

*Supporting Information for*

# Facile Preparation of Nitrogen-doped Graphene as a Metal-free Catalyst for Oxygen Reduction Reaction

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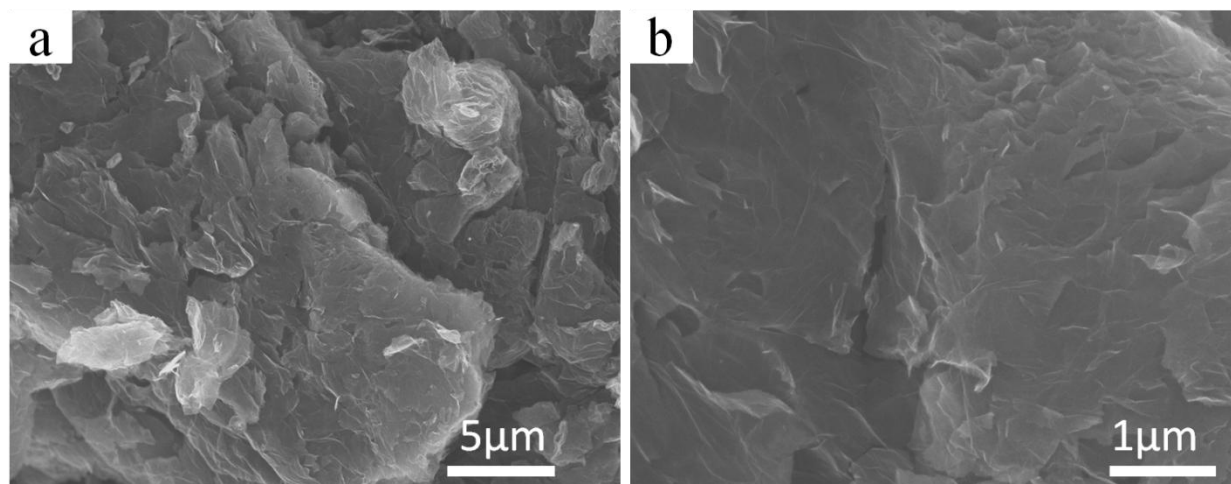
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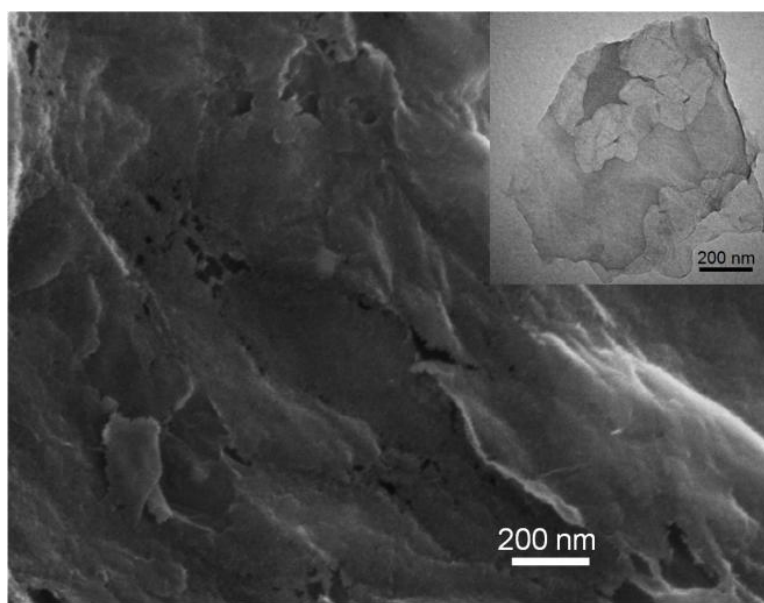
## 1. Supplementary structural characterizations



**Fig. S1** 0.5 mg/mL GO dispersion in water before (left) and after (right) adding 2.5 mg/mL melamine.



**Fig. S2** SEM images of graphene at (a) low magnification and (b) high magnification.



**Fig. S3** The SEM and TEM (inset) images of nG-900 showing the existence of holes in graphitic structure.

**Table 1** Peak assignment of FTIR spectra of GO and melamine.<sup>1,2</sup>

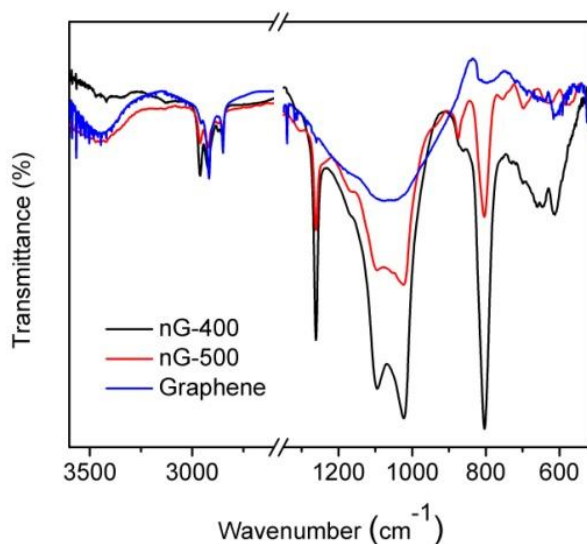
Peak position wavenumber (cm <sup>-1</sup> )	Assignment
GO	
3420 (broad)	O-H , absorbed water
1724	C=O (carboxylic and ketone)
1637	absorbed water
1582	unoxidized aromatic region
1382	O-H
1076 (broad)	C-O (phenolic, epoxy, and ketone groups)

Melamine

3470, 3426, 3338, 3130, 1650  
1562, 1468, 1431, 815  
1030

NH<sub>2</sub>  
1,3,5-s-triazine ring  
C-N

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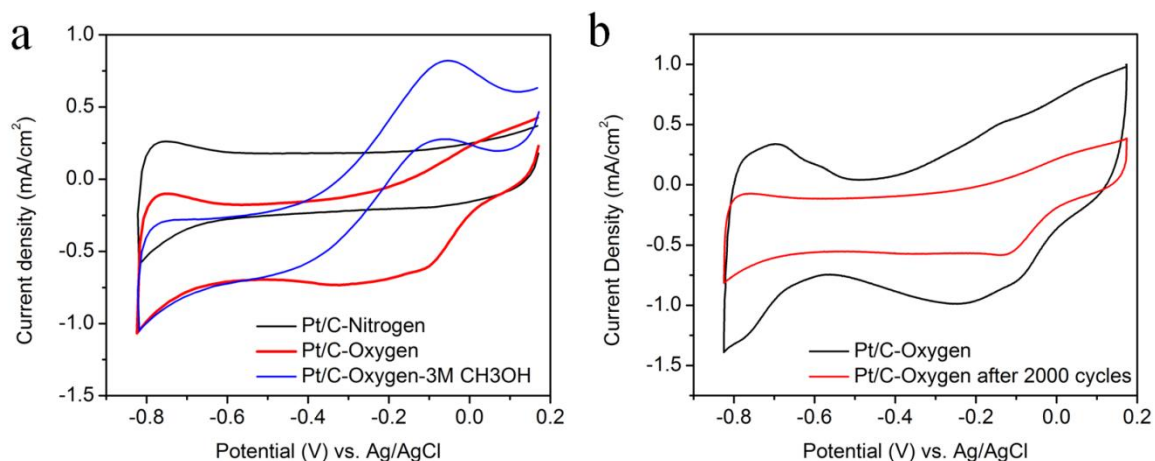


**Fig. S4** FtIR spectra of nG-400, nG-500 and graphene.

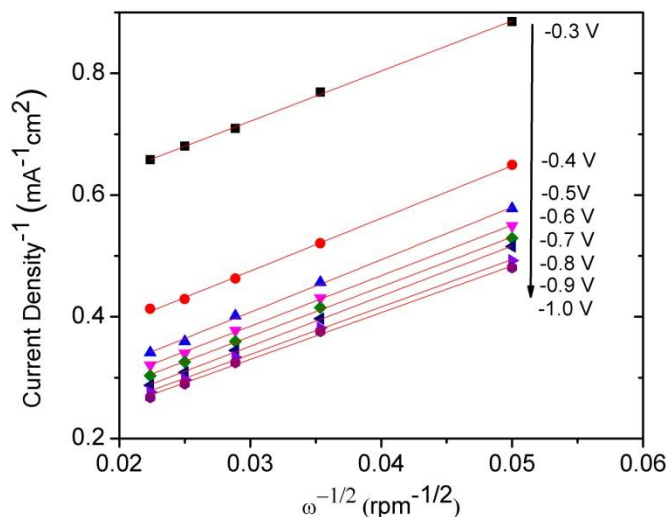
### Discussions on the mechanism on N doping

There are two possible pathways for N-doping during pyrolysis. The first pathway is that carbon nitride, produced by decomposition of melamine, acts as an intermediate for the formation of N dopant in NG. Another pathway is via chemical reactions of melamine with surface functional groups and subsequent thermal transformations during pyrolysis. To elucidate the doping mechanism for pyrolysis of GO-melamine, the following controlled experiments were carried out: 1) GO-melamine mixture was washed by copious water before pyrolysis to remove excessive melamine. It was found that the N content in resulting nG is significantly lower (< 3 %), indicating that excessive melamine, which are critical for the formation of carbon nitride, plays a role in doping process. However, we found that further increase the melamine/ GO ratio to 10 does not lead to a higher N content in nG, probably because only carbon nitride adjacent to graphene could be converted to nG. 2) The GO-melamine was pre-reduced before pyrolysis (300 °C in H<sub>2</sub>/Ar) to remove oxygen-containing functional groups that can react with melamine. The resulting nG from reduced GO-melamine has a N content of 7.41 %, which is closed to nG reported in main text, indicating the minor role of oxygen-containing functional groups in the doping process. Therefore, we conclude that the conversion of carbon nitride to nG is a dominate pathway for N-doping.

### 2. Supplementary electrochemical characterization of nGs and control samples



**Fig. S5** CVs of Pt/C (a) in nitrogen or oxygen saturated 0.1 M KOH solutions, and in the oxygen-saturated solution with 3M methanol; (b) before and after stability test (2000 cycles in oxygen saturated 1M KOH at a scan rate of 100 mV/s).

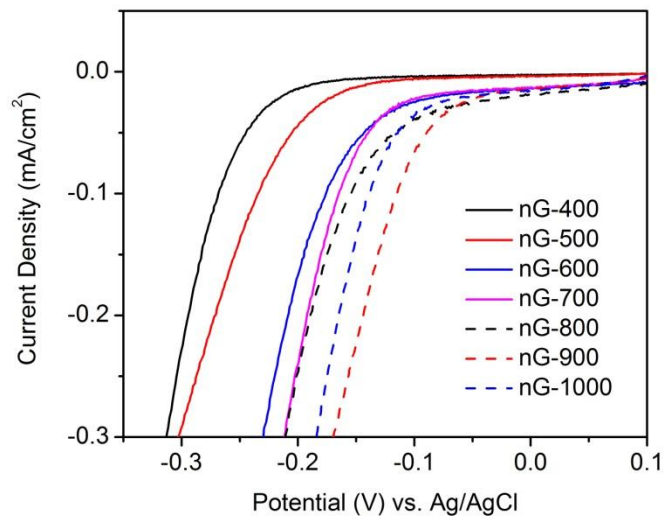


**Fig. S6** Koutecky–Levich plot of current density<sup>-1</sup> vs.  $\omega^{-1/2}$  at different electrode potentials. The number

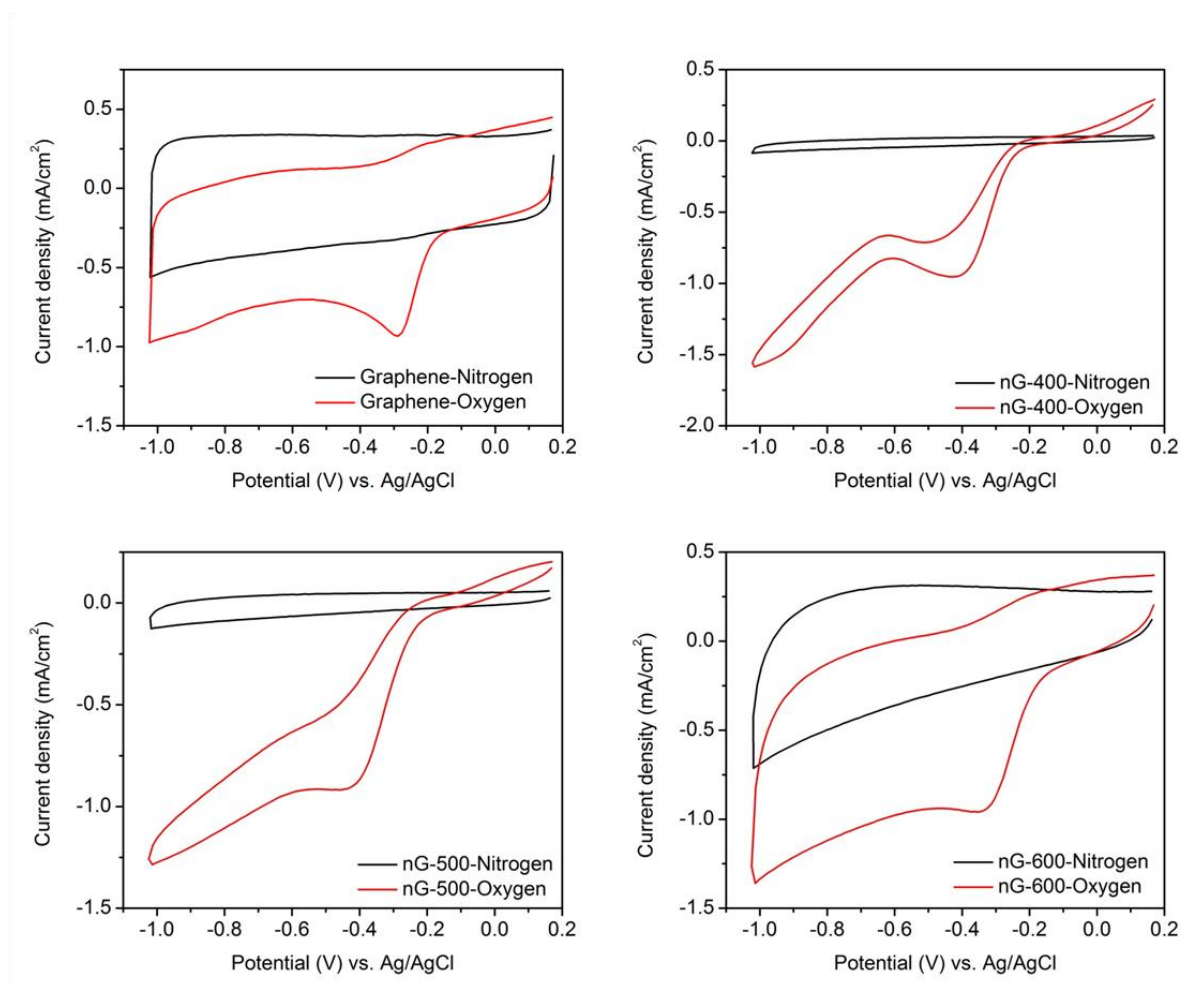
$$\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_K} = \frac{1}{B\omega^{1/2}} + \frac{1}{J_K},$$

of electron transfer is analyzed by the Koutecky–Levich equations:  $B = 0.2nFC_0(D_0)^{2/3}v^{-1/6}$  where  $J$ ,  $J_L$ ,  $J_K$  are measured current density, diffusion-limiting current densities and kinetic-limiting current density respectively.  $\omega$  is the rotation speed in rpm.  $F$  is the Faraday constant (96485 C/mol);  $D_0$  is the diffusion coefficient of oxygen in 0.1 M KOH ( $1.9 \times 10^{-5}$  cm<sup>2</sup>/s),

$\nu$  is the kinetic viscosity ( $0.01 \text{ cm}^2/\text{s}$ ), and  $C_0$  is the bulk concentration of oxygen ( $1.2 \times 10^{-6} \text{ mol/cm}^3$ ).  $0.2$  is a constant when the rotation speed is expressed in rpm.<sup>3</sup>



**Fig. S7** LSV curves of nGs in a 0.1 M oxygen saturated KOH at a scan rate of 10 mV/s.



**Fig. S8** CVs of graphene, nG-400, nG-500, and nG-600.

### Reference

1. Z. Y. Lin, Y. Liu, Y. G. Yao, O. J. Hildreth, Z. Li, K. Moon and C. P. Wong, *J. Phys. Chem. C*, 2011, **115**, 7120-7125.
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