**Supporting Information**

# Nitrogen-Doped Graphene as Efficient Metal-Free Electrocatalyst for Oxygen Reduction in Fuel Cells

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Figure S1 shows a SEM image of the N-graphene film while Figure S2 shows Raman spectra for both N-graphene and C-graphene films, indicating that nitrogen doping has introduced defects into the graphene structure. For the graphene films with a similar thickness (reflected by a similar intensity ratio of the G band (1580 $cm^{-1}$) to 2D band (2680 $cm^{-1}$), the N-graphene film shows a higher intensity for the D band (1350$cm^{-1}$) than that of C-graphene film ((Figure S2a)), as also reflected by the normalized spectra in Figure S2 (b). The appearance of D' band in 1620 $cm^{-1}$, albeit relatively small, provides an additional evidence for the N-doping induced defects in graphene structure.

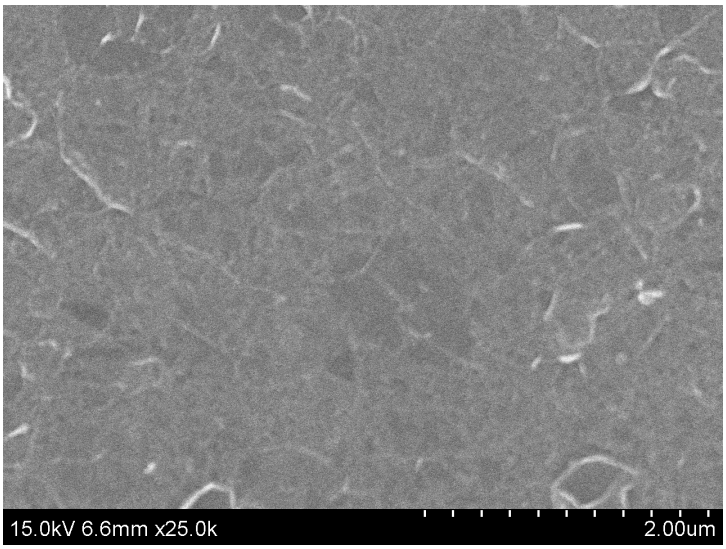


**Figure S1.** SEM image of the *as-synthesized* N-graphene film.

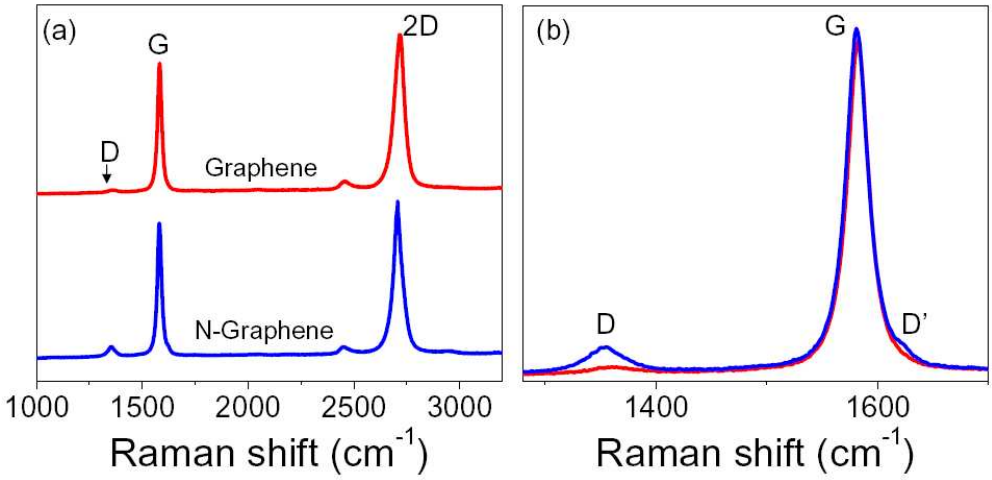


**Figure S2.** Raman spectra of N-graphene (blue) and C-graphene (red) films. (b) A partially magnified view of Raman spectra from (a) after normalization at the G band, showing a higher D band for N-graphene.

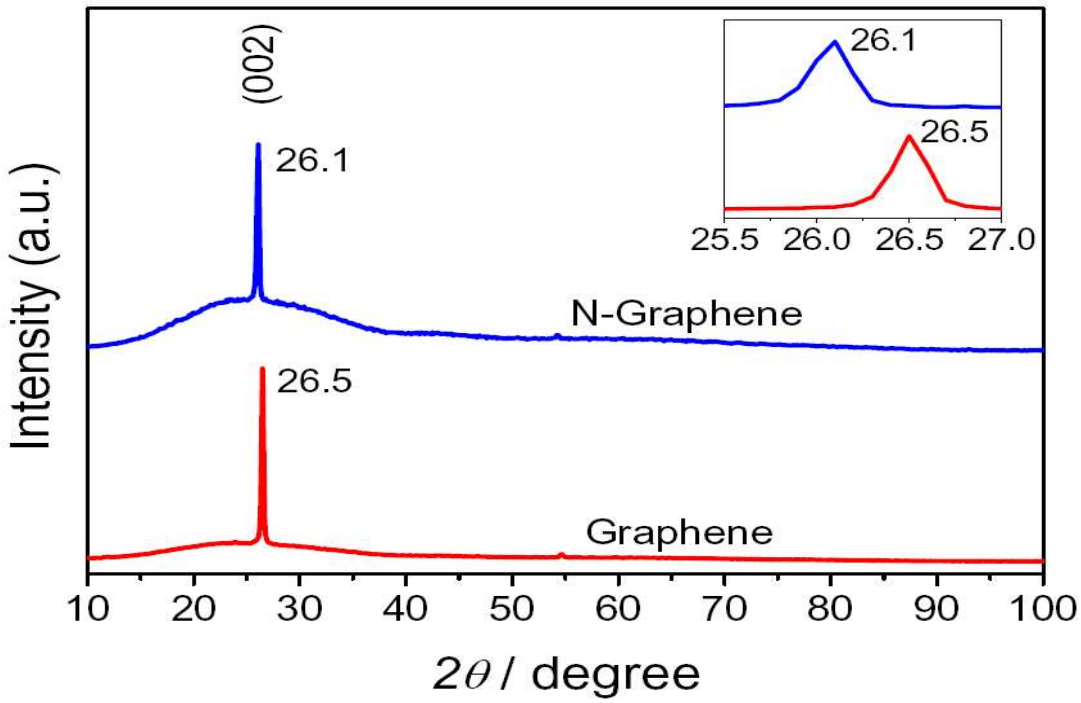


**Figure S3.** XRD profiles for N-graphene and C-graphene films. The (002) peak at 26.5° (2θ) for C-graphene film corresponds to a graphene layer with a d-spacing of 3.36 Å. The (002) peak at 26.1° (2θ) for N-graphene film corresponds to a interlayer spacing of 3.41 Å.

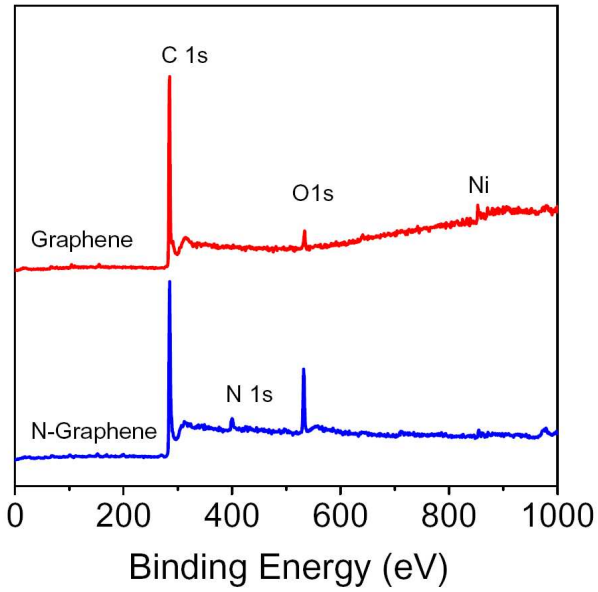


**Figure S4.** XPS survey spectra for N-graphene and C-graphene films, showing the presence of an N 1s peak and absence of the Ni peak for the N-graphene film.

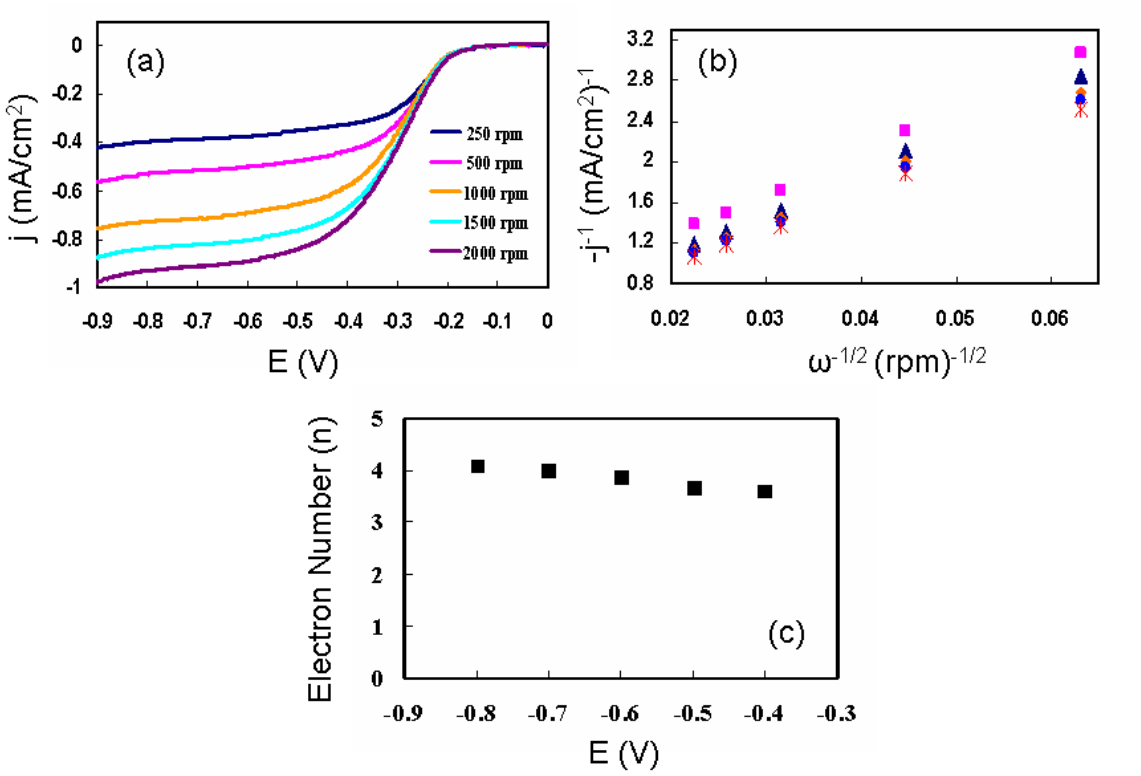


**Figure S5.** (a) Current-potential curves for ORR in air-saturated 0.1 M KOH on an N-graphene electrode at various rotation rates. (b) Koutecky-Levich plots for oxygen reduction on a N-doped graphene electrode in air-saturated 0.1 M KOH (data derived from (a). (c) The dependence of *n* on potential for the N-graphene electrode.

RRDE current-potential curves at various rotating speeds are shown in Figure S5(a). The limited diffusion currents are dependent on the rotating rates. The number of electrons involved in the ORR can be calculated from the Koutecky-Levich (K-L) equation:[1]

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

where $i_k$ is the kinetic current and ω is the electrode rotating rate. B is the K-L slope which is determined by

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

where $n$ represents the number of electrons transferred per oxygen molecule, F is the Faraday constant (F = 96485 C•mol$^{-1}$), $D_{O_2}$ is the diffusion coefficient of $O_2$ in 0.1 M KOH ($1.73 \times 10^{-5}$ cm$^2$•s$^{-1}$), $v$ is the kinematic viscosity (0.01 cm$^2$•s$^{-1}$) and $C_{O_2}$ is the bulk concentration of $O_2$ ($2.4 \times 10^{-7}$ mol•cm$^{-3}$).[2,3] The constant 0.2 is adopted when the rotation speed is expressed in rpm.

The K-L plots shown in Figure S5(b) is obtained from Figure S5(a). Both $i_k$ and B can be determined by the K-L curves. Figure S5(c) shows the dependence of $n$ on potential. It is found that there are 3.6-4 electrons transferred during ORR at the N-graphene electrode, confirming the highly efficient catalytic activity of the electrode.

**References**


(1) Tammeveski, K.; Tenno, T.; Claret, J.; Ferrater, C. Electrochemical Reduction of Oxygen on Thin-film Pt Electrodes in 0.1 M KOH. *Electrochimica Acta* **1997**, *42*, 893—897.

(2) Davis, R.E.; Horvath, G.L.; Tobias, C.W. The Solubility and Diffusion Coefficient of Oxygen in Potassium Hydroxide Solutions. *Electrochimica Acta* **1967**, *12*, 287—297.

(3) Tammeveski, K.; Kontturi, K.; Nichols, R.J.; Potter, R.J.; Schiffrin, D.J. Surface Redox Catalysis for $O_2$ Reduction on Quinone-modified Glassy Carbon Electrodes. *J. Electroanal. Chem.* **2001**, *515*, 101—112.