Supporting Information

Controlled Electrochemical Intercalation, Exfoliation and \textit{in situ} Nitrogen Doping of Graphite in Nitrate-Based Protic Ionic Liquids

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Experimental

Materials

Graphite rods were purchased from Goodfellow (99.997%, 3.0 mm diameter, UK) and Sigma-Aldrich (99.999%, 3.0 mm diameter, USA), respectively. Ethylammonium nitrate (EAN, 98%) was purchased from Io-li-tec (Germany) and used as received. All other chemicals were purchased from Sigma-Aldrich and used without further purification. Water used throughout this study was purified by a MilliQ water purifying system and has a resistance of 18.2 mΩ.

Electrochemical procedure

All electrochemical exfoliation experiments were carried out with a CHI 760 electrochemical workstation (CH Instrument, USA). The graphite rod was used as the working electrode, a Ag/AgCl and a Pt wire (or graphite rod) were used as the reference and counter electrode, respectively. The potential was held at 2.2 V vs. Ag/AgCl for 2 hours, and the precipitate prepared from this experiment was collected by filtration, and washed thoroughly with ethanol and water. The as-prepared nitrogen-doped graphene (N-graphene) was then dried at 40 °C overnight under vacuum.

Dried N-graphene (4 mg) was mixed with 1 ml 1:4 (v/v) ethanol and H₂O solution.
Then, 8 µL of 5 wt% Nafion (Sigma-Aldrich) solution was added into this mixture, and sonicated for more than 1h to form a homogeneous ink. Then, 3 µL and 6 µL of this ink was dropped casted on the surface of 3 mm diameter glassy carbon macrodisc electrode and 4 mm diameter glassy carbon rotating disk electrode, respectively, for further electrochemical characterization.

**Potential reference conversion**

In pure ionic liquids, a IUPAC recommended redox couple, ferrocene/ferrocenium (Fe\(^{0/+}\)), was used as the internal potential reference, and then converted to normal hydrogen electrode (NHE) reference using equation 1.\(^1\)

\[
E \text{ (vs. NHE)} = E \text{ (vs. } \text{Fe}^{0/+}) + 0.63 \text{ V} 
\]

where \(E \text{ (vs. NHE)}\) is the potential referenced against NHE, while \(E \text{ (vs. } \text{Fe}^{0/+})\) is the potential referenced against Fe\(^{0/+}\). For ionic liquid/water mixture, a Ag/AgCl was used as the reference electrode, and the potential was converted to NHE reference by equation 2.

\[
E \text{ (vs. NHE)} = E \text{ (vs. Ag/AgCl)} + 0.197 \text{ V} 
\]

where \(E \text{ (vs. Ag/AgCl)}\) is the potential obtained with a Ag/AgCl reference electrode.

**Physical characterization**

The as-prepared N-graphene was first dispersed in dimethylformide (DMF) to form a homogeneous solution. The solution was drop casted on the surface of indium tin oxide (ITO) coated glass then air-dried. The N-graphene coated ITO was then used as the sample for X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), X-ray Photoelectron Spectroscopy (XPS) and Raman Spectra characterization. For Transmission Electron Microscopy (TEM), samples were prepared by drop casting the N-graphene solution on the surface of copper grid, then dried in air.

**Calculation of number of electrons \((n)\) transfer in oxygen reduction reactions (ORR)**

The electron transfer number \(n\) was calculated using the Koutecky-Levich (K-L) equation:\(^2\)

\[
\frac{1}{i} = \frac{1}{i_k} + \frac{1}{Bi^0.5} 
\]

\(i\) is the kinetic limiting current, \(\omega\) is the rotating speed of the electrode, \(B\) is the slope
of K-L equation which can be determined by equation:

\[
B = 0.2 \ nF \left( D_{O_2} \right)^{2/3} \ \eta^{-1/6} \ \mathcal{C}_{O_2}
\]  

(4)

where \( n \) is the number of electrons transferred, \( F \) is the Faraday constant (96485 C mol\(^{-1}\)), \( D_{O_2} \) is the oxygen diffusion coefficient in 0.1 M KOH (1.73 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}), \( \eta \) is the kinetic viscosity (0.01 cm\(^2\) s\(^{-1}\)), and \( \mathcal{C}_{O_2} \) is the bulk concentration of O\(_2\) in air saturated 0.1 M KOH solution (2.4 \times 10^{-7} \text{ mol cm}^{-3}).
**Figure S1.** Cyclic voltammogram obtained with a graphite rod working electrode in EAN/H$_2$O (9/1, v/v) mixture at a scan rate of 0.1 V/s.

**Figure S2.** Anodic potential limit of neat EAN and EAN/H$_2$O (9/1, v/v) mixture obtained at a graphite rod working electrode at a scan rate of 0.1 V/s.
**Figure S3.** (a) Top view photograph of the electrochemical cell after exfoliation of graphite in EAN/water (9:1 v/v) at 2.2 V for 2 h. (b) The Tyndall effect of as-prepared N-graphene re-dispersed in DMF. (c) SEM image and (d) HRTEM image of the as-prepared N-graphene showing large area, few layer graphene are formed.

**Figure S4.** (a) High resolution C1s XPS spectrum of N-graphene.
Figure S5. XPS spectra of N-graphene prepared from EAN/water mixture at different volume ratios.

Figure S6. (a) Photograph of a graphite exfoliation in 70% nitric acid solution after 5 min at an applied potential of 2.2 V, (b) TEM image of precipitate obtained from graphite rod exfoliation in 70% nitric acid.
**Figure S7.** (a) Cyclic voltammograms obtained with a graphite rod working electrode in EAN/H$_2$O (9/1, v/v) mixture at a scan rate of 0.1 V/s at the 1st, 50th, and 100th cycle, respectively. (b, c) TEM and HRTEM images of N-graphene prepared from cyclic voltammetry exfoliation. (d) XPS survey spectra of N-graphene prepared from cyclic voltammetry exfoliation. Inset in (d) shows the high resolution N 1s XPS spectra of N-graphene.

**References:**