Supporting information

# Template-Free Synthesis of Porous Graphitic Carbon Nitride/carbon Composite Spheres for electrocatalytic Oxygen Reduction Reaction

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## Experimental section

### Material Synthesis

All chemical reagents were of analytical grade and used as starting materials without further purification. The pristine g-CN was prepared by a modified method reported previously.[1,2] In a typical synthesis of g-CN/C-1, 1.00 g (7.92 mmol) of melamine was dissolved in 40 mL of dimethyl sulfoxide (DMSO) at 35 °C, and 1.02 g (7.92 mmol) of cyanuric acid and 3.12 g (15.84 mmol) of D-glucose were both dissolved in 20 mL of DMSO under the same condition. Subsequently, the cyanuric acid and D-glucose solution was slowly dropped into the melamine solution. White precipitate was generated after reaction at 35 °C for 0.5 h, which was collected by centrifugation and washed with absolute ethanol. After drying in a vacuum oven at 80°C for 12h, the sample was calcined in a tube furnace with a heating rate of 2.3 °C min$^{-1}$ and maintained at 600 °C for 4 h under argon atmosphere. The carbon in the physically mixed g-CN+C was obtained by calcining D-glucose under the same condition. A series of samples were synthesized by altering the amounts of D-glucose while the mass of cyanuric acid and melamine remain unchanged. 7.80 g (39.60 mmol) of D-glucose is used to synthesize g-CN/C-2 and 15.60 g (79.20 mmol) of D-glucose is used to produce g-CN/C-3.

## Material Characterization

The samples were characterized by powder X-ray diffraction (XRD, Rigaku Mini Flex 600 X-ray generator, Cu Kα radiation, $\lambda = 1.5406$ Å) at a scanning rate of 1° min$^{-1}$ from 10° to 50°, scanning electron microscope (SEM, JEOL JSM-7500F microscope, operating voltage, 5 kV) and transmission electron microscopy (TEM, Philips Tecnai F20 operated at 200 kV). FTIR-650 spectrometer (Gangdong Co., Ltd., Tianjin, China) was used for the Fourier transform infrared (FT-IR) spectroscopy analysis in the range of 400–4000 cm$^{-1}$. Raman spectra were obtained using a confocal Raman microscope (DXR, Thermo-Fisher Scientific) at 532 nm excitation from an argon-ion laser. The specific surface area was analyzed using Brunauer-Emmett-Teller (BET) nitrogen adsorption/desorption isotherm at 77 K on a BELSORP-mini instrument. X-ray photoelectron spectroscopy (XPS) measurements were performed using a Kratos Axis Ultra DLD spectrometer employing a monochromated Al-Kα X-ray source ($h\nu$ = 1486.6 eV), hybrid (magnetic/electrostatic) optics, and a multichannel plate and delayline detector (DLD). Elemental analysis was obtained using a vario EL CUBE elemental analyser, Elementar Analysensysteme GmnH. Electrical conductivity measurements were conducted by pressing the samples into chips between two stainless steel electrodes and measuring the electrical resistance of the respective sample by ohm's law on Ametek Parstat 4000. The conductivity $\kappa$ was deduced using the equation: $\kappa = 1/\rho = h/(R*S)$, where $\rho$ is resistivity and S and h are the surface and thickness of the chips.

## Electrochemical characterization

Electrochemical measurements were carried out with a computer-controlled workstation bipotentiostats (AFCBP1, Pine Instrument) assembled with a modulated speed rotator (PHYCHEMI) in a three-electrode cell configuration at room temperature. The reference electrode was saturated calomel electrode (SCE), and the counter electrode was a platinum sheet. A glassy carbon electrode coated with a thin layer of catalyst was used as the working electrode. All potentials in this paper are against RHE. The electrode was made as follows: 3.0 mg of sample and 7.0 mg of carbon (Vulcan XC72) were mixed in 500 μL of ultrapure water and 500 μL of absolute ethanol. Then 50 μL of $Na^+$-exchanged Nafion solution was added into the mixture. After ultrasonically mixing for 30 min, 7 μL of the mixture was dropped onto the top surface of a rotation ring-disk electrode (RRDE). Finally, the ink was dried for 8 h at room temperature to form a thin catalyst film. Voltammetry and RRDE studies were carried out in 0.1 M aqueous KOH electrolyte saturated with high-purity $O_2$.

The overall electron transfer number per oxygen molecule involved in a typical ORR process can be calculated from the slope of Koutecky-Levich plots using the following equation:[3]

$$1/i = 1/i_{\mathrm{K}} + 1/i_d = 1/i_{\mathrm{K}} - 1/(0.62nFAv^{-1/6}C_{O2}D_{O2}^{2/3}\omega^{-1/2}) \qquad (1)$$

Where, $i_K$ is the kinetic current when the influence of mass transfer can be ignored, ω is the electrode rotating speed (rad $s^{-1}$), $n$ is the number of electrons transferred per oxygen molecule, $F$ is the Faraday constant, 96485 C $mol^{-1}$, $A$ is the electrode geometric surface area (cm$^2$), $v$ is the kinetic viscosity, $C_{O2}$ is the bulk concentration of $O_2$, and $D_{O2}$ is the diffusion coefficient of $O_2$ in 0.1 M KOH. The plot of $1/i$ versus $\omega^{-1/2}$ is linear.

The kinetic current is calculated from mass-diffusion correction based on the following equation:[4]

$$I_k = II_d/ (I_d - I) \tag{2}$$

For RRDE, the electron transfer number and the percentage of peroxide species ($y_{peroxide}$) relative to the total products is calculated based on the following equation:[5,6]

$$n = 4NI_d/ (NI_d + I_r) \tag{3}$$

$$y_{peroxide} = 200\ I_r/( NI_d + I_r) \tag{4}$$

$I_d$ and $I_r$ are disk and ring current, respectively. N is the current efficiency of RRDE.

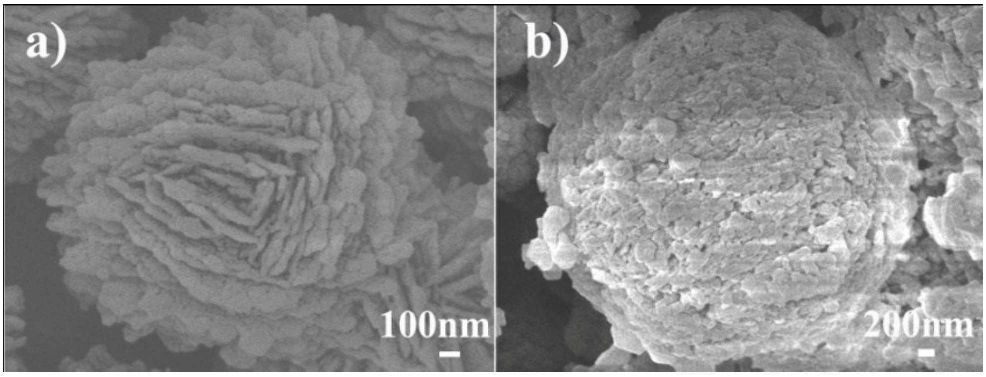

**Fig. S1** SEM images of a) MCA and b) precursor of g-CN/C.

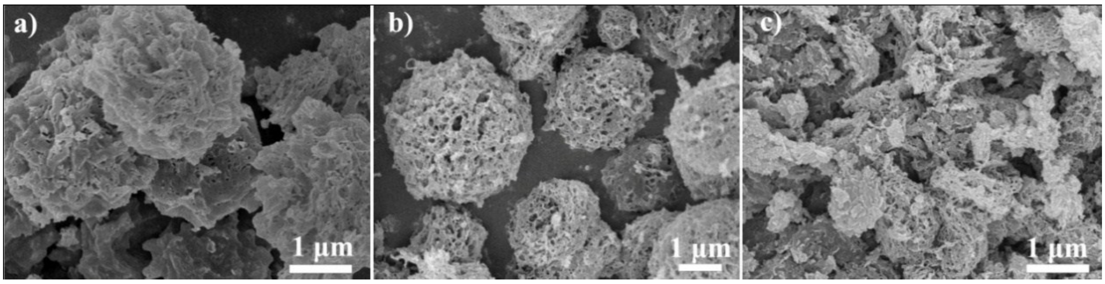

**Fig. S2** SEM images of g-CN/C calcined at a) 500 °C, b) 600 °C and c) 700 °C for 4h, respectively.

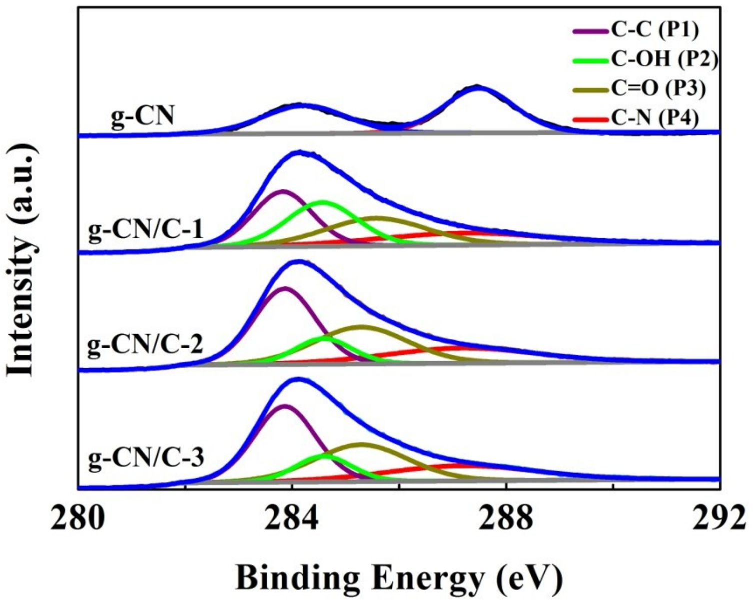

**Fig. S3** High-resolution XPS spectra of C 1s in samples.

**Table S1** The ratio of C/N in g-CN based on the atomic ratio of carbon and nitrogen and relative composition ratio (%) of four carbon components derived from decomposed XPS spectra.

| samples | C1s (atm. %)[a] | N1s (atm. %) | Relative composition ratio of carbon (%)[b] | | | | C/N[c] in g-CN |
|---|---|---|---|---|---|---|---|
| | | | P1 | P2 | P3 | P4 | |
| g-CN | 50.74 | 43.11 | 42.72 | 0 | 0 | 57.28 | 0.67 |
| g-CN/C-1 | 74.60 | 15.61 | 37.84 | 20.75 | 30.22 | 11.18 | 0.53 |
| g-CN/C-2 | 74.70 | 19.88 | 29.03 | 27.51 | 25.03 | 18.43 | 0.69 |
| g-CN/C-3 | 76.40 | 16.57 | 39.34 | 12.09 | 29.05 | 19.52 | 0.90 |

[a] atomic ratios of carbon and nitrogen in composites are obtained from the XPS results.

[b] different carbon percentages deconvoluted from the C1s XPS spectra of composites in Fig. S3.

[c] the ratio of C/N in g-CN is calculated via carbon present in C-N bonds divided by nitrogen, according to the equation C/N=P4*C1s/N1s.

**Table S2** The content of carbon and nitrogen in samples by elemental analysis.

| samples | C (wt %) | N (wt %) |
|---|---|---|
| g-CN | 34.11 | 60.50 |
| g-CN/C-1 | 40.26 | 50.35 |
| g-CN/C-2 | 53.81 | 33.75 |
| g-CN/C-3 | 65.03 | 26.09 |

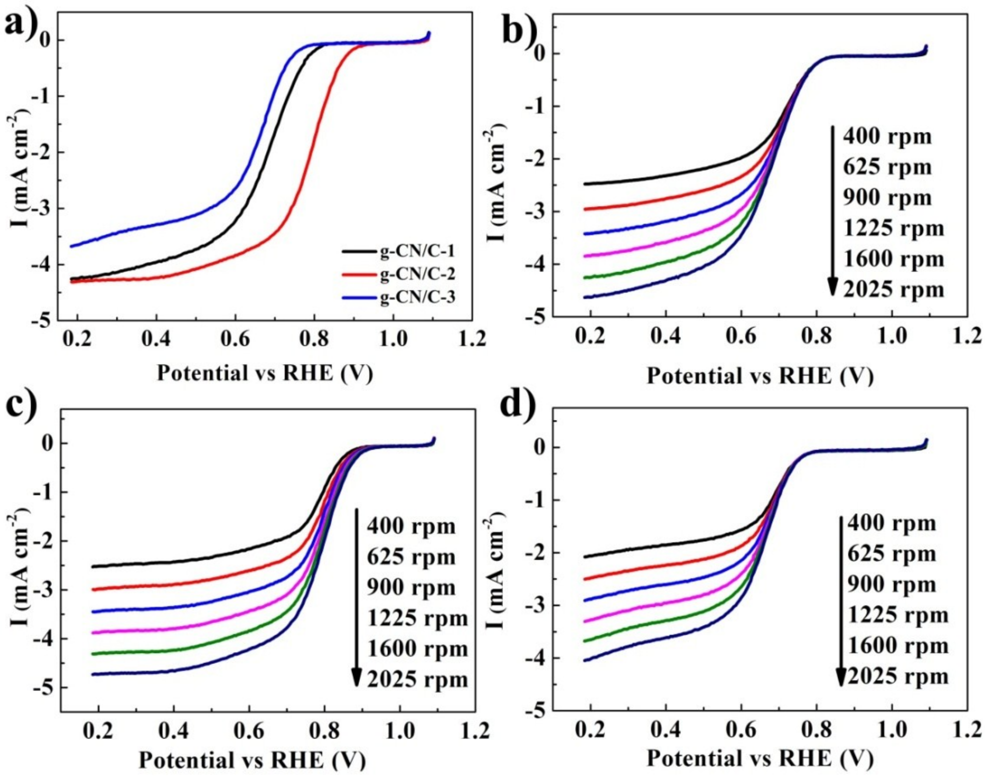

**Fig. S4** a) RDE results of the samples with different nitrogen contents. LSVs of b) g-CN/C-1, c) g-CN/C-2 and d) g-CN/C-3 on RDE at various rotation rates from 400 to 2025 rpm in $O_2$-saturated 0.1 M KOH solution at scan rate of 5 mV $s^{-1}$.

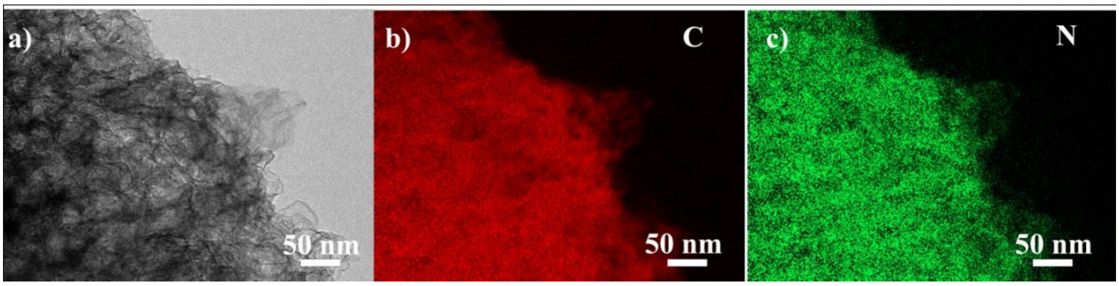

**Fig. S5** a) TEM image of g-CN/C-2, and b, c) the corresponding C- and N-elemental mappings.

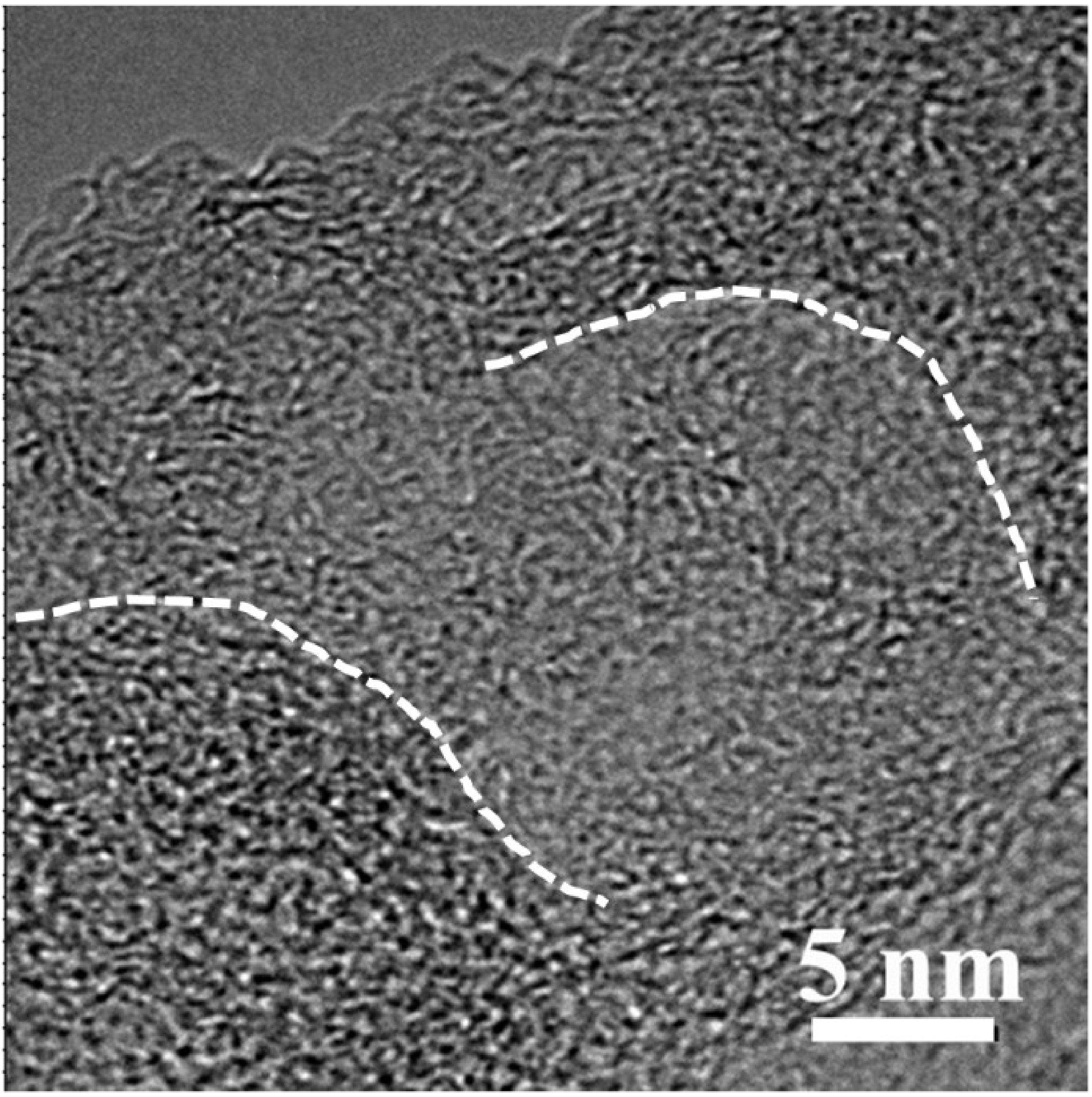

**Fig. S6** High-resolution TEM image of g-CN/C-2.

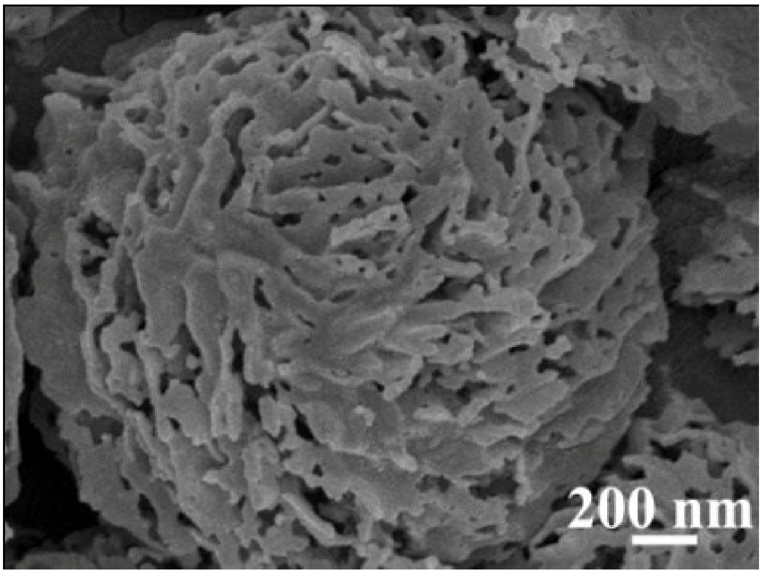

**Fig. S7** SEM image of g-CN.

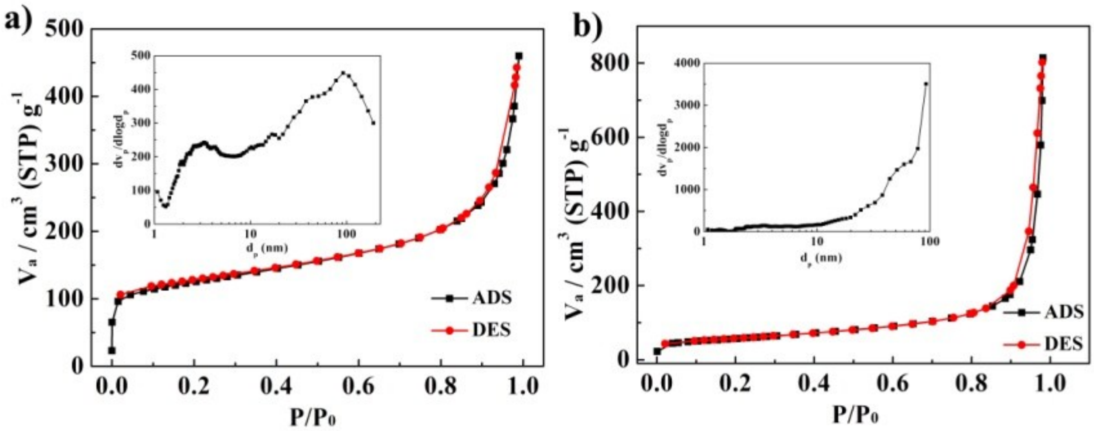

**Fig. S8** Nitrogen sorption isotherms of a) g-CN/C-2 and b) g-CN. The insets are the corresponding pore size distributions.

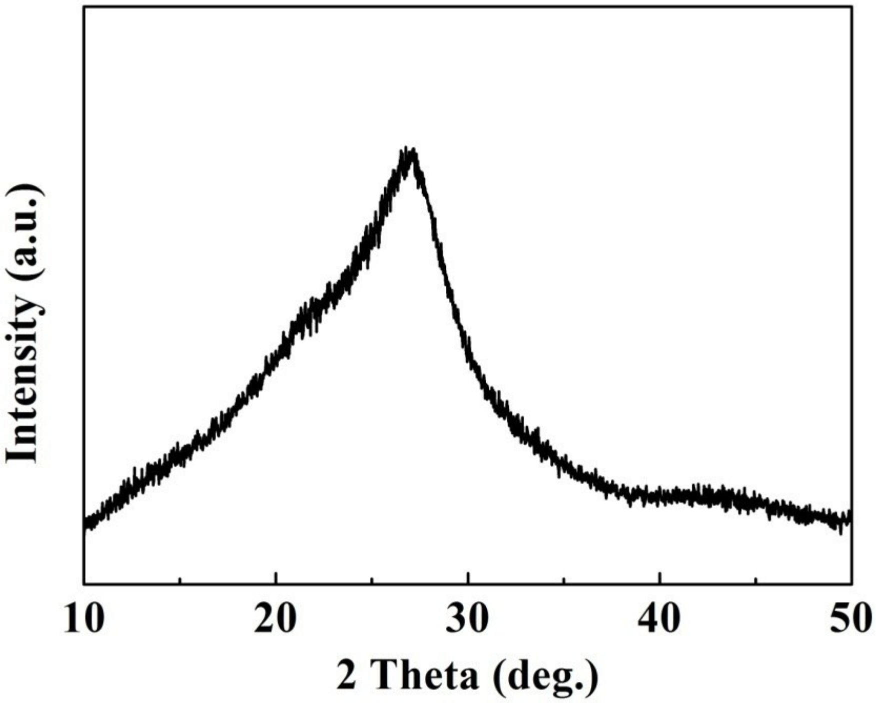

**Fig.S9** XRD pattern of g-CN/C-2.

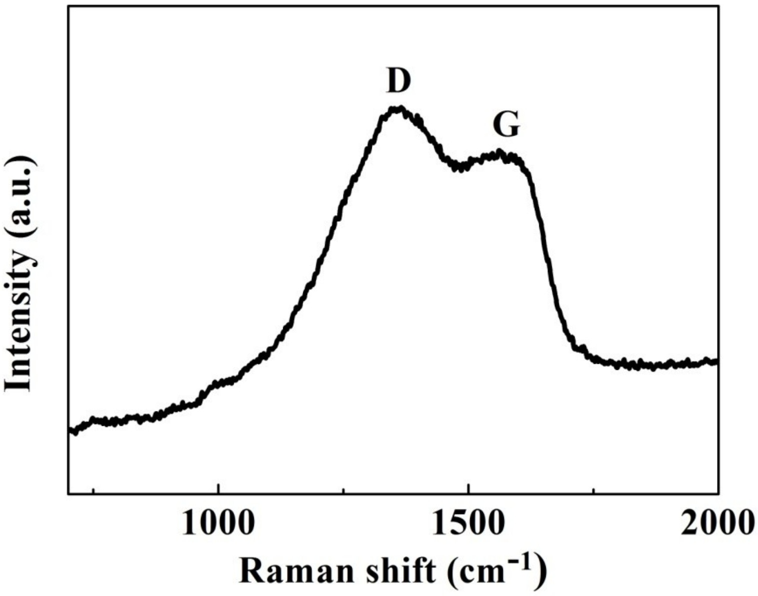

**Fig.S10** Raman spectrum of g-CN/C-2.

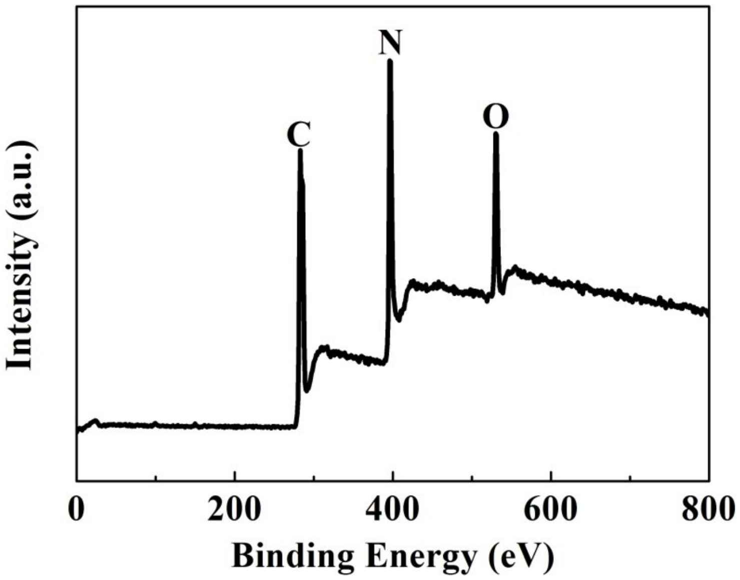

**Fig. S11** Survey scan XPS spectrum of g-CN/C-2.

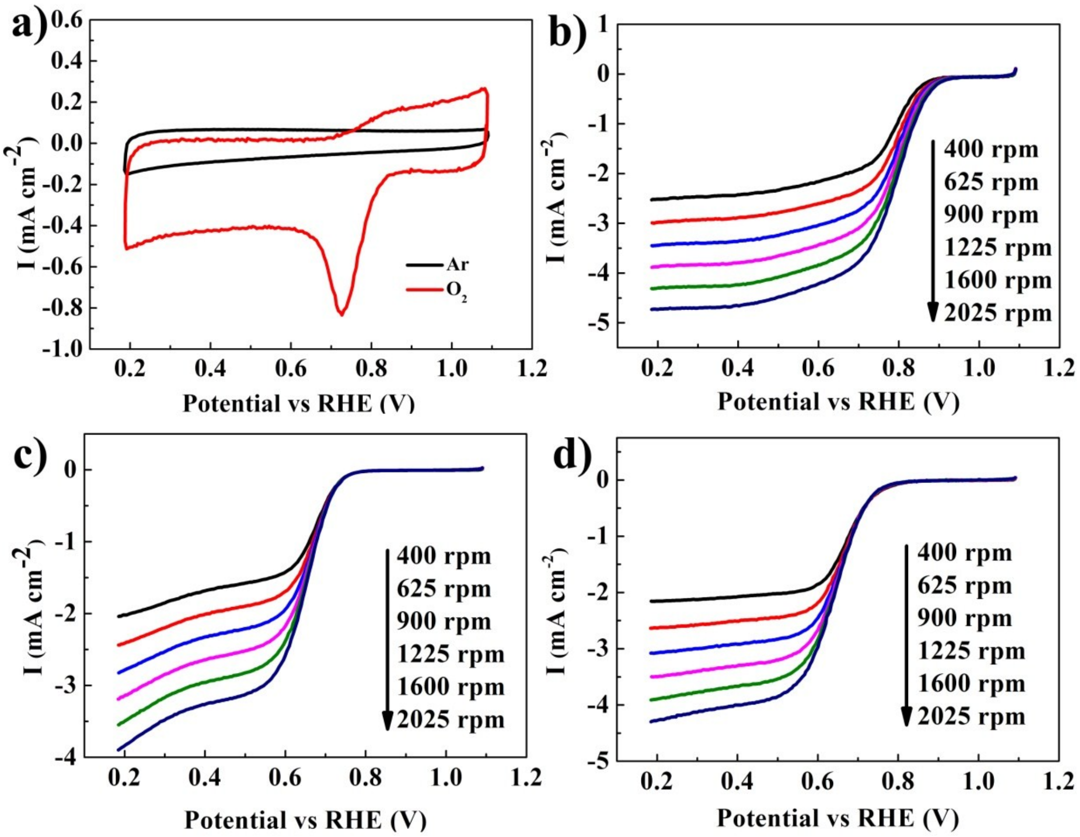

**Fig. S12** a) CVs of ORR on g-CN/C-2 in $O_2$-saturated 0.1 M KOH solution (red line) and Ar-saturated 0.1 M KOH solution (black line) at a scan rate of 20 mV $s^{-1}$. LSVs of b) g-CN/C-2, c) g-CN and d) g-CN+C on RDE at various rotation rates from 400 to 2025 rpm in $O_2$-saturated 0.1 M KOH solution at a scan rate of 5 mV $s^{-1}$.

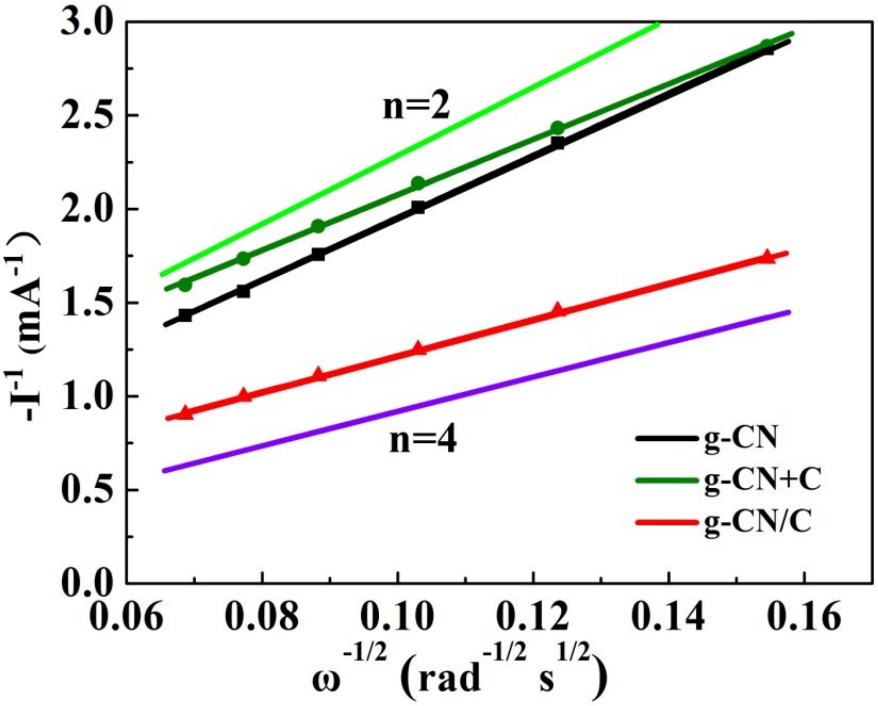

**Fig. S13** K-L plots based on Koutecky-Levich equation at 0.5 V of g-CN/C-2.

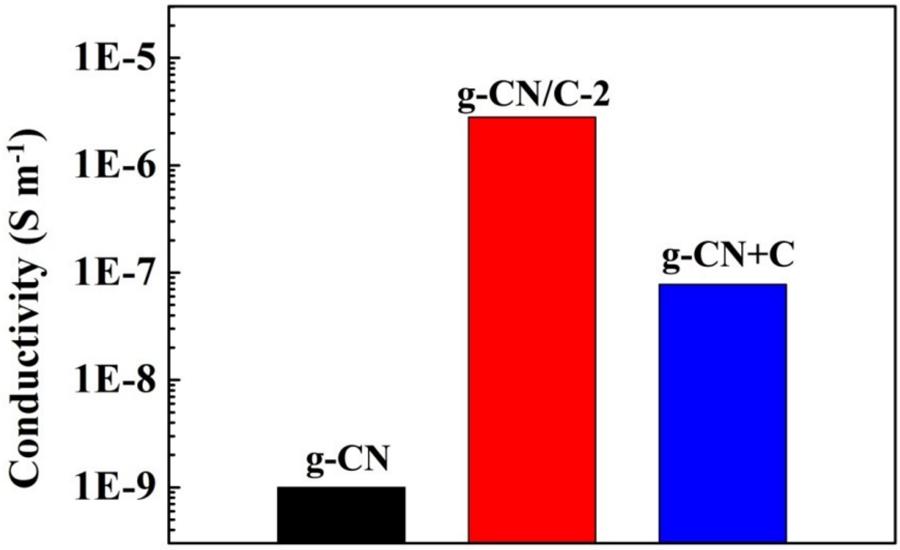

**Fig. S14** Electrical conductivity of g-CN, g-CN/C-2, and g-CN +C.

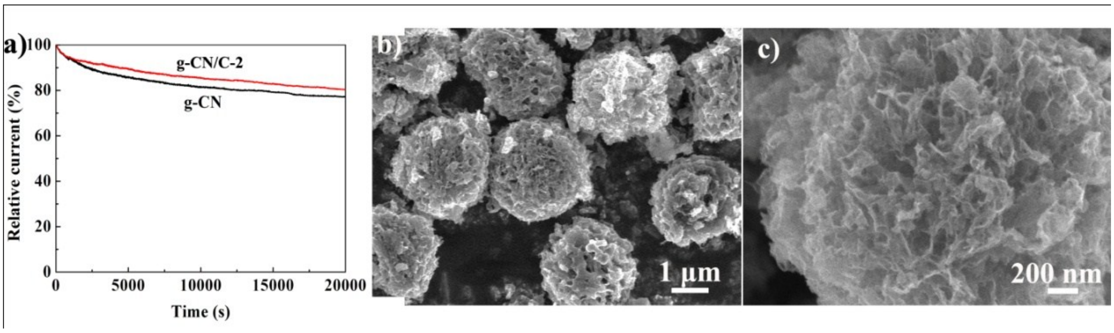

**Fig. S15** a) Current-time (i-t) chronoamperometric response of g-CN/C-2 and g-CN electrodes in $O_2$-saturated 0.1 M KOH solution at a rotation rate of 900 rpm. b and c) SEM images of g-CN/C-2 after catalyzing oxygen reduction in 0.1 M $O_2$-saturated KOH solution.

# References

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