Facile fabrication of N-doped three-dimensional reduced graphene oxide as a superior electrocatalyst for oxygen reduction reaction

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Abstract: Nitrogen-doped graphene materials provide the attractive potentials to replace the high-priced Pt and Pt-based catalysts for oxygen reduction reaction (ORR) to accelerate the industrialization of fuel cells (FCs). Herein, the nitrogen-doped three-dimensional reduced graphene oxide (N-3DrGO) catalysts have been prepared by a facile hydrothermal method using the raw materials of GO, melamine and formaldehyde. The N contents in N-3DrGO products vary from 3.12 to 9.69 at. % which can be easily regulated by adjusting the feed mass ratios of GO and melamine. It is found that a higher content of N does not necessarily result in enhanced electrocatalytic activity. Rather, with the highest total percentage of graphitic N and pyridinic N (69.2%), superior solvent dispersibility, as well as a smaller interfacial and charge-transfer resistance, the N-3DrGO catalyst obtained by a mass ratio of 1:1.5 between GO and melamine presents the most excellent activity towards ORR. As a catalyst using in FCs for ORR, the obtained N-3DrGO catalysts exhibit favorable electrocatalytic performance, excellent methanol tolerance and much enhanced durability compared with that of commercial Pt/C (20 wt%) catalyst in alkaline media. Furthermore, the above-mentioned approach is demonstrated to be a versatile method in fabricating N-3DrGO-based catalysts by introducing the foreign active atoms such as sulfur (S) to realize the N and S co-doping, which can further enhance the catalysts' ORR activity.

Key words: Fuel cells; N-3DrGO catalyst; oxygen reduction reaction; excellent methanol tolerance; enhanced durability¹

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1. Introduction

Fuel cells (FCs) as a clean energy have attracted global attention because of their high energy conversion efficiency, broad fuel sources, and quick start-up as well as the environmentally friendly to atmosphere [1, 2]. The paramount importance of electrochemical activity in FCs is the oxygen reduction reaction (ORR), which is dramatically influenced by the cathode catalysts at the process of ORR. Currently, platinum (Pt) and Pt-based materials are the proverbially used catalysts in FCs owing to their high efficiency [3-5]. However, their high expenditure and limited stability together with the poor durability hinder the commercialization of FCs. Therefore, enormous efforts [4-6] have been dedicated to the Pt-free catalysts based on the heteroatoms-doped (N, B, S, et al) and/or non-precious metals carbon materials. Li *et al.* [7] reported a metal-free electrocatalyst of N-doped graphene which exhibited an efficient electrocatalytic performance towards ORR. Liang *et al.* [8] reported an S and N dual-doped mesoporous graphene electrocatalyst with superior synergistically enhanced ORR property. Our research group [9] has previously fabricated B-doped three-dimensional reduced graphene oxide (3DrGO) by a one-pot supercritical fluid for ORR. Among the heteroatom-doped carbon-based materials, N-doped carbonaceous nanomaterials with high ORR property, outstanding fuels selectivity and long-term stability have been regarded as the hopeful candidates.

Graphene, a two-dimensional (2D) monolayer carbon material [10, 11], has attracted increasing attention because of their additionally unique properties. Unfortunately, for both graphene and doped graphene, the practical surface area and electrical conductivity can be significantly diminished by the aggregated graphene nanosheets owing to their interlayer van der Waals force or π - π conjugation. Recently, integrated from 2D graphene sheets, 3D graphene featured with an accessible surface area, good electrical conductivity, and efficient mass transfer, presents a great number of potential applications in

batteries, supercapacitors, energy conversion and FCs [12-14]. Thus, fabricating the FCs' cathode catalysts with good electrocatalytic activity has generated great interests. There are numerous methods that can be used to fabricate 3DrGO-based materials such as self-assembly, chemical vapor deposition (CVD) and template-assembly [4, 12]. For example, Zhou *et al.* [15] have developed a hard templating approach to synthesize 3D porous N-doped graphene foam for ORR, but the rigorous experiment requirements may restrict the application of this method. Liu *et al.* [16] have synthesized the 3D graphene foam/carbon nanotube composite films used in the electrode materials of supercapacitors by a hard template-directed CVD method. These usual approaches have confronted the shortcoming of weak mechanical stability due to the physical linkage nature of the 3D graphene networks. Typically, the 3D structure of the graphene network may be destroyed when this kind of materials are dispersed in the solvents. Furthermore, the experiment conditions of most methods are too rigorous to adopt, which makes them meet the difficulty in industrialization. Therefore, developing facile methods to synthesize 3DrGO-based materials with high mechanical stability is still a challenge.

In this paper, a facile hydrothermal method to synthesize the N-3DrGO catalyst has been introduced using the raw materials of GO suspension, melamine and formaldehyde. During the hydrothermal reaction process, the melamine formaldehyde resin (MFR) as a reported crosslinker [17] can be produced. The produced MFR can bond the GO sheets together and fill into the interlayer of GO sheets to avoid their aggregation. The fabricated N-3DrGO catalyst, with high specific surface area and abundant porous structures, exhibits desirable ORR activity and even better methanol tolerance and durability than that of commercial Pt/C catalyst. When introducing the sulfur (S)-containing precursor into the as-mentioned reaction system, the ORR activity can be further enhanced due to the synergistic effect of the co-doping of N and S. The results indicate that the versatility, easiness and superiority of this kind of approach in synthesizing the heteroatom-doped N-3DrGO catalysts, which is essential for preparing metal-free FCs'

cathode catalysts in large-scale production.

2. Experimental

2.1 Materials synthesis

GO was synthesized according to a modified Hummers method [18]. The N-3DrGO products were fabricated using a hydrothermal method with GO suspension, melamine and formaldehyde as the raw materials. In a typical procedure, melamine and formaldehyde aqueous solution (37%) at a molar ratio of 1:3 was added dropwise to a homogeneous GO suspension (10 mL, 10 mg/mL) under magnetic stirring for 2 h. The mass ratios between GO and melamine were adjusted to be 1:0.5, 1:1.5 and 1:2.5 for synthesizing the N-3DrGO products with different total N contents. Afterwards, the homogeneous mixture was moved into a 25 mL Teflon-lined autoclave and kept at 180°C for 12 h. Next, the autoclave was undisturbedly cooled to indoor temperature and the as-fabricated hybrid hydrogel was vacuum dried at 60°C for 24 h to obtain the xerogel. Finally, the dry xerogel was calcined at 750°C for 5 h in Ar atmosphere to obtain the ultimate N-3DrGO products. In addition, the obtained N-3DrGO products with the mass ratios between GO and melamine of 1:0.5, 1:1.5 and 1:2.5 was marked as N1-3DrGO, N2-3DrGO and N3-3DrGO, respectively.

2.2 Materials characterization

The morphologies of the products were characterized using a JEOL JSM-6700F scanning electron microscopy (SEM) and a Hitachi JEM-2100 transmission electron microscopy (TEM) operating at 200 kV. X-ray diffraction (XRD) analyses were carried out using a PW-1700 diffractometer with Cu K α ($\lambda=1.5405$ Å) radiation source. Raman spectra were collected on a J-Y T64000 Raman spectrometer with 532 nm wavelength of laser light at 5 mW. X-ray photoelectron spectroscopy (XPS) measurements were tested on a Thermos ESCALAB 250 spectrophotometer with Al-K α radiation. The specific surface areas and porous structures of the obtained products were characterized by a NOVA300e Quadrachrome adsorption instrument. The solvent dispersibility of

the electrodes was tested by a Nikon SMZ25 integrated microscope.

2.3 Electrochemical measurement

The electrochemical measurements were performed by a 760E electrochemical workstation in a normal tri-electrode with the auxiliary electrode of Pt wire and the reference electrode of Ag/AgCl. The N-3DrGO catalyst inks were prepared by ultrasonically dispersing the samples in a mixture solvent containing deionized water, isopropanol (99.5%) and Nafion (5%) with a volume ratio of 8/2/0.05 to form a homogenous catalyst ink (2 mg mL⁻¹). Then 10 µL of the as-mentioned ink was dropped onto the working electrode of a pre-polished glass carbon (GC) disk electrode with diameter of 5 mm and followed by drying at 60°C for 30 min. The catalyst of commercial Pt/C (20 wt%, Pt) was also measured similarly and used as a comparison group. EIS measurements were carried out in an O₂-saturated electrolyte at a frequency range from 100 kHz to 0.01 Hz. The potential range of the electrochemical measurement is from -1.0 to 0.2 V (*vs* Ag/AgCl) in a 0.1 M KOH aqueous solution. The recorded scanning rates of cyclic voltammograms (CVs) and linear sweep voltammetry (LSV) measurements are 50 mV s⁻¹ and 10 mV s⁻¹, respectively. Moreover, all the experiments were carried out under a N₂-saturated or O₂-saturated condition and the potential measurements were transformed to the RHE based on the following formula [19]:

$$E_{vs\ RHE}=E_{vs\ Ag/AgCl}+E^0_{Ag/AgCl}+0.059\ pH\ (\text{in volts}). \quad (1)$$

3. Results and discussion

The preparation schematic of the N-3DrGO product is depicted in Fig. 1. A homogeneous mixture containing melamine, formaldehyde and GO suspension was firstly hydrothermally treated in a Teflon-lined autoclave. In this process, the produced crosslinking agent of MFR can crosslink the GO sheets together and GO was thermally reduced at the same time to form the hybrid hydrogel. After that, the obtained hydrogel was then thermally dried to get the hybrid xerogel and the formed MFR can be confirmed by SEM analyses (in Fig. S1). When the filling agent of MFR occupied the interspace constituted by GO

sheets and provide a strict support, the hydrogel can avoid shrinking during the thermal drying process. Finally, in order to obtain a clean N-3DrGO product, the excess MFR would be removed by thermal treatment at the step of pyrolysis. After pyrolysis, the morphology of the N2-3DrGO (Fig. 2a, b) differs from that of before pyrolysis (in Fig. S1), which is due to the disappearance of MFR. With the mass ratio of GO and melamine altering, there are changeless in morphology and structure of the N2-3DrGO compared with the SEM images of N1-3DrGO and N3-3DrGO samples (in Fig. S2). From all the SEM images, it can be found that the N-3DrGO products have a multi-porous 3D architecture with freewill unpacked pores built from graphene layers. The TEM images can further demonstrate that the N-3DrGO products have a 3D porous structure constructed from the graphene nanosheets (in Fig. 2c, d).

The phase structure of the N-3DrGO samples was characterized by XRD analyses. Fig. 3a shows an obviously structural transformation when GO sheets were thermally reduced in Teflon-lined autoclave. A typical (002) diffraction peak of GO at 10.1° indicates its interlayer space of 0.88 nm. This big interlayer spacing can be ascribed to the emergence of carboxyl groups, hydroxyl and epoxy [20]. Such functional groups can be partly removed after hydrothermal reduction, which will lead to a smaller interlayer range. It is found that with the melamine input increased, the interlayer distances for N-3DrGO samples have decreased, which may be due to the more eliminated oxygen-containing functional groups by the introduced nitrogen. Meanwhile, the interlayer distance is calculated in order: N1-3DrGO ($d=0.67$ nm, $2\theta=13.2^\circ$) > N2-3DrGO ($d=0.41$ nm, $2\theta=21.6^\circ$) > N3-3DrGO ($d=0.40$ nm, $2\theta=22.1^\circ$). The interlayer spacing of all samples is bigger than that of the crude graphite ($d=0.34$ nm, $2\theta=26.5^\circ$), indicating that there still exists the functional groups in each N-3DrGO sample. Simultaneously, the obtained results of the reduction degree by Raman measurement (in Fig.3b) are consistent with the results of XRD. The intensity ratios of structural defects (D band at 1360 cm^{-1}) to pristine sp^2 lattice carbon (G band at 1590 cm^{-1}) (I_D/I_G) [21, 22] for N1-3DrGO, N2-3DrGO and

N3-3DrGO samples are calculated to be 1.11, 1.13, and 1.16, respectively. And the I_D/I_G values of all the N-3DrGO products are higher than that of GO sheets (0.94), which further indicate that GO has been partly reduced after hydrothermal treatment. Furthermore, according to the values of I_D/I_G , the mean crystalline size (L_a) of the N-3DrGO sample can be evaluated by the Tuinstra and Koenig (TK) equation [23]:

$$\frac{I(D)}{I(G)} = \frac{C(\lambda)}{La} \quad (2)$$

where $C(532 \text{ nm}) \sim 49.56 \text{ \AA}$ [24]. Therefore, the values of L_a for N1-3DrGO, N2-3DrGO and N3-3DrGO samples are calculated to be 44.65 $\text{\AA}$, 43.86 $\text{\AA}$ and 42.72 $\text{\AA}$, respectively, all of which are less than that of GO (52.7 $\text{\AA}$), indicating that GO has been reduced and nitrogen has been introduced into the hybrids after hydrothermal and pyrolysis process. Amongst the three N-3DrGO products, the minimal crystalline size is the N3-3DrGO sample due to the most adoption amount of melamine which leads to its maximum broken C-C bonds. These results demonstrate that the most defects introduced in sample N3-3DrGO during the nitrogen-doping process, which may bring negative influence to its solvent dispersibility and conductivity.

The N-3DrGO products with porous structures were also measured by a Quadrachrome adsorption instrument. The textual parameters of the three N-3DrGO samples are summarized in Table 1. It is clear seen that the specific surface areas of the N1-3DrGO, N2-3DrGO, and N3-3DrGO products determined by Brunauer-Emmett-Teller (BET) analysis (Fig. 4a) are 269, 318 and 380 $\text{m}^2 \text{g}^{-1}$, respectively. According to the density-functional-theory (DFT) calculation, the average pore sizes (Fig. 4b and Table 1) of them are counted to be 38.4, 37.1, and 38.1 nm, respectively. And the corresponding pore volumes of them are calculated to be 0.32, 0.45, and 0.58 $\text{cm}^3 \text{g}^{-1}$, respectively. These results have illuminated that the obtained N-3DrGO products have large specific surface areas and hierarchically distributed pores including micropores, mesopores, and macropores, but mainly based on the mesoporous architectures.

Table 1 Textural parameters of nitrogen sorption analysis for N-3DrGO products.

Sample	S_{BET} (m ² g ⁻¹)	Pore vol. (cm ³ g ⁻¹)	Pore size (nm)
N1-3DrGO	269	0.32	38.4
N2-3DrGO	318	0.45	37.1
N3-3DrGO	380	0.58	38.2

To further analyze the N contents and species, the elemental composition and bonding configuration of the N-3DrGO products were elucidated by XPS analysis. The survey spectra shown in Fig. 5a demonstrate the existence of carbon (C 1s, 284.1 eV), nitrogen (N 1s, 398.1 eV), and oxygen (O 1s, 533.1 eV) in the N-3DrGO products. Generally, the C 1s peak of pristine graphene is at 284.5 eV [25], and the shift of banding energy further confirms the existence of nitrogen in N-3DrGO products. The total N contents in the samples of N1-3DrGO, N2-3DrGO, and N3-3DrGO are counted to be 3.12, 7.78, and 9.69 at.% (Table S1), respectively, which indicates that the N-3DrGO products with different N contents can be obtained by simply adjusting the mass ratios of GO and melamine. As shown in Fig. 5b-d, the primary N 1s spectra include four typical peaks, which correspond to the pyridinic N (397.7 eV), pyrrolic N (398.9 eV), graphitic N (400.5 eV) and oxidized N (403. 1 eV), respectively. It is reported [26] that the pyridinic N stands for N atoms at the fringes or flaws of the graphene planes in a six-member ring, where every N atom combines with a couple of carbon atoms and contributes single p-type electron to the aromatic system. The pyrrolic N donates double p-electrons to the π -conjugated system, and it is located in the five-member rings of the graphene layers. The graphitic N is in the graphite plane and connects to tri-carbon atoms. It is believed [27] that the graphitic N and pyridinic N play remarkable roles for ORR, indicating that our-fabricated catalysts with different percentages of these two species N will present diverse ORR activities. Moreover, the XPS characteristic results together with the XRD patterns and Raman spectra as well as the BET analysis have demonstrated that the N-doped 3DrGO products with large specific

surface areas and multi-porous structures have been synthesized successfully.

The CVs were firstly measured to prove the ORR activity of the N-3DrGO electrodes. As illustrated in Fig. 6, the CVs with unapparent ORR peaks can be depicted under N₂-saturated conditions, while displaying a profound ORR peak in the O₂-saturated medium. Among the three catalysts, the N2-3DrGO electrode presents the highest onset/peak potential (0.694 V *vs* RHE) compared with that of N1-3DrGO (0.672 V) and N3-3DrGO (0.533 V) electrodes, which indicates that the N2-3DrGO electrode can absorb and reduce more oxygen molecules on its surface. However, the onset/peak potentials of all the N-3DrGO catalysts are still less than that of Pt/C catalyst (0.821 V). In order to further study the electrocatalytic performance of the obtained N-3DrGO catalysts, LSV measurements were also employed on the rotating disk electrode (RDE). Fig. 7a shows the polarization curves for diverse electrodes at the same rotation rate of 1600 rpm with O₂-saturated 0.1 M KOH. The ORR performance of the different catalysts is summed up in Table S2. Though it can be found that all the N-3DrGO catalysts exhibit desirable ORR performance, the ORR onset potentials of the N1-3DrGO (0.861 V *vs* RHE), N2-3DrGO (0.894 V), and N3-3DrGO catalysts (0.882 V) are still less than that of the Pt/C catalyst (0.918 V). Furthermore, the N2-3DrGO electrode (Fig. 7a) shows a satisfactory half-wave potential ($E_{1/2}$ =0.695 V *vs* RHE) and a relatively large diffusion-limiting current (-3.90 mA cm^{-2}), which is better than that of the N1-3DrGO electrode (0.638 V, -3.36 mA cm^{-2}) as well as the N3-3DrGO electrode (0.627 V, -3.25 mA cm^{-2}). However, it is of course less than that of the Pt/C electrode (0.792 V, -4.75 mA cm^{-2}). The ORR activity of the N2-3DrGO is superior to many reported catalysts such as the rGO/CTAB (cetyltrimethylammonium bromide) hybrid [28], X-doped rGO (X= F, Cl, Br and I) [29], Carbon quantum dots (CQDs) [30], N-doped colloidal graphene QDs [31], but still inferior to some other reported catalysts such as N-doped carbon nanoflakes [32], spinel ZnCo₂O₄/N-doped carbon nanotube composite [33], spinel CuCo₂O₄/N-rGO composite [34]. Furthermore, the Tafel plots for

ORR in the regions with low current density are derived from the corresponding RDE data according to the following equation [35]:

$$J_k = \frac{J \times J_d}{J_d - J} \quad (3)$$

where J_k is the kinetic current density, J is the tested current density and J_d is the diffusion-limiting current density. As depicted in Fig. 7b, the N2-3DrGO catalyst displays a smaller Tafel slope (99 mV dec^{-1}) compared with that of the N1-3DrGO (120 mV dec^{-1}) and N3-3DrGO (137 mV dec^{-1}) catalysts, which is more close to that of commercial Pt/C catalyst (76 mV dec^{-1}). The above results further illustrates that a more enhanced reaction dynamics and high inherent electrocatalytic property towards ORR is the N2-3DrGO electrode.

The results of CV together with LSV as well as the Tafel plots are coincident, all of which have demonstrated the superiority ORR activity of the N2-3DrGO catalyst, indicating that there is an excellent ratio between GO and the melamine for the best catalytic performance. It is In the process of our experiment, we found that although the N3-3DrGO catalyst has the maximum total N content, the ORR activity is still lower than that of the N2-3DrGO catalyst. On one hand, the total percentage of the active N species (Table S1) of graphitic N and pyridinic N (68.0%) in N3-3DrGO is lower than that of the N2-3DrGO catalyst (69.2%). On the other hand, the highest introduced defects (Fig. 3b) make the N3-3DrGO sample present poorer solvent dispersibility (Fig. S3) as well as a relatively larger interfacial and charge-transfer resistance (Fig. S4) compared with that of the N2-3DrGO catalyst. When the total N content is too low, the low active sites (61.2%) in N1-3DrGO lead to poor catalytic activity. Meanwhile, the large interfacial and charge-transfer resistance (Fig. S4) caused by the most remaining oxygen-containing functional groups (C/O atomic ratio is 2.01 in Fig. 5a) is another reason why the N1-3DrGO catalyst exhibits lower ORR activity. To sum up, the N2-3DrGO catalyst with the highest total percentage of the active N [36], superior solvent dispersibility together with small interfacial and charge-transfer resistance presents the most

favorable catalytic activity towards ORR.

The reaction kinetic of the ORR performance was further studied with diverse rotating speeds varied from 225 to 2500 rpm. The J_d values of the N1-3DrGO (Fig. S5a), N2-3DrGO (Fig. 7c), N3-3DrGO (Fig. S5c) and Pt/C catalysts (Fig. S5e) increase with the increasing of rotation rate (ω), but the onset potentials are still almost constant. The relevant Koutecky-Levich plots ($-J^{-1}$ vs. $\omega^{-1/2}$) are calculated by the following formula [37, 38]:

$$\frac{1}{J} = \frac{1}{J_k} + \frac{1}{J_d} = \frac{1}{J_k} + \frac{1}{B\omega^{1/2}} \quad (4)$$

$$B = 0.62nFC_0D_0^{2/3}\mu^{-1/6} \quad (5)$$

where B and ω are the reciprocal of the slope and the angular velocity of the electrode, respectively, n is the transferred electrons for ORR, F is the Faraday constant ($F=96485 \text{ C mol}^{-1}$), μ is the kinematic viscosity of the electrolyte ($0.01 \text{ cm}^2 \text{ s}^{-1}$), D_0 is the diffusion coefficient of O_2 in 0.1 M KOH ($D_0=1.9\times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$), and C_0 is the concentration of O_2 ($C_0=1.2\times 10^{-6} \text{ mol cm}^{-3}$). It can be seen that the N1-3DrGO (Fig. S5b), N2-3DrGO (the inserted picture of Fig. 7c), N3-3DrGO (Fig. S5d) and Pt/C catalysts (Fig. S5f) at different potentials present a linear relationship. As shown in Fig. 7d, the average n values (from 0.1 to 0.6 V vs RHE) of the N2-3DrGO catalyst is calculated to be 3.58, which is even higher than that of Pt/C (3.48), demonstrating that the ORR process of this catalyst follows a four-electron transfer pathway. In contrast, the N1-3DrGO and N3-3DrGO electrodes exhibit much lower average n values of 2.17 and 3.03, respectively (Fig. 7d). These results illuminate that the ORR process in the catalysts of N2-3DrGO and N3-3DrGO is dominated by a four-electron transfer pathway except for that of the N1-3DrGO dominated by a two-electron process.

In order to the practical utilization in fuel cells, the methanol poisoning effect and stability should be further investigated due to the well-known easiness crossover effect of the methanol molecules. Therefore, the catalytic selectivity performance of the N2-3DrGO sample, chosen as an example, was

tested in a 0.1 M KOH with 1 M methanol. For comparison, a control group of Pt/C electrode (Fig. 8b) was also measured. After adding the methanol, the ORR signals tested at approximately 0.842 V are disappeared in the CV curve of the Pt/C electrode. Meanwhile, the current intensity corresponding to methanol oxidation of the Pt/C at potential of 0.965 V increases dramatically. However, the CV curves of the N2-3DrGO electrode obtained with and without methanol having no significant difference can be seen in Fig. 8b, indicating that the electrocatalyst of the N2-3DrGO electrode is free from poisoned by methanol. The electrocatalytic selectivity measurement results illuminate that the N2-3DrGO catalyst not only presents a desirable ORR activity, but also has better methanol selectivity than that of Pt/C.

Besides the methanol poisoning effect, the durability of the N2-3DrGO and Pt/C catalysts were also assessed through CV measurements at the scanning speed of 100 mV s^{-1} . It can be clearly seen that only a little decline of current and a neglected variation of the ORR peak have happened on the N2-3DrGO electrode (Fig. 9b) before and after 2000 continuous cycles. However, an obvious decline of current (Fig. 9a) can be found in Pt/C electrode after 2000 persistent cycles. Moreover, only 11.8 mV degradation can be observed in the N2-3DrGO electrode (Fig. 9d) after 2000 scanning cycles, while the degradation of Pt/C reaches to about 23.2 mV (Fig. 9c). The above CV results together with the LSV measurement results illuminate that the fabricated N-doped 3DrGO catalysts have a highly electrochemical stability and durability than that of Pt/C, which is paramount importance in the practical applications of FCs.

To verify the versatility and reliability of this kind of synthesis method in fabricating N-3DrGO-based catalysts, the S precursor of benzyl disulfide, taken as an example, is also introduced into the reaction system after hydrothermal reaction without changing other reaction condition and the detailed research work will be published elsewhere. Fig. 10a is the SEM image of the N and S co-doped 3DrGO (NS-3DrGO) sample, in which no obvious changes have been

found compared with that of N-3DrGO sample (Fig. 2a, b) illuminating that the 3D architecture has been kept and the reliability of this method is also demonstrated. The XPS measurement result (Fig. 10b) indicates that the atoms of S have been introduced into the N-3DrGO product successfully. It can be seen clearly from the CV curves (Fig. 10c) that the NS-3DrGO catalyst (0.723 V) has a more positive O₂ reduction peak than that of N-3DrGO catalyst (0.694 V), and a closer ORR activity compared with commercial Pt/C (Fig. 6d). LSV curve (Fig. 10d) of the NS-3DrGO catalyst shows a close onset potential (0.882 V) with that of the N-3DrGO catalyst (0.894 V). The half-wave potential and diffusion-limiting current density of the NS-3DrGO catalyst are 135 mV and 34 mA cm⁻² higher than that of the N-3DrGO catalyst and both of these key parameters are much more close to the commercial Pt/C catalyst (Fig. 6d), indicating the ORR activity of the N-3DrGO can be further enhanced by introducing foreign S atoms. The above results demonstrate that our reported synthesis method is a versatile and reliable approach in fabricating N-3DrGO-based catalyst, and easily changing the reaction precursor can realize co- or multi-doped 3DrGO catalysts without destroying the 3D architecture.

4. Conclusions

In summary, a facile fabrication strategy to synthesize the N-doped 3DrGO electrocatalysts has been developed using the raw materials of GO, formaldehyde, and melamine. The total N content in the N-3DrGO products vary from 3.12 to 9.69 at. %. With large specific surface area and multi-porous architecture, the N-3DrGO catalysts display favorable ORR performance. Especially, the N2-3DrGO catalyst exhibits the most outstanding ORR activity which may be due to the highest total percentage of the active N, superior solvent dispersibility and a small interfacial and charge-transfer resistance. Furthermore, the N-3DrGO electrocatalyst present much better electrochemical stability and durability than that of Pt/C catalyst. After introducing S atoms and realizing N and S co-doping, the catalyst exhibits much better ORR activity than that of N-3DrGO catalyst indicating the versatility and reliability of this

smart synthesis method, which possibly makes it a promising strategy to obtain different kinds of N-3DrGO-based catalysts for ORR.

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Figure captions

Fig. 1 Preparation schematic of the N-3DrGO products, (a) self-assembly crosslinking effect of GO, melamine and formaldehyde by hydrothermal treatment to form hybrid hydrogel; (b)

thermal drying of the hydrogel to form the hybrid xerogel, and (c) pyrolysis step of the xerogel to form a covalently bonded N-3DrGO products

Fig. 2 The SEM images (a, b) and the TEM images (c, d) of N2-3DrGO sample

Fig. 3 (a) XRD patterns of the N1-3DrGO, N2-3DrGO, and N3-3DrGO products, the patterns of graphite and GO are included for comparison; (b) the Raman spectra of GO, N1-3DrGO, N2-3DrGO, and N3-3DrGO products

Fig. 4 (a) Nitrogen adsorption/deposition isotherms and (b) the pore size distribution of the N1-3DrGO, N2-3DrGO and N3-3DrGO products, respectively

Fig. 5 (a) XPS survey spectra of the N1-3DrGO, N2-3DrGO, N3-3DrGO products, and (b-d) are the corresponding N 1s spectra, respectively.

Fig. 6 CVs of the catalysts: (a) N1-3DrGO, (b) N2-3DrGO, (c) N3-3DrGO and (d) Pt/C on GC electrode in N₂- and O₂-saturated 0.1 M KOH with a scan rate of 50 mV s⁻¹

Fig. 7 (a) ORR polarization curves of the N1-3DrGO, N2-3DrGO, N3-3DrGO and Pt/C catalysts at a rotation rate of 1600 rpm and a scan rate of 10 mV s^{-1} ; (b) is the corresponding Tafel plots derived from the RDE data; (c) LSV curves of ORR of the N2-3DrGO catalyst obtained at different rotating rates, the inserted picture is the corresponding Koutecky-Levich (K-L) plots at different electrode potentials on N2-3DrGO electrode; (d) the average n values of the different electrodes at diverse electrode potentials

Fig. 8 CVs of the (a) N2-3DrGO and (b) Pt/C catalysts on GC electrodes in O_2 -saturated 0.1 M KOH with and without addition of methanol (1 M) at a scan rate of 10 mV s^{-1}

Fig. 9 CVs of (a) Pt/C and (b) N2-3DrGO catalysts; (c, d) are the corresponding ORR polarization curves before and after 2000 scanning cycles

Fig. 10 (a, b) are the SEM image and XPS survey of the NS-3DrGO sample, respectively; (c, d) are the CV curves and LSV polarization curves of the N-3DrGO and NS-3DrGO catalysts, correspondingly

Graphical abstract