N-CF-1000-4) have higher limiting current densities than that of the corresponding undoped carbon materials (CMK-3-1000). This result further supports the CV observations described above, and strongly indicates the significance of TH introduction for ORR catalytic activity enhancement. Furthermore, from Fig. 4b, we can also observe that the onset potential for



Fig. 4 (a) CVs for various catalysts obtained under different mass ratios of sucrose to TH, (b) LSV curves for various catalysts and a Pt/C catalyst at a rotation rate of 1600 rpm. Chronoamperometric responses of S–N–CF-1000 and Pt/C catalyst, (c) with 3 M methanol added at around 90 s, and (d) at -0.40 V in an O2-saturated 0.1 M KOH solution.

S-N-CF-1000 is close to that of the Pt/C catalyst, and that its current density is higher than that of the Pt/C catalyst. These results suggest that the ORR catalytic activity of S-N-CF-1000 is better than those of commercial Pt/C catalysts. Considering their physical parameters (Table S1[†]) and morphological characters, it is believed that such excellent performances for the S-N-CF-1000 may be attributed to the synergistic effect, which includes high catalytic sites for ORR provided by high S-N heteroatom loading,¹⁴ excellent reactant transport caused by hierarchical pore structures¹⁹ and high electron transfer rate provided by 3D continuous networks. To further prove the role of S-N-CF-1000 in the ORR electrochemical process, we also performed RDE measurements at various rotation speeds (see Fig. S4 and Table S1⁺). The number of electron transfers for S-N-CF-1000 is calculated to be 3.96, which indicates a fourelectron-transfer reaction. The calculated limited-kinetics current density (I_k) is 11.69 mA cm⁻² at -0.40 V. The electrocatalytic activity of S-N-CF-1000 is comparable to those of NPMCs (e.g., N-doped CNTs).^{5,6} The above results further confirm that S-N-CF-1000 is a promising metal-free NPMC with high catalytic activity for ORR.

As a control experiment, the influence of the annealing temperature on the electrocatalytic properties of the carbon materials was further explored. Fig. 5a and b show the CV and LSV measurement curves for carbon materials obtained at 600-1000 °C. Their physical parameters, corresponding experimental data, and electrochemical activity data are listed in Table S1.[†] From Fig. 5a, it can be seen that the carbon material obtained at 1000 °C (S-N-CF-1000) shows the highest peak current and most positive ORR peak potential of all the samples. The results of LSV measurements, shown in Fig. 5b, also support the CV observations, and all the observations strongly indicate that S-N-CF-1000 has the best ORR activity amongst these co-doped carbon materials. It is believed that the improved graphitic degree as a result of restoring defects at higher temperature in the S-N-CF-1000 samples may be one of the factors contributing to the significantly enhanced catalytic activity. The bonding configurations should also be an important factor for ORR. The detailed relationship between catalytic activity and microstructure for these co-doped carbon foams needs to be further investigated.

Possible crossover effects and stability of the catalyst materials are both important parameters for evaluation of their practical application in fuel-cells. Chronoamperometric



Fig. 5 CVs (a) and LSV curves at a rotation rate of 1600 rpm (b) for various catalysts obtained under different annealing temperature.

responses to methanol introduced into an O2-saturated electrolyte were therefore measured for both S-N-CF-1000 and a commercial Pt/C catalyst. It can be seen from Fig. 4c that after the addition of 3 M methanol at 90 s, no noticeable change was observed in the ORR current at the S-N-CF-1000 electrode. In contrast, the ORR current for the Pt/C catalyst decreased sharply. These results indicate that S-N-CF-1000 has a good ability for avoiding crossover effects. The durabilities of the S-N-CF-1000 were also compared by holding them at -0.40 V for 6 h in an O₂-saturated 0.1 M KOH solution. Fig. 4d shows that the resulted chronoamperometric response for S-N-CF-1000 exhibited very slow attenuation, and a high relative current of 90.5% still persisted after 6 h. The stability of the S-N-CF-1000 is comparable to that of the previously reported metal free ORR catalysts (e.g., nitrogen-doped ordered mesoporous graphitic arrays).6,7,9 These results confirm that S-N-CF-1000 has potential uses in direct methanol and alkaline fuel-cells.

Conclusion

In summary, a new type of 3D S–N co-doped carbon foams with hierarchical pore structures have been fabricated through a convenient, economical, and scalable route. The foams exhibit excellent catalytic activity, good stability, and a high methanol tolerance compared to the commercial Pt/C catalyst. Our results not only develop a new type of catalysts with excellent electrocatalytic performance by a commercially valid route, but also provide useful information for further clarification of the relationship between the microstructures of metal-free carbon materials and catalyst properties for ORR. More importantly, the idea to design hierarchical pore structures could be applied to other catalytic materials and serve as a general strategy for improving the activity of various ORR catalysts.

Acknowledgements

The work was supported in part by grants from NSFC (51002106, 21273163, 21005055, 21173259) and NSFC for Distinguished Young Scholars (51025207), ZJST (2012R10014-08), NSFZJ (R4090137) and ZJED Innovative Team for S. Huang.

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