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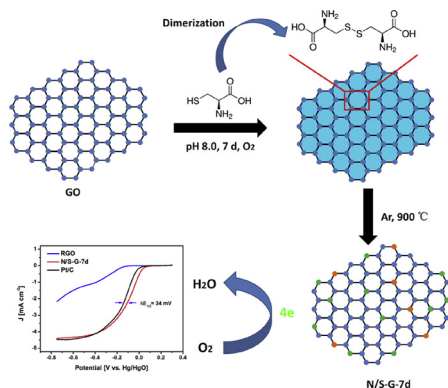
Nitrogen/sulfur-doping of graphene with cysteine as a heteroatom source for oxygen reduction electrocatalysis



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GRAPHICAL ABSTRACT



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ABSTRACT

Heteroatom-doped graphene have encouraged intensive research as promising metal-free oxygen reduction reaction (ORR) electrocatalysts but the correlation between the precursor material and final ORR activity remains unclear. In this work a series of nitrogen/sulfur (N/S)-doped graphene catalysts were synthesized by modifying graphene oxide (GO) with cysteine as a N/S source and sequential thermal annealing. It is disclosed that the cysteine-GO reaction time shows a significant influence on the ORR activity of N/S-doped graphene. A unique process of oxidation-induced *in situ* disulfide formation is further found to be involved in the synthesis of optimal N/S-doped graphene, which displays ORR activity superior to commercial Pt/C in alkaline media. This work suggests that the heteroatom source itself and careful optimization of reaction conditions are critical to obtain high performance doped-graphene electrocatalyst.

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1. Introduction

Heteroatom-doped carbon has emerged as a type of promising oxygen reduction reaction (ORR) catalysts since the pioneer work by Dai and coworkers in 2009 [1–3]. The enhanced ORR activity

is believed to originate from heteroatom-disturbed electro-neutrality of sp^2 carbon in the graphitic framework to favor the adsorption of molecular oxygen and subsequent electrochemical reduction [2,4–8]. Dually-doped carbons were further explored as this strategy offers more flexibility to modulate the electronic structure by optimizing doping sites, dopant densities, and dopant ratio for possible synergistic effect [9–17]. Accumulating evidence has unveiled that both the doping density and doping site of the

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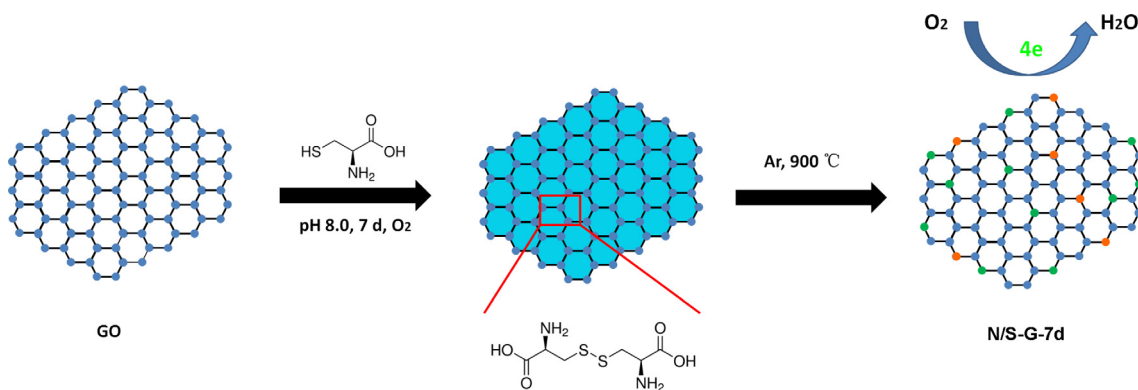


Fig. 1. Schematic showing the synthesis of N/S co-doped graphene.

heteroatom are significantly important to the final ORR activity [5,18,19]. In most cases, heteroatom-doping of carbon was achieved by thermal annealing of a precursor material composed of a carbon host with modified heteroatom source. It is not fully understood yet regarding how heteroatoms are conjugated into different sites of the host carbon lattice during the high temperature process, which restricts the rational design and synthesis of doped carbon for ORR catalysis.

Cysteine is a well-known sulfur-containing redox amino acid implicated in various biological systems [20,21]. It has been used as a precursor to synthesize N/S-doped carbon quantum dots [22]. Due to the presence of reductive thiol, cysteine possesses considerable reducing ability and is able to be oxidized by dissolved oxygen at neutral pH to form a cystine dimer [23]. At the same time, cysteine is able to bind to graphene oxide (GO) surface via electrostatic attraction and/or hydrophobic interaction [24] or via the ring-opening of epoxides on GO sheets [25].

Considering the abundant chemistry of cysteine and its various ways binding to GO, in this work we used it as a green N/S source to functionalize GO under different reaction condition, followed by annealing in an inert Argon atmosphere to synthesize N/S-doped graphene catalysts. Systematic characterizations and electrochemical comparisons unveiled that although N/S-doping is successfully achieved in all synthesized catalysts, their ORR activity varies significantly upon the change of the cysteine-GO reaction time. The optimal catalyst demonstrates ORR performance superior to commercial Pt/C in alkaline media. A unique process of oxidation-induced *in situ* disulfide formation with optimal grafting density is further disclosed to be critical in the synthesis of the optimal catalyst, as shown in Fig. 1. This work suggests that the heteroatom source itself and careful optimization of reaction conditions are critical to obtain high performance doped-graphene electrocatalyst, and thus may offer a valuable clue on the rational design of metal-free ORR electrocatalysts.

2. Experimental

GO was prepared using the modified Hummers method [26,27]. Graphite powder (0.5 g) and sodium nitrate (NaNO_3 , 0.5 g) were mixed with concentrated sulfuric acid (H_2SO_4 , 98%, 23 mL) and stirred for 30 min in an ice bath. Potassium permanganate (KMnO_4 , 3.0 g) was slowly added into the mixture with vigorous stirring. The mixture was further stirred for 1 h in a 35 °C water bath before water (40 mL) was slowly added under vigorous stirring. The mixture was stirred for 30 min at 90 °C. Finally, 100 mL of water was added to the mixture, followed by hydrogen peroxide (H_2O_2 , 30%, 3.0 mL). After cooling down to room temperature, the products were collected by using centrifugation, and washed with 5 wt%

HCl and deionized water for several times. The yellow-brown suspension of GO was obtained by dispersing the products in water with the assistance of ultrasonication.

To synthesize N/S-doped graphene, cysteine (2.0 mg mL^{-1}) was added to GO suspension (1.0 mg mL^{-1}) and the pH of the final solution was around 5.0–6.0, which was further adjusted to 8.0 with 0.1 M KOH solution. After stirring the mixture at ambient atmosphere for 7 d, the product was collected by centrifugation, freezing-dried, and annealed at 900 °C (Ar atmosphere, heating rate of 5 °C min^{-1} , maintaining at 900 °C for 3 h), as shown in Fig. 1. This catalyst was denoted as N/S-G-7d. For comparison, N/S-G-1d, N/S-G-4d and N/S-G-14d were also obtained by adjusting the cysteine-GO reaction time to 1, 4 and 14 d, respectively. GO was also processed with the same annealing procedure to obtain thermally reduced GO (RGO).

An Autolab PGSTAT302N potentiostat system was used for electrochemical measurements in a three-electrode cell with Pt foil as the counter electrode. Hg/HgO/1M KOH electrode was used as the reference electrode, to which all potentials reported in present work are referring. Also the potential could be easily converted to the one versus Reversible Hydrogen Electrode (E_{RHE}) by using the Nernst equation:

$$E_{RHE} = E_{\text{Hg}/\text{HgO}} + 0.059 \times \text{pH} + E_{\text{Hg}/\text{HgO}}^0$$

where the pH is the electrolyte pH (13 in this case) and the $E_{\text{Hg}/\text{HgO}}^0$ is 0.098 V versus Normal Hydrogen Electrode (NHE). The working electrode was prepared by casting catalyst slurry (dispersing 2.0 mg of catalyst and 50 μL of 5 wt% Nafion solution in 1.0 mL of ethanol) onto glassy carbon electrode (2.0 mm diameter, 5 μL applied for cyclic voltammetry CV measurements, and 5.0 mm diameter, 25 μL applied for linear scanning voltammetry, LSV measurements) and the solvent was allowed to naturally evaporate at room temperature. Before each experiment, the freshly prepared electrolyte (0.1 M KOH) was bubbled with pure N_2 or O_2 for 30 min.

Fourier transform infrared (FTIR) spectra were measured on Nicolet FTIR 6700 spectrophotometer. X-ray photoelectron spectrum (XPS) was collected on an ESCALAB 250Xi system from Thermo Fisher. Transmission electron microscopy (TEM) and Scanning electron microscopy (SEM) images were obtained on a JEM-2100 system and a JSM-7800F system from JOEL, respectively. Raman spectra were collected on a RENISHAW inVia Raman Microscope with 532 nm excitation.

3. Results and discussion

The annealing temperature was first optimized and 900 °C was chosen as the optimal temperature for thermal treatment of the precursor, as shown in Fig. S1. The ORR activity of as-prepared N/

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