Supporting Information

Controlled Electrochemical Intercalation, Exfoliation and *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 ^{o}C overnight under vacuum.

Dried N-graphene (4 mg) was mixed with 1 ml 1:4 (v/v) ethanol and H_2O 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 ($\mathrm{Fc}^{0/+}$), was used as the internal potential reference, and then converted to normal hydrogen electrode (NHE) reference using equation 1.[1]

$$E\ (\text{vs. NHE}) = E\ (\text{vs. Fc}^{0/+}) + 0.63\ \text{V} \qquad (1)$$

where E (vs. NHE) is the potential referenced against NHE, while E (vs. $\mathrm{Fc}^{0/+}$) is the potential referenced against $\mathrm{Fc}^{0/+}$. 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.

$$E\ (\text{vs. NHE}) = E\ (\text{vs. Ag/AgCl}) + 0.197\ \text{V} \qquad (2)$$

where E (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]

$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{B\omega^{0.5}} \qquad (3)$$

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

$$B = 0.2\, nF\, (D_{O_2})^{2/3}\, \upsilon^{-1/6}\, C_{O_2} \qquad (4)$$

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 (1.73×10^{-5} cm^2 s^{-1}),[3] υ is the kinetic viscosity (0.01 cm^2 s^{-1}), and C_{O_2} is the bulk concentration of O_2 in air saturated 0.1 M KOH solution (2.4×10^{-7} mol cm^{-3}).[4]

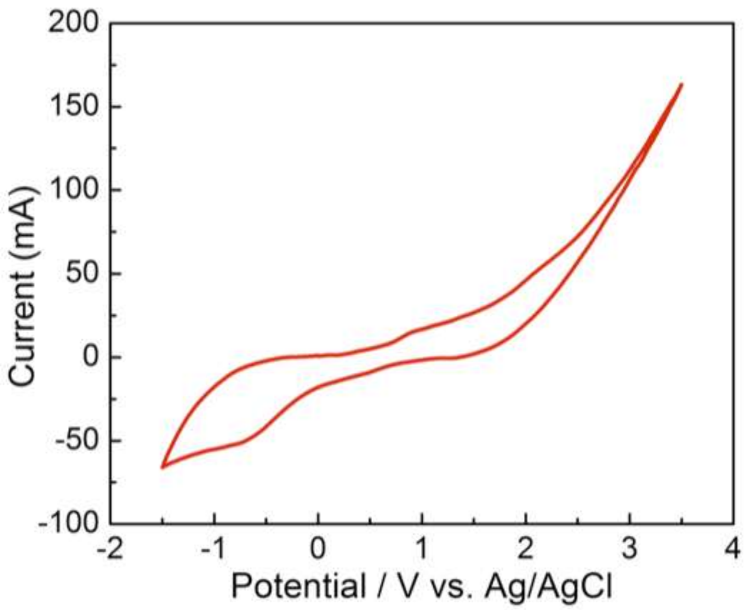

Figure S1. Cyclic voltammogram obtained with a graphite rod working electrode in EAN/H_2O (9/1, v/v) mixture at a scan rate of 0.1 V/s.

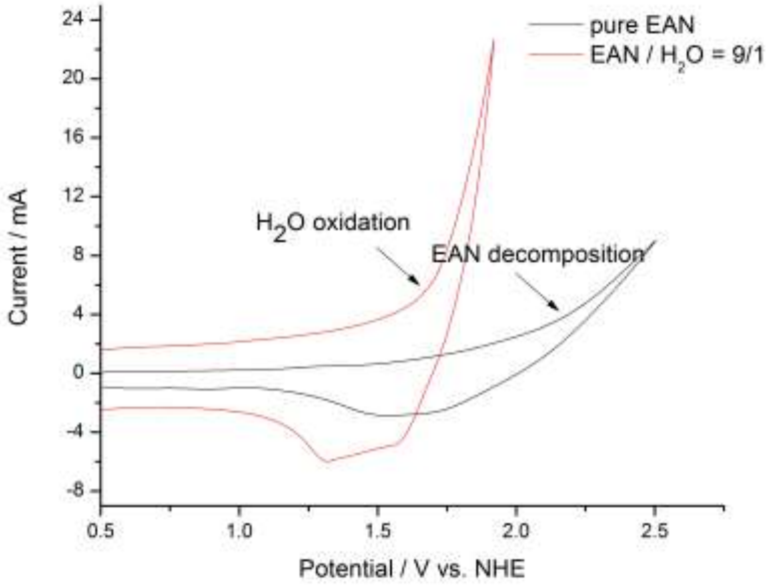

Figure S2. Anodic potential limit of neat EAN and EAN/H_2O (9/1, v/v) mixture obtained at a graphite rod working electrode at a scan rate of 0.1 V/s.

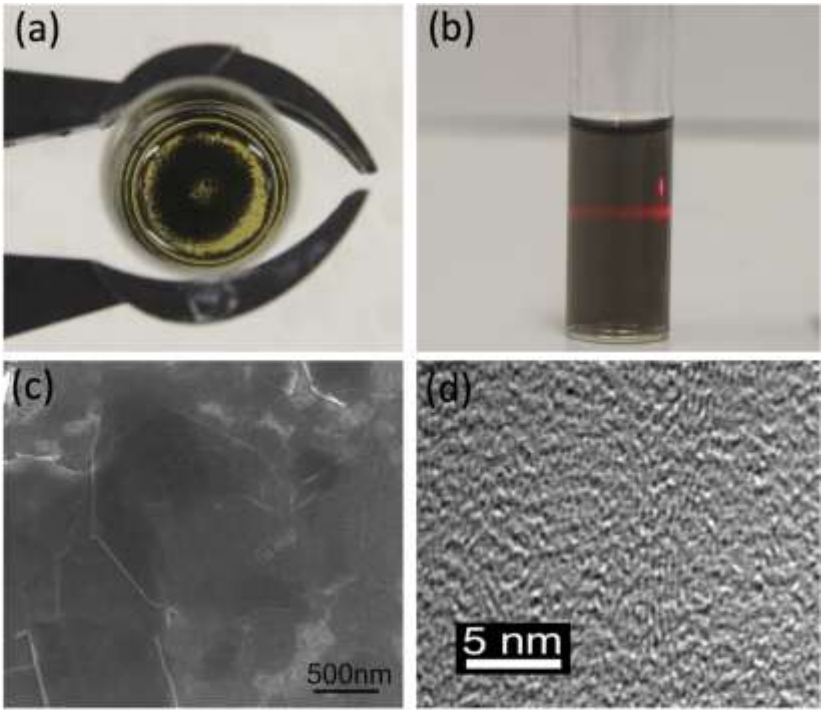

Figure S3. (a) Top view photograph of the electrochemical cell after exfoliation of graphite in EAN/water (9:1 v/v) at 2.2 V for 2 h. (b) The Tyndall effect of as-prepared N-graphene re-dispersed in DMF. (c) SEM image and (d) HRTEM image of the as-preapred N-graphene showing large are, few layer graphene are formed.

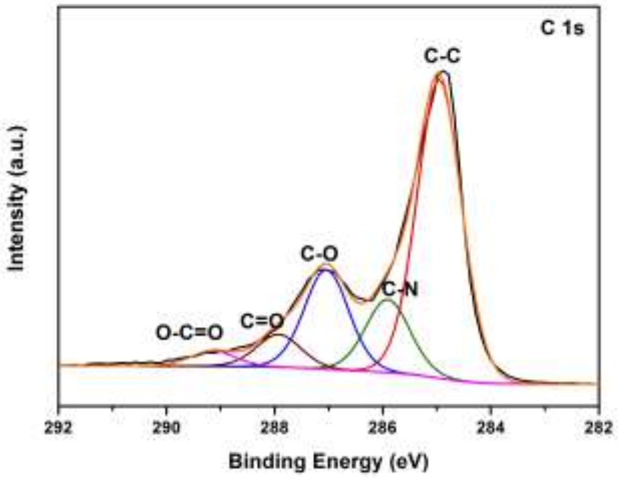

Figure S4. (a) High resolution C1s XPS spectrum of N-graphene.

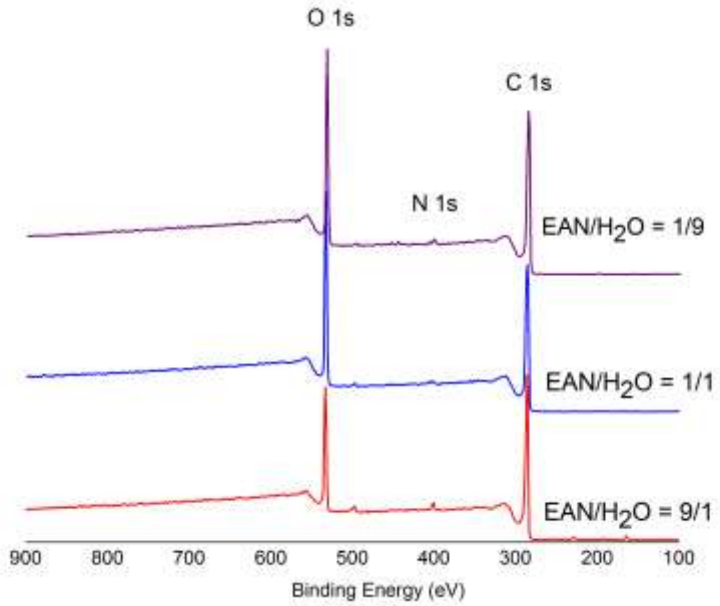

Figure S5. XPS spectra of N-graphene prepared from EAN/water mixture at different volume ratios.

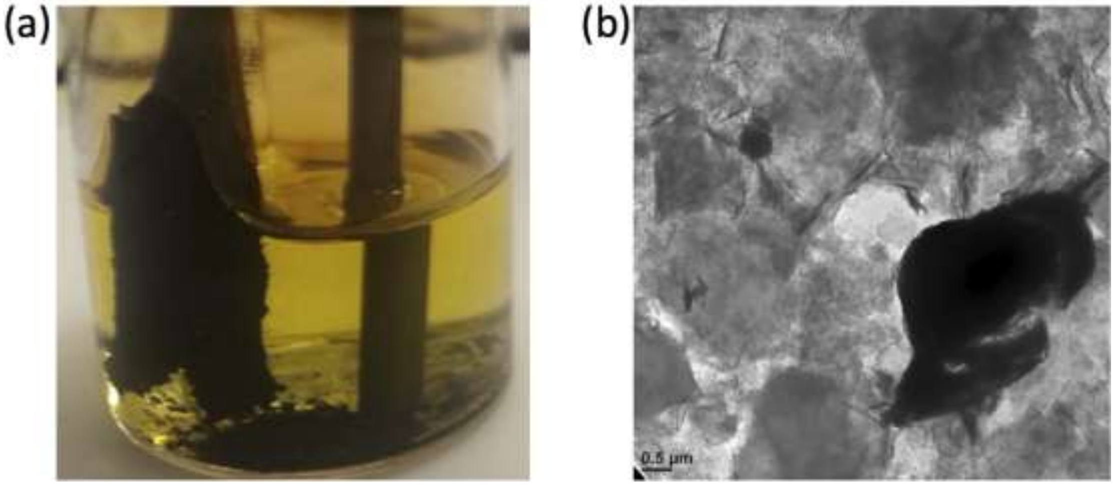

Figure S6. (a) Photograph of a graphite exfoliation in 70% nitric acid solution after 5 min at an applied potential of 2.2 V, (b) TEM image of precipitate obtained from graphite rod exfoliation in 70% nitric acid.

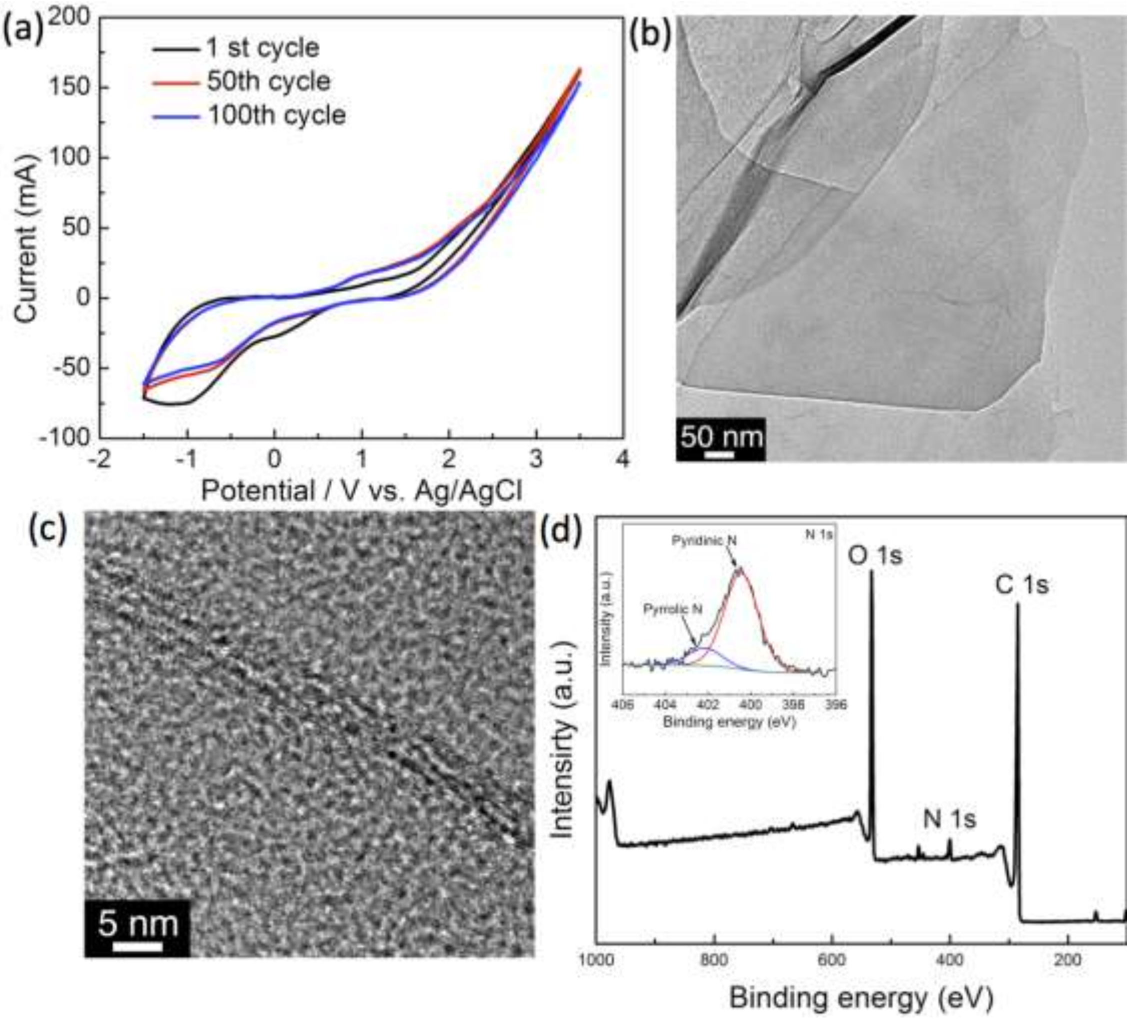

Figure S7. (a) Cyclic voltammograms obtained with a graphite rod working electrode in EAN/H_2O (9/1, v/v) mixture at a scan rate of 0.1 V/s at the 1st, 50th, and 100th cycle, respectively. (b, c) TEM and HRTEM images of N-graphene prepared from cyclic voltammetry exfoliation. (d) XPS survey spectra of N-graphene prepared from cyclic voltammetry exfoliation. Inset in (d) shows the high resolution N 1s XPS spectra of N-graphene.

References:

1. V. V. Pavlishchuk and A. W. Addison, *Inorg Chim Acta*, 2000, **298**, 97-102.
2. K. Tammeveski, T. Tenno, J. Claret and C. Ferrater, *Electrochim Acta*, 1997, **42**, 893-897.
3. G. L. H. R.E. Davis, C.W. Tobias, *Electrochim Acta*, 1967, **12**, 11.
4. L. T. Qu, Y. Liu, J. B. Baek and L. M. Dai, *Acs Nano*, 2010, **4**, 1321-1326.