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Nitrogen and Sulfur Dual-Doped Reduced Graphene Oxide: Synergistic Effect of Dopants Towards Oxygen Reduction Reaction

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ABSTRACT

We describe a facile single-step non-hydrothermal chemical route for the synthesis of N and S dual-doped reduced graphene oxide (SN-rGO) and the synergistic effect of N and S in oxygen reduction reaction (ORR). The reduction of graphene oxide (GO) and dual doping of rGO are achieved in one-step with a single doping agent in ethylene glycol. SN-rGO has pyridinic and pyrrolic nitrogen and thiophenic sulphur and it has N/C and S/C atomic ratio of 0.12 and 0.08, respectively. The atomic percentage of pyridinic N (66%) is significantly higher than pyrrolic N (34%). The electrocatalytic performance of SN-rGO towards ORR is examined in terms of onset potential, kinetic current density, number of electrons transferred, durability and methanol tolerance in alkaline solution. SN-rGO shows excellent electrocatalytic activity with an onset potential of −15 mV (Hg/HgO) and it tends promotes the four electron pathway. The activity of SN-rGO is superior to that of rGO doped only with N and S (N-rGO and S-rGO) and undoped rGO. The comparison of the ORR activity of SN-rGO with N-rGO and S-rGO indicates the synergistic effect of heteroatoms of SN-rGO in the electrocatalytic reaction. SN-rGO is highly durable and completely silent towards the anode fuel methanol.

1. Introduction

Development of highly efficient and stable metal-free electrocatalyst for the cathodic reduction of oxygen in fuel cells and metal air batteries received significant interest among the scientific community. This is due to the fact that the traditional state-of-the-art Pt-based catalysts are very expensive, scarce and the electron transfer kinetics of ORR on Pt is rather sluggish. Moreover, they are not durable and have intolerance towards anode fuel such as methanol and formic acid. It has been estimated that more than 30-50% of the fuel cell cost is actually due to the catalyst used in the membrane electrode assembly, which is the heart of the fuel cell [1,2]. The high cost of the catalyst limits the commercialization of fuel cells for practical applications. Several efforts are being taken to identify/synthesize new inexpensive electrocatalyst without compromising the activity [3–9]. In the recent past, the nanoscale Pt and Pt-based binary and ternary alloy and core-shell electrocatalysts and non-precious metal oxide-based catalysts have been exploited for ORR [8,10–14]. However, these catalysts lack durability and do not have high tolerance towards anode fuels. Most of the high performance ORR catalysts are highly capable of oxidizing the anode fuels [15]. Although the metal oxide-based catalysts are cost-effective, the poor electronic conductivity limits their catalytic performance. Very recently, the carbon-based materials have emerged as a promising metal-free catalyst for energy conversion and storage applications [7,9,16]. The as-synthesized N, S and B-doped mesoporous carbon and graphene/reduced graphene oxide (rGO) have been explored as a cathode catalyst for ORR [9,16–18]. The catalytic activity of these materials is comparable to those of the Pt-based material, though the actual mechanism is still unclear [18]. To date, among the heteroatom doped carbon-based catalysts, the nitrogen doped rGO (N-rGO) is known to efficiently catalyze ORR [19–27]. The chemical and electronic environment of N on the carbon framework strongly influences the catalytic activity. For instance, it has been demonstrated that the presence of large amount of pyridinic and graphitic N in the carbon network significantly enhances the electrocatalytic performance of N-rGO towards ORR [25–27].

Dual doping of rGO with two different heteroatoms is a promising approach to further improve the catalytic performance. Such dual doping with N, B or P has been explored in the recent past to facilitate the electron transfer of ORR [28–31]. A handful of papers report the dual doping of rGO with N and S and their catalytic activity towards ORR [32–38]. Most of these methods involve multi-steps, time-consuming tedious procedures and require very high temperature. For instance, Su et al. synthesized

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N and S doped 3-dimensional graphene framework by hydrothermal method at 180 °C for 10 h [35]. Liang et al. reported an interesting approach for the synthesis of dual doped mesoporous graphene using colloidal silica template at the temperature of 900 °C [32]. Xu et al. synthesized N and S doped few-layered graphene oxide for ORR using chemical vapour deposition [36]. Very recently, Ai et al. synthesized N and S doped graphene for catalytic and battery applications; the doping of heteroatom onto the carbon network and reduction of GO was achieved in two different steps involving 36 h and very high temperature [33]. The thermal annealing of GO with suitable S and N doping agents at high temperature (900 °C) is known to yield co-doped rGO [34,37].

Our group is interested in the development of efficient nanoelectrocatalyst for fuel cell applications [11,12,39,40]. Recently, we have demonstrated the electrocatalytic performance of a hybrid material derived from N-rGO and transition metal oxide [40]. The synergistic effect of N-rGO and metal oxide significantly improved the electrocatalytic performance of the hybrid catalyst. In an effort to develop a low cost metal-free electrocatalyst, herein we describe a rapid low temperature one-step chemical route for the synthesis of N and S dual doped rGO and its electrocatalytic performance towards ORR. The main focus of the study is to demonstrate a simple non-hydrothermal route for the single-step chemical doping of rGO with N and S and to explore the effect of dual doping in the electrocatalytic activity towards ORR. Our synthetic approach is very simple and the dual-doped catalyst has excellent electrocatalytic activity.

2. Experimental

2.1. Reagents and materials

Graphite and polyvinyledine fluoride (PVDF) were purchased from Sigma-Aldrich. $KMnO_4$, $NaNO_3$, H_2SO_4, Na_2S, thiourea, ethylene glycol (EG), urea, HCl and ammonia were obtained from Merck, India. All the solutions used in this experiment were made of Millipore water (Milli Q system).

2.2. Synthesis of GO

GO was synthesized according to modified Hummer's method by the exfoliation of graphite [41]. Concentrated H_2SO_4 (50 mL) was slowly added to a mixture of graphite powder (1 g) and $NaNO_3$ (1 g) in a 500 mL round-bottom flask at 0 °C. Then solid $KMnO_4$ (6 g) was added to the reaction mixture and it was stirred continuously for 1 h at room temperature. The mixture was then diluted with 200 mL of water. After 15 min, 30% H_2O_2 solution (~5 mL) was added to the reaction vessel until the gas evolution ceased. The exfoliated graphite was then separated from the reaction mixture by centrifugation. The residue was then washed thoroughly with 5% HCl solution to remove the sulfate ions. The washing was continued until the supernatant gave a negative test for the sulphate ions with $BaCl_2$ solution. The yellow-brown residue obtained after repeated washing with HCl was further washed with copious amounts of Millipore water and dried in vacuum.

2.3. Synthesis of SN-rGO, N-rGO and S-rGO

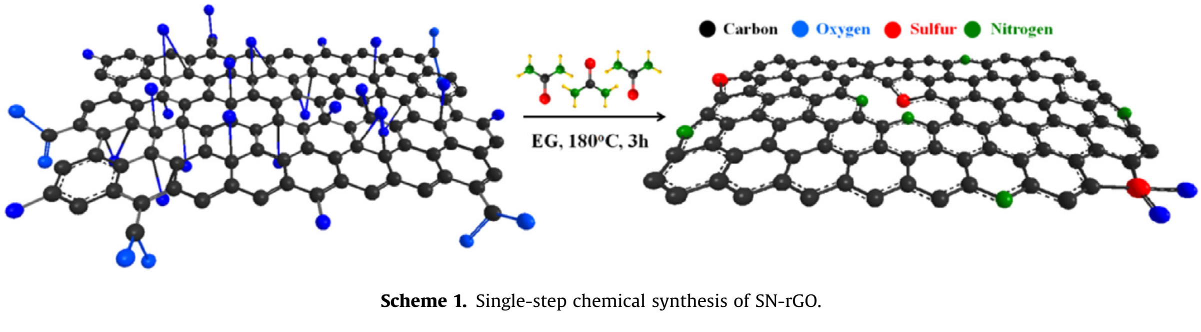
In a typical synthesis of SN-rGO, GO (20 mg) was dispersed in 20 mL of EG by ultrasonication for 1 h. The GO dispersion was then added to thiourea solution (1 mM) in EG. The mixture was again sonicated for 30 min and then transferred to a round bottom flask and subjected to reflux for 3 h at 180 °C (Scheme 1). After completion of the reaction, the product was collected by centrifugation and thoroughly washed with Millipore water and alcohol. The thus obtained SN-rGO was then dried in vacuum oven for 12 h at 80 °C. The N-rGO and S-rGO were synthesized at an identical procedure using urea and Na_2S as doping agent.

2.4. Electrode preparation

The glassy carbon (GC) rotating disk (RDE) and GC-Pt rotating-ring-disk electrodes (RRDE) were polished well with fine emery paper and alumina (0.05 μm) slurry and sonicated in Millipore water for 10-15 min to remove the physically adsorbed impurities. These electrodes were washed repeatedly with copious amount of Millipore water and dried. The binder solution was prepared by mixing PVDF (1 mg) in 1 mL N-methyl-2-pyrrolidone (NMP). The catalyst ink was prepared by mixing appropriate amount of SN-rGO (0.4 mg) and binder solution (200 μL) and sonicated for 2 h. An aliquot of 10 μL of the catalyst ink was drop casted uniformly on the surface of RDE and RRDE and dried at ambient temperature. The loading of the catalyst on the electrode surface was kept at 0.1 mg/cm^2 in all the cases.

2.5. Materials characterization

Transmission electron microscopic (TEM) measurements were performed with JEOL JEM 2010 (TEM) at an operating voltage of 200 kV. Scanning electron microscopic (FESEM) measurements were carried out with FEI NOVA NANOSEM 450 field emission scanning electron microscope. Energy dispersive X-ray microanalyzer (BRUKER EDAX) attached to the FESEM was used for elemental compositional analysis. X-ray photoelectron spectral (XPS) profile was acquired with Theta Probe, Thermo Fisher Scientific, UK. Raman spectral measurement was performed using a Jobin Yvon Horiba T64000 spectrometer (France) with an excitation source of Argon Krypton mixed ion gas laser (488 nm, Spectra Physics, USA). Conductivity measurement was carried out using Vander Pauw 4 probe electrical measurement unit (supporting information). All electrochemical experiments were carried out in a two-compartment three-electrode cell with Hg/HgO reference, Pt wire counter and GC RDE and GC disk Pt ring RRDE working electrodes. Autolab potentiostat/galvanostat (302 N) workstation



Scheme 1. Single-step chemical synthesis of SN-rGO.