Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting Information for

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

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1. Supplementary structural characterizations

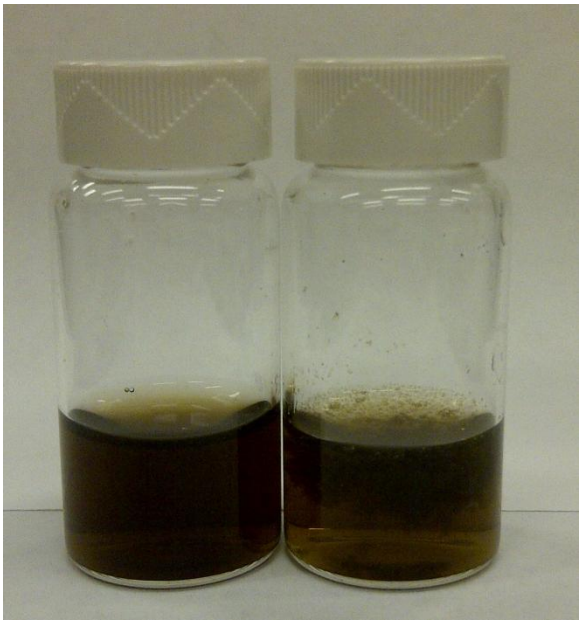

Fig. S1 0.5 mg/mL GO dipersion in water before (left) and after (right) adding 2.5 mg/mL melamine.

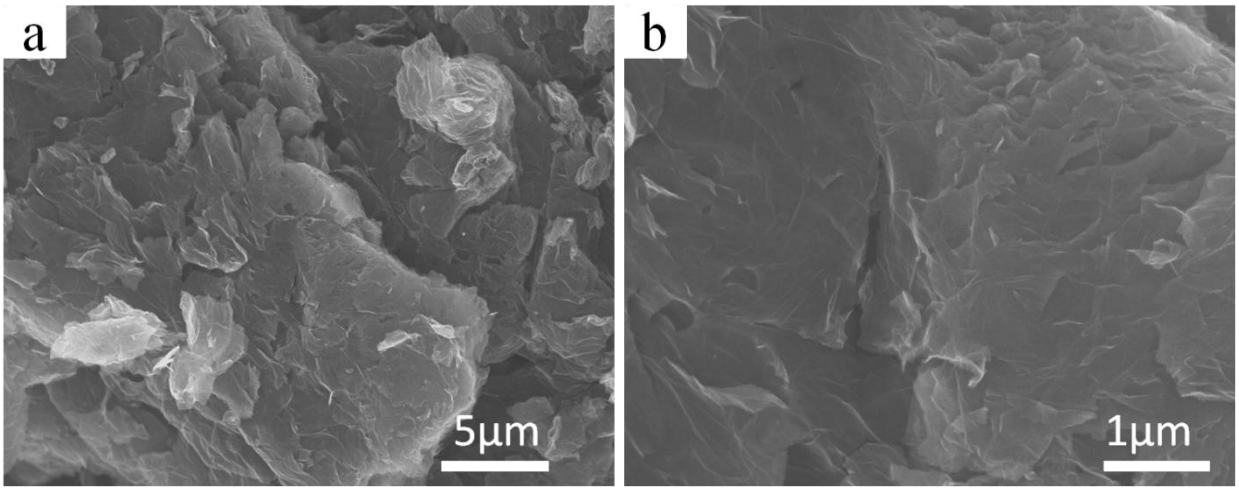

Fig. S2 SEM images of graphene at (a) low magnification and (b) high magnification.

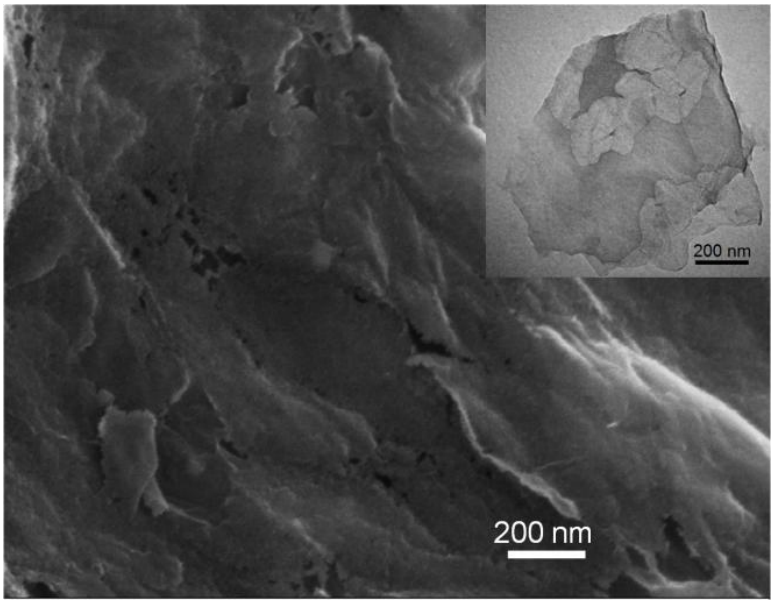

Fig. S3 The SEM and TEM (inset) images of nG-900 showing the existence of holes in graphitic structure.

Table 1 Peak assignment of FTIR spectra of GO and melamine.[1, 2]

Peak position wavenumber (cm^{-1})	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	NH_2
	1562, 1468, 1431, 815	1,3,5-s-triazine ring
	1030	C-N

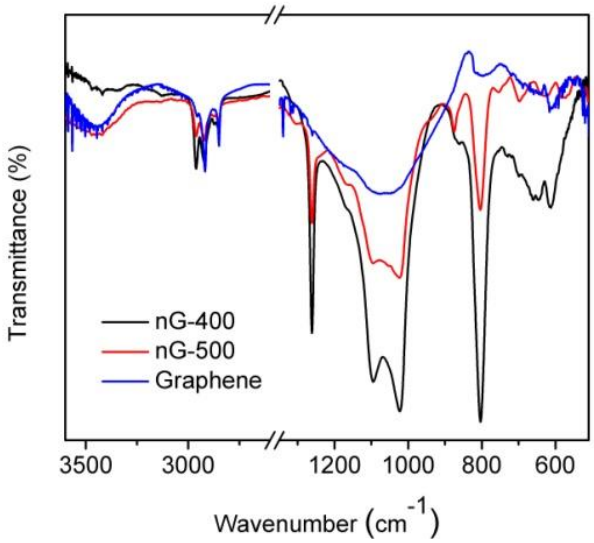

Fig. S4 FtIR spectra of nG-400, nG-500 and graphene.

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_2/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. Supplimentary electrochemical characterization of nGs and control samples

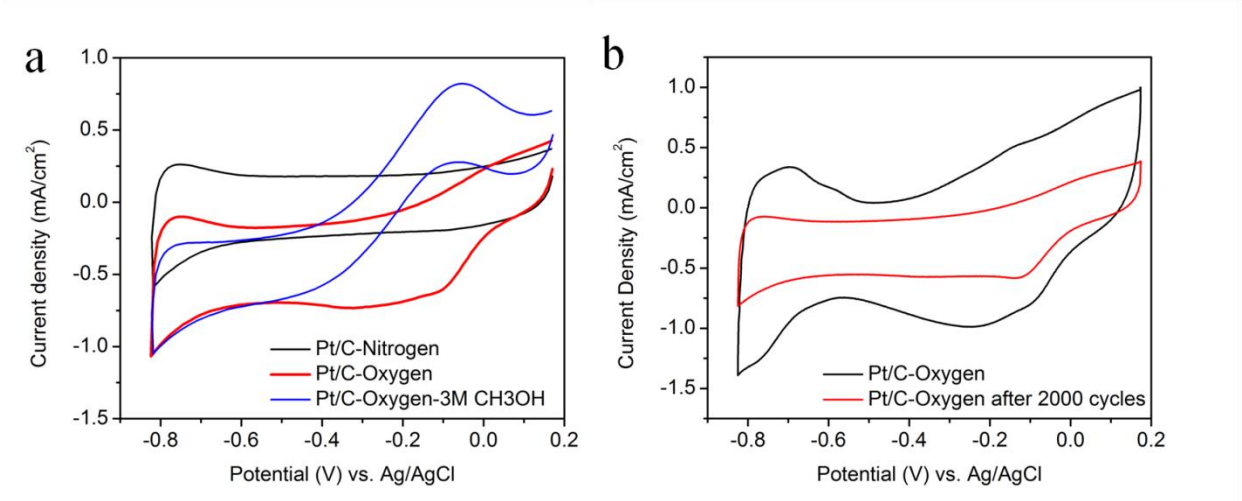

Fig. S5 CVs of Pt/C (a) in nitrogen or oxygen saturated 0.1 M KOH solutions, and in the oxygen-saturated solution with 3M methanol; (b) before and after stability test (2000 cycles in oxygen saturated 1M KOH at a scan rate of 100 mV/s).

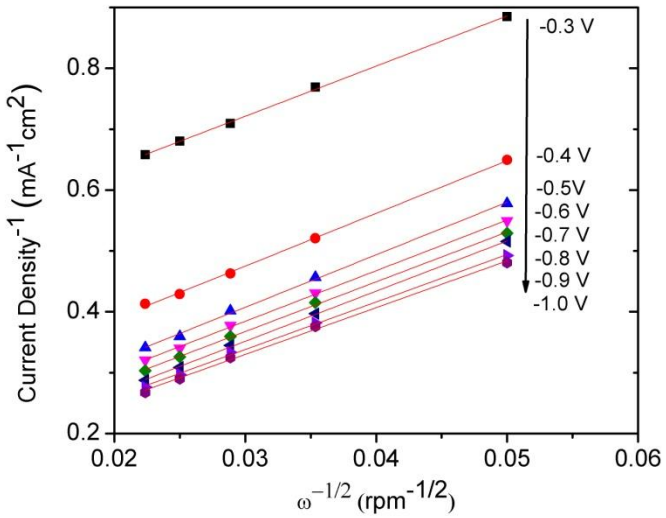

Fig. S6 Koutecky–Levich plot of current density^{-1} vs. $\omega^{-1/2}$ at different electrode potentials. The number of electron transfer is analyzed by the Koutecky–Levich equations: $\frac{1}{J}=\frac{1}{J_L}+\frac{1}{J_K}=\frac{1}{B\omega^{1/2}}+\frac{1}{J_K}$, $B=0.2nFC_0(D_0)^{2/3}v^{-1/6}$ where J, J_L, J_k are measured current density, diffusion-limiting current densities and kinetic-limiting current density respectively. ω is the rotation speed in rpm. F is the the Faraday constant (96485 C/mol); D_0 is the diffusion coefficient of oxygen in 0.1 M KOH (1.9×10^{-5} cm^2/s),

υ is the kinetic viscosity (0.01 cm^2/s), and C_0 is the bulk concentration of oxygen (1.2×10^{-6} mol/ cm^3). 0.2 is a constant when the rotation speed is expressed in rpm.[3]

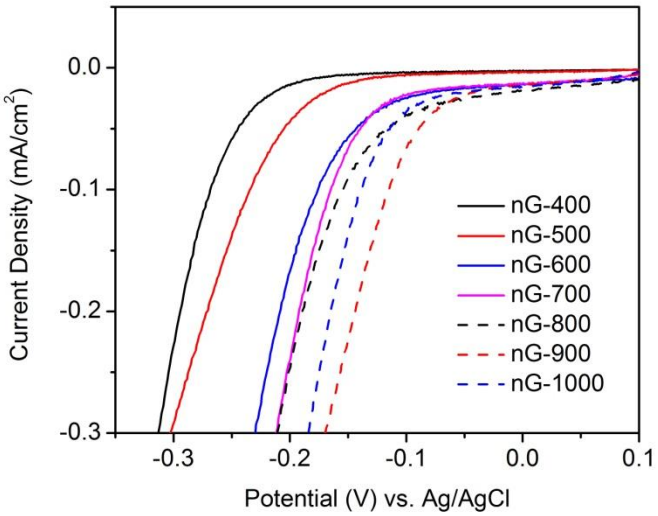

Fig. S7 LSV curves of nGs in a 0.1 M oxygen saturated KOH at a scan rate of 10 mV/s.

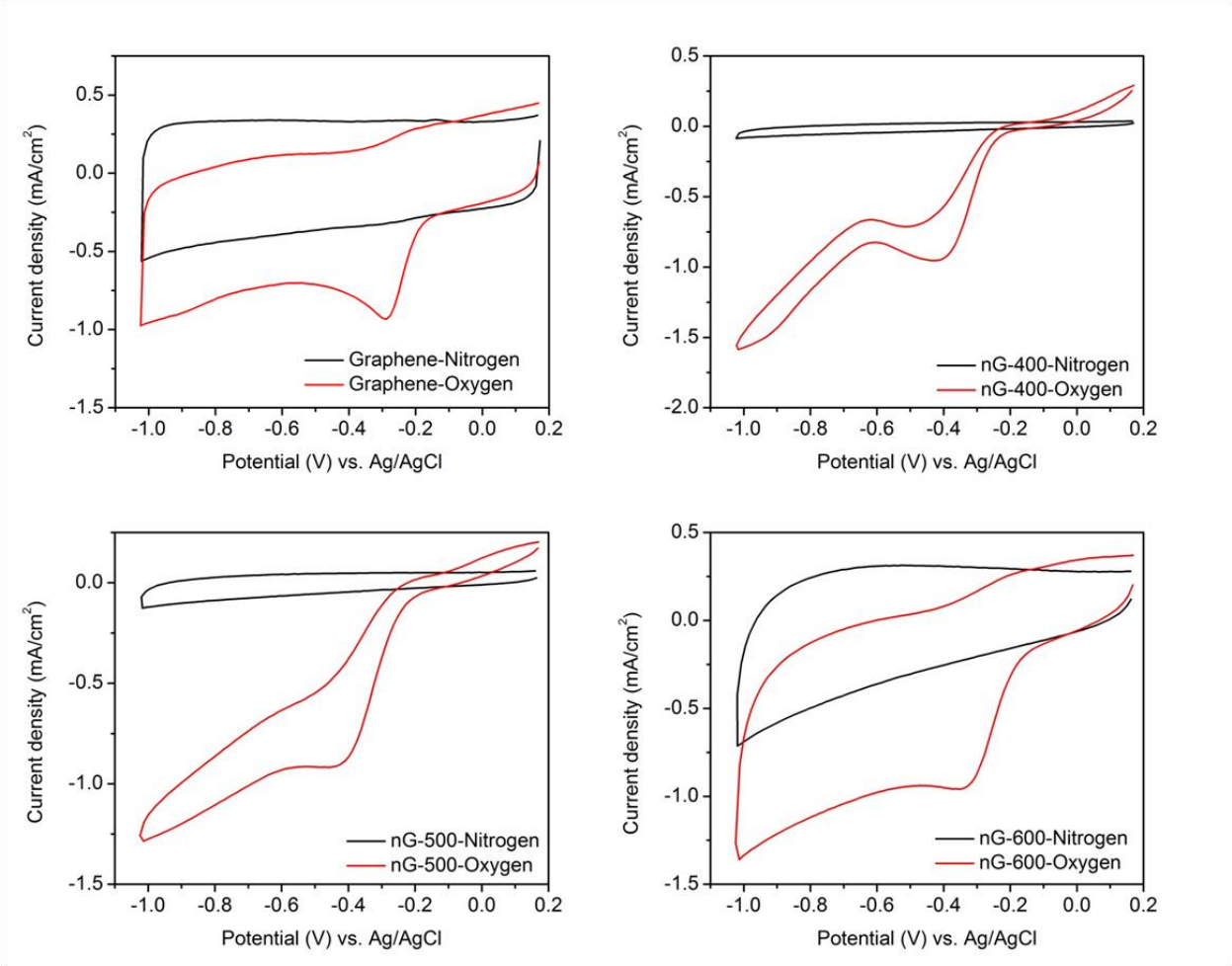

Fig. S8 CVs of graphene, nG-400, nG-500, and nG-600.

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.
2. L. Costa and G. Camino, *J. Therm. Anal.* 1988, **34**, 423-429.
3. S. Y. Wang, D. S. Yu and L. M. Dai, *J. Am. Chem Soc.*, 2011, **133**, 5182-5185.