Simple preparation of nanoporous few-layer nitrogen-doped graphene for use as an efficient electrocatalyst for oxygen reduction and oxygen evolution reactions

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ABSTRACT

We prepared nitrogen-doped graphene (NG) by simple pyrolysis of graphene oxide and polyaniline, which was selected as the N source. The resulting NG contains 2.4 at.% N, of which as high as 1.2 at.% is quaternary N. Electrochemical characterizations reveal that the NG has excellent catalytic activity toward oxygen reduction reaction (ORR) in an alkaline electrolyte, including a desirable four-electron pathway for the formation of water, large kinetic-limiting current density, long-term stability and good tolerance to methanol crossover. In addition, we demonstrate that the NG also has high catalytic activity toward oxygen evolution reaction (OER), rendering its potential application as a bi-functional catalyst for both ORR and OER.

1. Introduction

Graphene, a single layer carbon atoms covalently bonded into a hexagonal lattice, processes many intriguing physical and mechanical properties. Deliberate doping of graphene with heteroatoms, such as B, N or O, can effectively tailor its electronic properties and chemical reactivity, leading to enhanced performance of doped graphene [1–3]. In particular, nitrogen-doped graphene (NG) has attracted much attention recently due to its enticing performance in supercapacitors [4], lithium-ion batteries [5], advanced catalyst support [6], and catalysis for oxygen reduction reaction (ORR) [7–10]. Among these, electrocatalysis of ORR is one of the most promising applications of NG because of the high catalytic activity, superior reliability, and its potential to replace expensive Pt-based catalyst for fuel cells and metal-air batteries.

The material property and performance of NG depend strongly on the bonding configuration of N atoms in graphene lattice. Fig. 1a shows schematically the bonding configurations of typical N functionalities present in NG, including N atoms doped into graphene basal plane (quaternary N), N atoms in six-member ring (pyridinic N) and five-member ring (pyrrolic N), and N atoms bonded with O atoms (oxidized N). Quaternary N is shown to be vital to ORR catalytic activity [11–13]. Moreover, quaternary N is the most beneficial functionality for enhancing the capacitance of graphene in supercapacitor [4]. Further, pyridinic N is predicted to have higher reversible capacity in lithium ion battery by a recent theoretical study [14]. Therefore, it is very important to achieve high percentage of desirable N functionalities to optimize the materials performance.

To date, a variety of methods have been developed to prepare NG. While NG with high percentage of quaternary or pyridinic N dopant has been obtained by carefully tuning the growth parameters in a chemical vapor deposition (CVD) process [15,16], the extreme low yield limits its applicability to fundamental studies. Other existing approaches show less controllability over the bonding configuration of N dopant,
including segregation growth [17], arc-discharge of graphite [18], solvothermal synthesis [19], and post-treatment of graphene/graphene oxide (GO) with NH3, hydrazine or nitrogen-plasma [4,20–22]. Furthermore, most of these complex processes are either prohibitively expensive (limited to laboratory scale production) or involving toxic precursors. Therefore, a rational approach to control the N-doping process is highly desirable, which determines not only the nature of N functionalities and the resulting NG performance, but also the cost effectiveness for large-scale production and practical applications.

Recent studies have demonstrated that the pyrolysis of GO with a low-cost N source, such as urea [9] and melamine [8,10], is a versatile method for large-scale production of NG with flexible control over the N bonding configurations. It is found that the nature of N functionalities in the resulting NG is largely determined by the structure of N source and the pyrolysis temperature [9,10]. Here we report our findings in the synthesis of NG via pyrolysis of graphene oxide with polyaniline (PANI), which was selected as the N source because the structural similarity of its N atoms to quaternary N may facilitate the formation of quaternary N during pyrolysis. Fig. 1b schematically depicts the synthetic approach, where a conformal layer of PANI is coated on GO surface, forming GO–PANI composite (GO–PANI). The GO–PANI is further pyrolyzed to convert PANI to NG that attaches on graphene surface. In this process, GO acts as a structuring agent that guides the formation of thin-layer PANI and thermally derived NG. The effect of pyrolysis temperature has been systematically studied. We found that 1000 °C appears to be an optimal pyrolysis temperature that produces NG with excellent catalytic activity and outstanding durability toward ORR. Accordingly, the structure and ORR catalytic activity of NG sample pyrolyzed at 1000 °C (NG-1000) are discussed in detail (samples are denoted as NG-temperature, where the temperature refers to the pyrolysis temperature). In addition to ORR, we also examined the electrocatalytic properties of NGs for oxygen evolution reaction (OER), an important reaction for many energy storage and conversion processes in regenerative fuel cells and rechargeable metal–air batteries, etc. [23,24].

2. Experimental

2.1. Material synthesis

GO was prepared using the Hummers’ method. To prepare GO–PANI composite, 200 mg GO was dispersed in 40 mL water by sonication. Concentrated HCl was added into GO suspension to form a 1 M solution. After that, 100 mg aniline monomer was added into the GO solution. A catalyst solution of 0.17 g (NH4)2S2O8 in 1 M HCl was added. The reaction was carried out for 24 h. Then the GO–PANI composite was collected by vacuum filtration and washed with copious water. The GO–PANI composite was dried at 55 °C overnight. The NG was prepared by pyrolyzing GO–PANI composite at 1000 °C for 30 min in an Ar atmosphere. The undoped graphene was prepared by pyrolyzing GO at 1000 °C for 30 min in an Ar atmosphere and used as a control sample. Pure PANI is prepared in the same way without adding GO.

2.2. Characterizations

Transmission electron microscopy (TEM, JEOL100 CX) and scanning electron microscopy (SEM, LEO 1530) equipped with an EDS detector (Oxford Instruments) were used to image the morphology of NGs. The nitrogen adsorption/desorption isotherm was collected using a Micromeritics TriStar II sorptometer (Micromeritics Instrument Corporation, USA). Powder X-ray diffraction (XRD) analysis was carried out with a Philips X’pert II powder diffractometer, using Cu Kα radiation (45 kV and 40 mA). The X-ray photoelectron spectroscopy (XPS) was carried out with a Thermo K-Alpha XPS. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out on a simultaneous DSC–TGA analyzer (SDT Q600, TA Instruments Co.). Raman characterization was carried out using a LabRAM ARAMIS, Horiba Jobin Yvon with a 532-nm-wavelength laser. Fourier transform infrared spectroscopy (FTIR) characterization was performed at ambient temperature with a FTIR spectrometer (Nicolet, Magna IR 560).

2.3. Electrochemical characterizations

The electrochemical properties of NG were tested in a three-electrode system. A Pt wire and Ag/AgCl electrode filled with
saturated KCl aqueous solution were used as the counter electrode and reference electrode respectively. The electrolyte was 0.1 M aqueous KOH solution which was purged by nitrogen or oxygen for 10 min prior to the electrochemical test. To prepare the NG-loaded working electrode, NG was dispersed in the mixture water and isopropanol (V:V = 4:1) containing 0.05 wt.% Nafion. 10.00 µL of 1 mg/mL NG dispersion was transferred onto a glassy carbon electrode (GC, 3 mm diameter, 0.07065 cm² geometric area) and dried at 80 °C. The NG loading was calculated to be 141 µg/cm². The control sample graphene and Pt/C (20 wt.% Pt, Alpha Aesar) on GC were prepared in the same way. Cyclic voltammetry (CV) and Linear scan voltammetry (LSV) were measured on a Versastat 2-channel system (Princeton Applied Research). The electrocatalytic activities toward ORR were also measured using a rotating disk electrode (Pine Instrument, MSR Analytical Rotator) with a scan rate of 10 mV/s. 28 µL of 1 mg/mL NG dispersion was transferred onto the GC electrode (5 mm diameter, 0.196 cm² geometric area) embedded in a PTFE holder, and dried in air at 80 °C for 1 h. A platinum wire was used a counter electrode. The 0.1 M KOH solution was prepared as electrolyte and saturated with oxygen by bubbling with oxygen gas for 30 min before measuring ORR activities. The potential was controlled by a potentiostat (Solartron, SI 1286).

3. Results and discussion

GO–PANI was synthesized via an in situ polymerization reaction, where aniline monomer was polymerized in an acidic GO solution using ammonium persulfate as the catalyst. The GO acts as a structuring agent so that a uniform layer of PANI was coated on GO sheet (Fig. 2a). In comparison, PANI nanorods were obtained without adding GO (Supplementary Fig. S1). The GO–PANI sheets stack into a 3D porous structure as a result of the introduction of PANI (Fig. 2b), which changes the attractive/repulsive force ratio between GO sheets [25,26]. This phenomenon has been discussed in previous studies on GO-conducting polymer hydrogels [25,26]. Clean multi-layer graphene with lots of wrinkles was produced after pyrolysis, as shown in Fig. 2c. The semi-transparent nature of NG-1000 under TEM observation indicates a small thickness. The SEM image shown in Fig. 2d reveals that the 3D assembly

Fig. 2 – (a) TEM and (b) SEM image of GO–PANI; (c) TEM and (d) SEM image of NG-1000.
of NG-1000 was largely preserved after pyrolysis. The 3D architecture leads to a high portion of meso- and micro-pores. Fig. 3 shows the nitrogen adsorption/desorption isotherm of NG-1000, which has a type-IV curve with an H2-type of hysteresis loop [27]. The Brunauer–Emmett–Teller (BET) surface area of NG-1000 is measured to be \( \frac{377}{\text{m}^2/\text{g}} \) with an average pore diameter of \( \frac{11.5}{\text{nm}} \) (Fig. 3 inset). The XRD pattern of NG-1000 shown in Supplementary Fig. S2 has a broad peak at \( \frac{26.2}{\text{}} \), corresponding to an inter-layer spacing of \( \frac{0.340}{\text{nm}} \) that is close to \( \frac{0.335}{\text{nm}} \) for graphite.

X-ray photoelectron spectroscopy (XPS) is used to probe the chemical composition and structure of NGs. As shown in Fig. 4a, the survey spectrum of NG-1000 reveals the presence of C, N and O without any other impurities. The N content is found to be 2.4 at.%. The successful N-doping was also confirmed by elemental mapping using energy dispersive spectroscopy (Supplementary Fig. S3). The high resolution N 1s spectrum was used primarily to determine the bonding configurations of N atoms in NG. As seen in Fig. 4a inset, the peak deconvolution suggests four components in NG-1000 centered at 398.2, 400.0, 401.0, and 403.0 eV, corresponding to pyridinic N, pyrrolic N, quaternary N and oxidized N, respectively [28,29]. The quaternary N percentage is as high as 51.1%, which is vital to high catalytic activity. In addition, the high resolution C 1s spectrum shows a peak centered at 284.7 eV, and a tail at higher binding energies that is caused by hetero N and O atoms in NG (Supplementary Fig. S4a). Moreover, the deconvolution of high resolution O 1s spectrum suggests that the O atoms exist in –OH groups and absorbed water molecules (Supplementary Fig. S4b).

The evolution of N functionalities during pyrolysis was investigated by plotting the percentages of N functionalities with respect to the pyrolysis temperature, as shown in Fig. 4b. The N atoms in as prepared GO–PANI exist in imine and amine groups (Supplementary Fig. S5). After being pyrolyzed, pyridinic N forms as a result of the crosslinking of PANI chains [30,31], while pyrrolic N is generated from amines N [9,10]. When increasing the pyrolysis temperature, the decomposition and re-construction of PANI lead to a monotonic decrease in percentage of the pyrrolic N,1 and an in-

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1 It is impractical to distinguish pyrrolic N and amine N because their XPS peaks are very close. Here pyrrolic N represents both pyrrolic N and residual amine N. However, we believe the contribution of amine N is very small due to its thermal unstability.
crease in percentage of the pyridinic N and quaternary N, suggesting a transformation of pyrrolic N to pyridinic N and quaternary N. Moreover, the pyridinic N percentage drops at temperatures greater than 700 °C, due probably to the transformation of pyridinic N to quaternary N. The change in N functionalities during pyrolysis of GO–PANI is generally consistent with our previous findings [9,10].

The pyrolysis of PANI was monitored by simultaneous differential scanning calorimetry–thermogravimetric analysis (Supplementary Fig. S7), which reveals several major physical changes and chemical reactions during the pyrolysis of PANI, including the loss of adsorbed water at ~100 °C, desorption of volatile compounds and dopant between 200 and 300 °C, and structural decomposition of PANI at temperatures greater than ~350 °C. It was also reported that the cross-linking reaction of PANI occurs at temperature above 170 °C [30,31]. These chemical reactions of PANI are in line with transformations of N functionalities in NG. The structural change of NGs during pyrolysis was further investigated using Raman and FTIR spectroscopies. Raman spectroscopy is useful to measure the structural disorder in graphene materials. Fig. 4c shows the Raman spectra of GO–PANI and NGs pyrolyzed at different temperatures. It is found that the $I_D/I_G$ ratio decreases from 1.17 initially for GO–PANI to 0.95–0.99 for NG-300–NG-600, due to thermal reduction of GO. Then the $I_D/I_G$ ratio starts to increases to ~1.1 for NG-800–NG-1100 due to the decomposition of epoxy and hydroxyl groups that leads to the in-plane C–C crack. As shown in Fig. 4d, the FTIR spectrum of GO–PANI shows characteristic peaks for both GO and PANI. Peaks at ~3440, 1632, and 1384 cm$^{-1}$ could be attributed to O–H stretching in hydroxyls and physisorbed water, HOH bending in physisorbed water, and C–O bending in phenol groups respectively [32]. The broad peak between 1000 and 1200 cm$^{-1}$ results from the stretching of C–O and C–C. PANI has characteristic peaks at ~1464 cm$^{-1}$ from the benzenoid structure, ~1300 cm$^{-1}$ from the C–N stretching of a secondary aromatic amine, and ~1237 cm$^{-1}$ from the C–N $^+$ stretching in the polaron structure [33]. As the GO–PANI being pyrolyzed at 300 °C, the peak at ~1562 cm$^{-1}$, a shoulder peak in GO–PANI, becomes very obvious, which could be attributed to C–C

![Graph](image_url)

Fig. 5 – Electrocatalytic activity of NG-1000 toward ORR and OER. (a) CV curves of NG-1000 in nitrogen or oxygen saturated 0.1 M KOH with a scanning rate of 100 mV/s. (b) RDE measurement of NGs in oxygen saturated electrolyte with a scanning rate of 10 mV/s. Inset is the Koutecky–Levich plots at different potentials. (c) CV curves of NG-1000 in nitrogen saturated 0.1 M KOH with a scanning rate of 100 mV/s. (d) LSV of NG-1000, graphene, Pt/C and glassy carbon electrode in 0.1 M KOH with a scanning rate of 10 mV/s.
stretching in reduced GO and the quinonoid structure of PANI [2,23]. Moreover, the peaks at ~1632, ~1300 and 1237 cm\(^{-1}\) disappear, due to the removal of physisorbed water and the decomposition of PANI. In the spectrum of NG-400, the peak at 1464 cm\(^{-1}\) are much diminished as a result of the decomposition of benzoid structure. Finally in NG-1000, O–H in phenols, C–O and C–N are major residual functional groups.

The catalytic properties of NG-1000 were investigated in a conventional three-electrode system. As seen in Fig. 5a, cyclic voltammetry (CV) of NG-1000 reveals a pure capacitive current background in nitrogen saturated electrolyte. In oxygen saturated electrolyte, a prominent cathodic current appears with a peak centered at ~0.22 V, indicating a high ORR catalytic activity. Rotating disk electrode (RDE) measurement was used to characterize the kinetics of ORR catalyzed by NG-1000, as shown in Fig. 5b. The number of electron transfer is calculated to 3.8–3.9 between ~0.35 and ~0.5 V from the Koutecky–Levich plots (Fig. 5b inset), suggesting that the ORR on NG-1000 surface produces water via a desirable four-electron pathway. The kinetic limiting current is 8.9 mA/cm\(^2\) at ~0.35 V, and up to 11.6 mA/cm\(^2\) at ~0.40 V. Moreover, the reliability test of NG-1000 showed superior long-term stability and resistance to methanol crossover to the commercial Pt/C catalyst. After 2000 CV cycles in oxygen saturated electrolyte, the CV curve of NG-1000 showed minimal changes, whereas the CV curve of Pt/C showed a significant reduction of area and cathodic current. Moreover, the addition of 3 M methanol did not hinder the ORR on NG-1000. In contrast, methanol oxidation reaction occurred on Pt/C that greatly suppressed the ORR (Supplementary Fig. S8). Supplementary Table S1 compares the performance of NG-1000 with those previous reports [7–10,34,35]. It is clear that our NG-1000, though with a moderate N-doping level (2.4 at.%), shows a superior catalytic performance, owing to a high percentage of quaternary N.

It was found the ORR catalytic activity of NG depends strongly on the pyrolysis temperature. The numbers of electron transfer at ~0.35 V are 3.21, 3.31, 3.93, and 3.48, respectively, for NG-800, NG-900, NG-1000, and NG-1100 (Supplementary Fig. S9). This dependence is resulted from the previously mentioned evolution of NG structure during pyrolysis. As shown in Fig. 4b, quaternary N content increased with pyrolysis temperature, leading to a higher catalytic activity. However, at temperature greater than 1000 °C, the decomposition of N functionalities occurred, which lowers the N content (N content in NG-1000 is 1.1 at.%) and the resulting catalytic activity.

We extended the CV potential range step by step to water oxidation regime to study the catalytic activity of NG-1000 toward OER. As seen in Fig. 5c, the large anodic current appears when the electrode potential was scanned between ~0.6 and 0.8 V, indicating the occurrence of OER on NG-1000 surface. Moreover, the evolved oxygen can be reduced, leading to a cathodic current peak in the OER regime. When the potential was further extended to 1.0 V, the OER current and the resulting ORR current increased dramatically. The ORR current also increased with the number of cycles due probably to the accumulation of evolved oxygen. It was found that OER catalytic activity of NG-1000 is higher than those of undoped graphene, the commercial Pt/C catalyst, and the glassy carbon electrode, as evidenced by the linear scan voltammetry (LSV) curves of these materials shown in Fig. 5d. However, NGs pyrolyzed at 800–1000 °C show similar LSV curves in OER regime as shown in Supplementary Fig. S10, indicating that the OER activity of NG is less dependent on the pyrolysis temperature compared to that of ORR.

4. Conclusion

We developed a facile method for large-scale preparation of NG via pyrolysis of GO and PANI. Due to the structural similarity between N atoms in PANI and quaternary N, a high quaternary N percentage of up to 51% (relative to N dopant) was obtained, which is critical to ORR activity of NG. As a result, the NG exhibits an excellent catalytic activity toward ORR with a superior long-term stability and tolerance to methanol crossover. In addition, we found that NGs also shows high OER catalytic activity. Thus, it is ideally suited as catalyst for reversible air (O\(_2\)) electrodes for fuel cells and metal–air batteries.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbon.2012.10.039.

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