



Soft template-assisted method for synthesis of nitrogen and sulfur co-doped three-dimensional reduced graphene oxide as an efficient metal free catalyst for oxygen reduction reaction



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ABSTRACT

Developing earth-abundant materials to replace platinum (Pt)/Pt-based materials is an inevitable tendency for the progress of fuel cells due to the practical application limits. Recently, heteroatoms doped (N, S et al.) carbon materials, such as carbon nanotubes and graphene, have attracted great interests because of their amazing electrochemical activity towards oxygen reduction reaction (ORR). Herein, nitrogen and sulfur dual-doped three-dimensional reduced graphene oxide (NS-3DrGO) catalysts have been synthesized by a soft template-assisted approach followed by heat-pyrolysis treatment. Results indicate that with high specific surface area, sufficient porous structures, as well as the well-dispersed and doped atoms of N and S, the NS-3DrGO catalysts possess high onset/half-wave potentials together with large diffusing-limiting current density and present a four-electron transfer process in alkaline media. Specifically, at a relatively higher annealing temperature of 950 °C, the NS-3DrGO catalyst presents the optimal ORR activity compared with the others, which may be due to its highest amount (74.8 at. %) of the two active nitrogen species (pyridinic N and graphitic N) and the highest amount (79.8 at. %) of active thiophene-S together with the desirable specific surface (391.9 m² g⁻¹) area and multi-porous structure. Furthermore, the NS-3DrGO catalysts also exhibit superior methanol tolerance and favorable durability.

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1. Introduction

It is reported that introducing heteroatoms (N, B, P, S et al.) into carbonaceous materials can dramatically improve their electrocatalytic activity towards oxygen reduction reaction (ORR), a key reaction process in fuel cells' (FCs') cathode [1–4]. Recently, metal-free catalysts of the heteroatoms doped carbon materials possess the potentials in replacing the state-of-the-art precious platinum (Pt) and Pt-based catalysts, which is much meaningful for reducing the cost of FCs and accelerating the FCs' industrial progress [5–8]. Basically, after doping the foreign atoms, the intrinsic electrical neutrality of the sp² carbon in carbonaceous materials was destroyed leading to the formation of activated sites, which can act as the electrocatalytic centers for resultful adsorption of oxygen molecules [9]. Recent researches [1–3,10,11] have demonstrated

that realizing the dual-doping or multi-doping (B/N, N/S, P/N/S et al.) heteroatoms into carbon materials can improve the number of activated centers and reach synergetic effects to further enhance the ORR performance when compared with that of the single-doped carbon. Besides considering the heteroatoms selection, controlling the structure and morphology of these carbonaceous materials is also a paramount factor for the catalytic property advancing. The high specific surface area and multi-porous structures of the carbon materials [9] also play significant roles in improving the ORR activity due to the relatively large charge transport efficiency and more exposed active sites. Zheng et al. [12] have demonstrated that after incorporating of C₃N₄ into a mesoporous (~8 nm) carbon, the electron transfer efficiency has increased obviously, which is useful for the improvement of electrocatalytic activity. Liu et al. [13] reported that a sulfur and nitrogen co-doped three-dimensional carbon foams with hierarchical pore structures exhibit high ORR activity. However, amongst the synthesis methods, many of them have application limits due to the rigorous experiment conditions or the toxic and harmful raw

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materials. Therefore, finding facile synthesis approach and fabricating the dual-doped or multi-doped carbon materials with high specific surface area as well as hierarchical-porous structures are vital significance for developing the efficient metal-free catalysts.

Among the various carbon materials, Graphene, with numerous fascinating properties such as large theoretical specific surface area (S_{BET}) and excellent electrical conductivity, is a promising carbonaceous material choice for ORR catalysts [14–16]. However, the aqueous dispersibility of graphene is much poor, which in great extent limits the practical applications of graphene. It is well-known that many of experiments need manipulated in water system, indicating that graphene has its drawbacks in broad utilization. Meanwhile, the graphene sheets are very likely to aggregate together because of their interlayer π - π conjugation or van der Waals force [17], which will reduce the realistic S_{BET} of graphene. Thus, developing three-dimensional reduced graphene oxide (3DrGO) with high S_{BET} and hierarchical-porous structure is a potential way to solve these problems by using the ingredient of GO, having a good aqueous dispersibility due to the existing of the oxygen-containing functional groups on its surface. Our previously report [18] has employed a facile and environmentally friendly approach to fabricate the N-doped three-dimensional reduced graphene oxide (N-3DrGO) catalyst, but the ORR activity of this kind of N-3DrGO catalyst is moderate. Therefore, great efforts should be made to further improve its ORR activity.

The melamine formaldehyde resin (MFR) reported recently [19] can be used as a crosslinking agent to bond GO sheets together, which can be used to fabricate robust nitrogen-doped 3D porous graphene. Herein, the MFR was not only used as a nitrogen source, but also used to crosslink GO sheets together by a soft template-assisted method during the hydrothermal process. Simultaneously, in order to integrate sulfur into the hybrid for achieving nitrogen and sulfur co-doped three-dimensional reduced graphene oxide (NS-3DrGO) catalyst, the nontoxic benzyl disulfide (BD) was chosen as the sulfur source. Due to the high S_{BET} together with hierarchical-porous structure and well-dispersed N and S atoms, the obtained NS-3DrGO catalyst fabricated by the facile soft template-assisted method followed with heat treatment, exhibits superior electrocatalytic activity towards ORR. Specifically, the NS-3DrGO catalyst pyrolyzed at 950 °C, holding well-distributed N and S (1.69 at% N and 1.13 at% S) together with a desirable S_{BET} of 391.9 m² g⁻¹ as well as mesoporous structure, presents the optimal ORR performance compared with that of the others. Furthermore, the NS-3DrGO catalysts exhibit superior methanol tolerance and favorable long-term durability, which are ultra-significant for FCs' catalysts in practical applications.

2. Experimental

2.1. Synthesis of NS-3DrGO catalyst

GO was synthesized according to an improved Hummers method [20]. In a typical procedure, the homogeneous GO aqueous dispersion (10 mL, 10 mg/mL) was firstly prepared in a 30 mL vial. And then, 0.15 g melamine and 0.27 mL formaldehyde aqueous solution (37 wt%) were added into the vial with vigorous stirring for 2 h to form a homogeneous mixture. Afterwards, the above mixture was transferred into an autoclave and kept at 180 °C for 12 h to obtain the hybrid hydrogel. Next, the obtained hybrid hydrogel was put into a 100 mL beaker and then added with 0.5 g benzyl disulfide powders as well as additional 40 mL deionized (DI) water under drastic stirring for 2 h. Subsequently, the mixed solution was dried at 80 °C for overnight to get the hybrid xerogel. Finally, the as-prepared xerogel was pyrolyzed at different temperature (650 °C, 750 °C, 850 °C, 950 °C) for 5 h under argon atmosphere to form the

N and S co-doped 3DrGO catalysts. Specifically, the product pyrolyzed at diverse temperatures was marked as NS-3DrGO-X, where X denoted pyrolysis temperature.

2.2. Physical characterizations

X-ray diffraction (XRD) tests were conducted on PW1700 diffractometer using a Cu K α ($\lambda = 1.5405 \text{ \AA}$) radiation source (Philips Co.). Raman spectra were collected on a Thermofisher Raman spectrometer with 532 nm wavelength incident laser light at a laser power of 5 mW. The Brunauer-Emmett-Teller (BET) method was utilized for confirming the S_{BET} by adsorption of N₂ using a NOVA300e 250 volumetric adsorption instrument. Density functional theory (DFT) was used to calculate the pore size distribution. X-ray photoelectron spectra (XPS) were characterized on Kratos XSAM-800 spectrometer with the excitation source of Mg K α . Scanning electron microscopy (SEM) with a XL30 ESEM FEG field emission scanning electron microscope was carried out at 20 kV. Transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM), high-annular dark-field scanning transmission electron microscopy (STEM), element mapping analysis together with energy dispersive spectroscopy (EDS) were performed on Tecnai G2 F30 S-Twin electron microscope operating at 300 kV.

2.3. ORR measurements

The electrochemical experiments were carried out on a CHI 760E Autolab with three-electrode system, in which Pt wire, Ag/AgCl, and glassy-carbon rotating disk electrode (RDE) (with 5 mm in diameter), bought from PINE instruments, were used as the counter electrode, reference electrode, and working electrode, respectively. In order to obtain the catalyst film, 20 μ L of the catalyst ink (2 mg/mL, dispersed in a mixture solvent of DI water, isopropanol (99.5%) and Nafion (5%), V/V/V:8/2/0.05) was coated onto the pre-polished working electrode and dried at 60 °C. For comparison, the commercial Pt/C (20 wt%) electrode with half loadings (0.1 mg/cm²) was also measured. The electrocatalytic activity of all the catalysts was conducted at room temperature in a N₂-saturated or O₂-saturated 0.1 M KOH media. The cyclic voltammetry (CV) was recorded at a sweep rate of 50 mV s⁻¹ and the linear sweep voltammetry (LSV) was recorded at a scanning rate of 10 mV s⁻¹ at 1600 rpm with continuous O₂ flowing to ensure the O₂ saturation. The measurement potentials varied from -0.2 V to 1.0 V and converted to values versus the reversible hydrogen electrode (RHE) in all figures. Furthermore, the catalyst methanol tolerance and stability were tested by current-time (*i-t*) chronoamperometric responses at -0.35 V vs Ag/AgCl at a rotating rate of 1600 rpm.

3. Results and discussion

As depicted in Fig. 1, preparation of the NS-3DrGO products includes three main procedures: a) crosslinking of GO by the addition of melamine and formaldehyde using a hydrothermal method; b) homogenous mixing of BD with the hybrid hydrogel and c) final pyrolysis of the hybrid xerogel to obtain the nitrogen and sulfur co-doped 3DrGO electrocatalyst. In step a), the product of MFR, resulted from melamine and formaldehyde, can be obtained in the hydrothermal process, which can act as a crosslinking agent to bond GO sheets together and fill in the space of GO sheets. Subsequently, in step b), BD was added into the hydrogel mixture with vigorous stirring to get a homogeneous suspension. After well-mixed, the above mixture was then thermally dried at 80 °C for overnight to get the hybrid xerogel.

Finally, in step c), many of the unstable agents can be removed

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