

## Electronic Supplementary Information

# Engineering Self-assembled N-doped Graphene/Carbon Nanotube Composites towards Efficient Oxygen Reduction Electrocatalysts †

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### Experimental details

#### Chemicals and materials

Graphite (SP-1, Bay Carbon, MI), melamine (Sigma-Aldrich), N,N-Dimethylformamide (DMF, Beijing Chemical Reagent Ltd.), nitric acid (Beijing Chemical Reagent Ltd.), hydrochloric acid (Beijing Chemical Reagent Ltd.), NaNO<sub>3</sub> (Beijing Chemical Reagent Ltd.), KMnO<sub>4</sub> (Beijing Chemical Reagent Ltd.) and Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (Sigma-Aldrich) were used without further purification. Carbon nanotubes (CNT, Shenzhen Nanotech Port Co. Ltd.) were refluxed at 80 °C in concentrated nitric acid for 3h before subsequent experiments.

#### Synthesis of N-rGO-CNT

The graphene oxide (GO) was prepared with modified Hummers method.<sup>1</sup> In a typical synthesis of N-rGO-CNTs-0.2, CNT (40 mg) and melamine (240 mg) were sonicated in DMF solution (240 mL) for 1 h and then GO solution (3.08 mL, 2.6 mg/mL) was added into the mixture, followed by sonication for 1h. After stirred at room temperature overnight, the mixture solution was dried via rotary evaporation at 85 °C. Followed, the N-rGO-CNTs-0.2 was prepared by annealing the dried mixture in a programmable tube furnace under Ar atmosphere at 900 °C for 1h at a ramp rate of 20 °C/min. The samples of N-rGO-CNTs-1, N-rGO-CNTs-0.6 and N-rGO-CNTs-0.1 were obtained by only adjusting the amount of GO solution and melamine (15.39 mL GO solution and 400 mg melamine for N-rGO-CNTs-1, 9.23 mL GO solution and 320 mg melamine for N-rGO-CNTs-0.6, 1.54 mL GO solution and 220 mg melamine for N-rGO-CNTs-0.1).

### Synthesis of N-rGO

N-rGO sample was prepared in parallel with the same method as that for N-rGO-CN-0.2 except for no addition of CNT.

### Synthesis of N-CNT

N-CNT sample was prepared in parallel with the same method as that for N-rGO-CNT-0.2 except for no addition of GO solution.

### Synthesis of Fe-N-rGO-CNT

Fe-N-rGO-CNT was prepared in parallel with the same method as that for N-rGO-CNT-0.2 except for the addition of 81.70 mg  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  in preparing CNT and melamine mixture.

### Characterization

The morphologies of all materials were characterized by scanning electron microscope (JSM 6701, JEOL, Japan) operating at 10 kV and transmission electron microscope JEM-2100F (JEOL, Japan), working at an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) spectra were recorded on a VG ESCALab220i-XL with a monochromic  $\text{Mg K}\alpha$  source.

### Electrochemical measurements

All electrochemical measurements were carried out via a standard three electrode cell system on an electrochemical workstation (CHI 760E, ChenHua, Shanghai, China) at room temperature. Glass carbon rotating disk electrode (RDE) in a diameter of 3 mm coated with catalysts was used as work electrode. Standard  $\text{Ag}/\text{AgCl}$  (3 M  $\text{KCl}$  solution) reference electrode and Pt foil were used as reference electrode and counter electrode, respectively. Before each test, RDE was mechanically polished with 0.05  $\mu\text{m}$  alumina slurry and then washed with ethanol to obtain a clean surface. For the preparation of working electrode, 2 mg catalyst was dispersed in 800  $\mu\text{L}$  ethanol and sonicated for 15 minutes to form a homogeneous ink. 17  $\mu\text{L}$  ink was loaded on clean glassy carbon electrode to achieve a catalyst loading of 600  $\mu\text{g}/\text{cm}^2$ . After that, 2  $\mu\text{L}$  nafion (0.5 wt.%) solution was dropped onto electrode surface. After dry in air, the electrode was ready for test. Commercial Johnson-Matthey Pt/C (20 wt.% Pt loading) was used for comparison and Pt loading on electrode was 25.5  $\mu\text{g}/\text{cm}^2$ . All LSV curves were recorded on RDE at certain rotating speed controlled by CTV101 Speed Control Unit (Radiometer Analytical S.A., France).

The electron transfer number involved in ORR at catalysts was calculated by the Koutecky-Levich equation as follows:

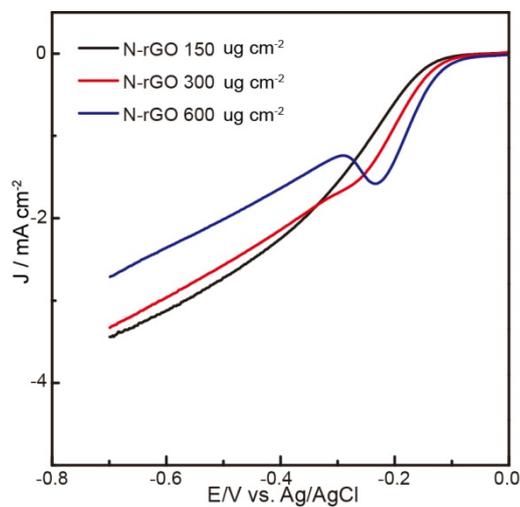
$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{B\omega^{0.5}}$$

Where  $j_k$  is the kinetic current and  $\omega$  is the rotating rate of electrode.  $B$  can be determined from the slope of the K-L plots based on the Levich equation:

$$B = 0.62nF(D_0)^{2/3}\nu^{-1/6}C_0$$

Where  $n$  represents the electron transfer number,  $F$  is the Faraday constant ( $F = 96485 \text{ C/mol}$ ),  $D_0$  is the diffusion coefficient of  $\text{O}_2$  in 0.1 M  $\text{KOH}$  ( $1.9 \times 10^{-5} \text{ cm}^2/\text{s}$ ),  $\nu$  is the kinetic viscosity ( $0.01 \text{ cm}^2/\text{s}$ ), and  $C_0$  is the bulk concentration of  $\text{O}_2$  ( $1.2 \times 10^{-3} \text{ mol/L}$ ). The constant 0.62 is adopted when the rotating speed is expressed in  $\text{rad/s}$ .

**Fig. S1** Polarization curves of N-rGO at different catalyst loading recorded in 0.1 M O<sub>2</sub>-saturated KOH at a scan rate of 10 mV/s and rotation speeds of 1600 rpm.



**Table S1** Binding energy position of pyridinic type, pyrrolic type, and quaternary type nitrogen used in the deconvolution of the XPS N1s peaks of N-rGO-CNT-0.2.

	pyridinic-N (eV)	pyrrolic-N (eV)	quaternary-N (eV)
N-rGO	398.31	399.41	400.96
N-CNTs	398.79	400.15	400.89
N-rGO-CNTs-0.2	398.67	399.69	401.19

## References

1 Hummers, W. S. and Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339-1339.