Short communication

A one-pot method to synthesize high performance multielement co-doped reduced graphene oxide catalysts for oxygen reduction

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ABSTRACT

A Fe, N and S multielement co-doped reduced graphene oxide (Fe–N–S/rGO) was successfully prepared using a one-pot method by directly pyrolyzing a mixture of graphene oxide (GO), $FeCl_3$, melamine and sulfur in N_2 flow, during which deoxidization of GO and multielement co-doping are realized simultaneously. This catalyst shows excellent oxygen reduction activity in an alkaline medium, with an onset potential of 0.95 V (vs. RHE) and a kinetic-limiting current density of 4.78 mA cm^{-2} at 0.68 V (vs. RHE), which is superior to that of commercial Pt/C. Furthermore, it exhibits long-term stability, excellent methanol tolerance and high selectivity for the four-electron reduction pathway.

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1. Introduction

Doped carbon materials as oxygen reduction reaction (ORR) catalysts in fuel cell cathodes have attracted a great deal of attention for their distinct advantages: relative cost-effectiveness and good catalytic performance [1–5]. Among these materials, graphene-based doped carbon catalysts, including doped graphene and doped graphene oxide, are promising due to graphene's unique physical and chemical properties [6]. Some researchers using multi-heteroatom doped graphene/graphene oxide have achieved excellent ORR performance, resulting from both the increased number of dopant heteroatoms and synergistic effects between the dopants [7,8]. Nitrogen and sulfur co-doped graphene is reported to be an efficient cathode catalyst for the ORR [8,9], yielding a performance superior to that of mono-heteroelement doped catalysts. However, none of these have yet to perform as highly as commercial Pt/C.

The use of transition metals to improve the performance of N-doped carbon catalysts has been widely confirmed and reported [10–12]. Herein, we suggest a one-pot method for preparing a reduced graphene oxide catalyst co-doped with Fe, N and S. The catalyst exhibits excellent ORR activity, even superior to that of commercial Pt/C. To our knowledge, this is the first time a reduced graphene oxide catalyst co-doped with Fe, N and S has been prepared for application in the ORR.

2. Experimental

2.1. Preparation of the catalysts

Fe–N–S/rGO was prepared by a one-pot method. First, GO, $FeCl_3$, melamine and sulfur, in a mass ratio of 1:5:5:0.06, were thoroughly mixed by milling in a mortar. Next, the mixture was pyrolyzed at 850 °C for 30 min in N_2 flow, and then leached with acid. The resulting material is denoted as Fe–N–S/rGO. For comparison, Fe–N/rGO, N–S/rGO, N/rGO and S/rGO were also prepared using the same procedure. The GO used in this work was prepared by a simple approach, in which graphite oxide powder was thermally expanded at 850 °C for 30 min under N_2 atmosphere [13].

2.2. Characterization

Electrochemical measurements were performed on an electrochemical workstation (Ivium, Netherlands) coupled with a rotating disk electrode (RDE) system (Pine, USA) in a three-electrode system. The catalyst electrode was prepared by dropping 20 μL of 5 mg/mL catalyst ink on the glassy carbon disk (5 mm in diameter). A Pt wire and Ag/AgCl electrode (3 M NaCl) were used as the counter electrode and reference electrode, respectively. The Ag/AgCl electrode (3 M NaCl) was calibrated with respect to a reversible hydrogen electrode (RHE). The electrolyte was 0.1 M aqueous KOH solution. Rotating ring-disk electrode (RRDE) voltammograms were recorded on a CHI 750E electrochemical workstation (CH Instruments, USA) using a ring-disk electrode (5 mm in diameter for the Pt disk) at 1600 rpm. All the cyclic voltammetry (CV),

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linear sweep voltammetry (LSV) and RRDE voltammograms were performed with a scanning rate of 10 mV s^{-1} at room temperature.

3. Results and discussion

3.1. Morphology and structure

Fig. 1a,b,c,d shows SEM and TEM images of the Fe–N–S/rGO. The Fe–N–S/rGO shows a typical morphology of graphene. These curled and wrinkled graphene sheets, stacked together in a disorderly fashion, could easily form a porous structure, and such a structure was confirmed by BET testing. The high-resolution TEM image insets in Fig. 1c and d show well-defined graphitic lattice fringes, indicating good crystallization of the Fe–N–S/rGO nanosheets. No metallic nanoparticles can be observed in the TEM images.

The I_D/I_G value (Raman) of Fe–N–S/rGO ($I_D/I_G \approx 1.09$) is larger than that of GO ($I_D/I_G \approx 0.87$) (Fig. 1e), indicating that the number of defects and the amount of graphitic carbon greatly increased. As shown in
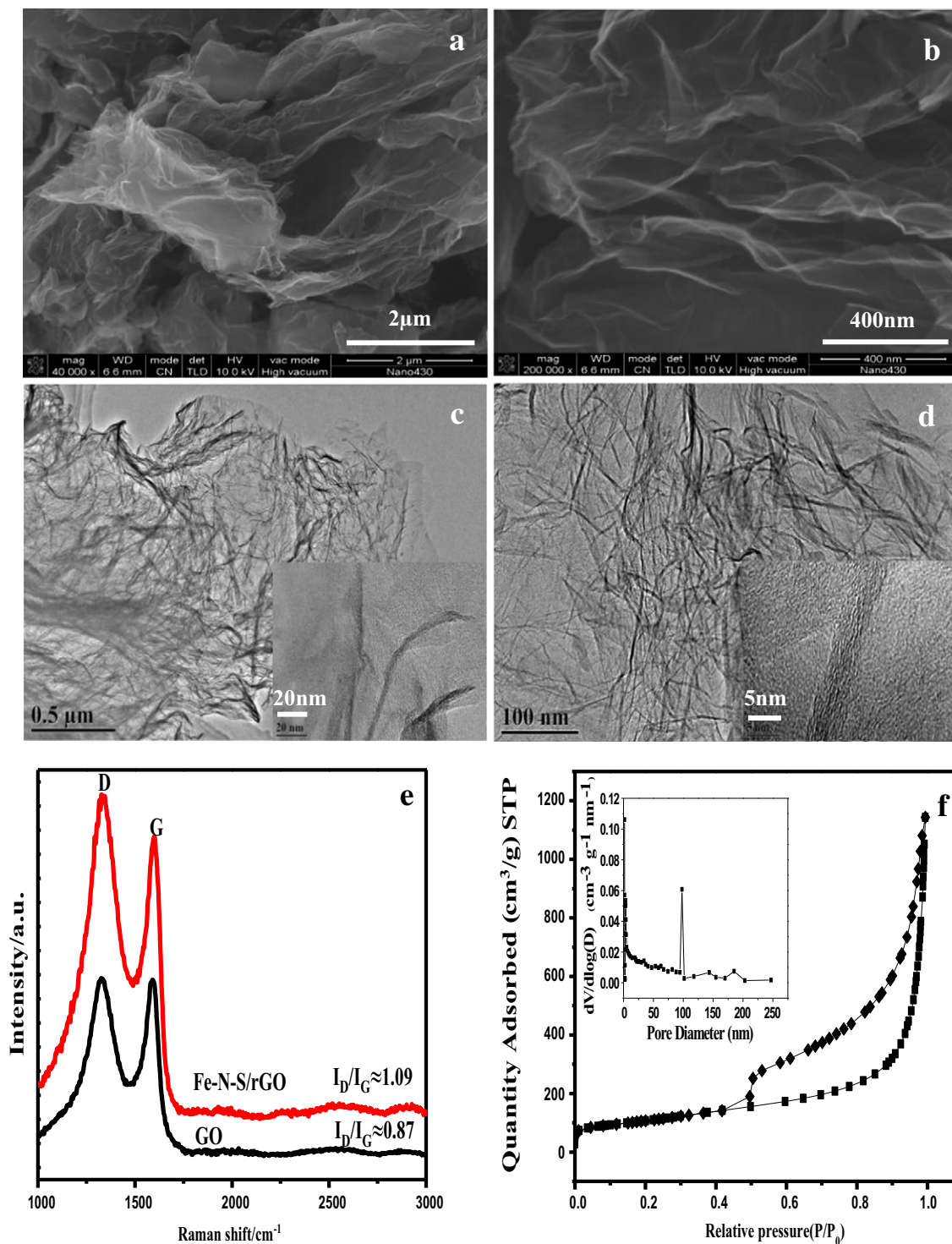

Fig. 1. SEM (a, b) and TEM (c, d) images of Fe–N–S/rGO, Raman spectra of Fe–N–S/rGO and GO (e), and nitrogen adsorption–desorption isotherms and (inset) the corresponding pore-size distribution of Fe–N–S/rGO (f).