Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Functions in Cooperation for Enhanced Oxygen Reduction Reaction: The Independent Roles of Oxygen and Nitrogen Sites in Metal-free Nanocarbon and Their Functional Synergy

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Experimental Detail

Synthesis of Graphene Oxide (GO)

Typically, 2.0 g of expandable graphite flake (GrafGuard 160-50-N, Graftech, USA) was mixed with 120 mL concentrated H_2SO_4 (98%, Sigma-Aldrich), followed by addition of 12.0 g $KMnO_4$ (BJH Chemicals) at ambient condition. The temperature of the mixture was raised to 60 °C in a water bath with continuous stirring over 4 hours and then cooled. After cooling back to room temperature, 150 mL of water and 5.0 mL H_2O_2 (30% in water, Merck) were added to the mixture, turning the solution into a yellow-orange color. The reaction solution was centrifuged at 4400 rpm for 30 minutes and the resulting supernatant decanted away. This process was repeated several times until the solution maintained at pH 7 over > 4 repeated centrifugations. The purified graphite oxide-water dispersion was subjected to probe ultrasonication to yield GO. The GO dispersion was then evaporated in 80 °C oven in air to obtain GO power in loose turbostratic stacking for a better exfoliation result. The resulting brown GO powder was collected for ICP-OES analysis and thermal exfoliation and reduction at 1000 °C. The metal content (Mn) was < 0.01 wt%.

The preparation of GO nanoribbon (GONR) underwent the same procedure except the starting graphite material was replaced by a purified multi-walled carbon nanotube (CNT), provided by Institute of Metal Research, Chinese Academy of Sciences. The metal contents (Fe, Mn) of GONR were also < 0.01 wt%.

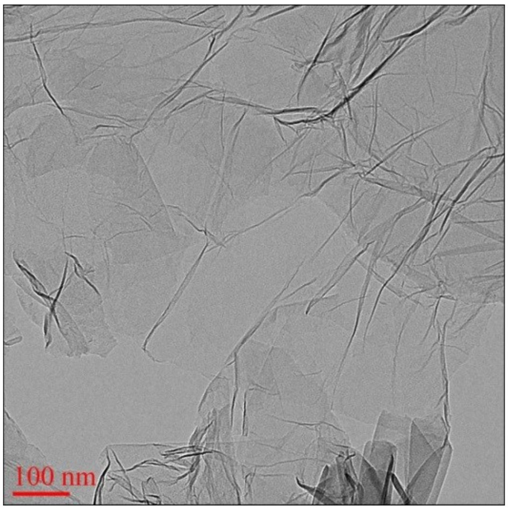

Figure S1. A TEM image of purified GO before thermal exfoliation.

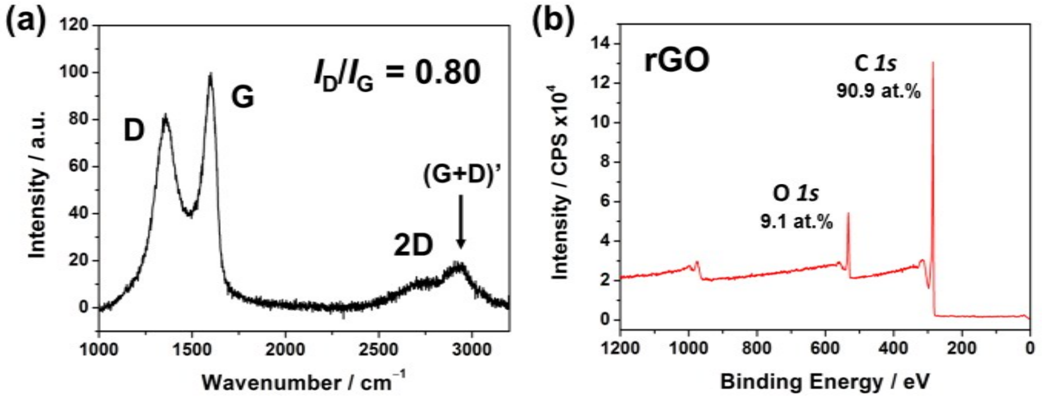

Figure S2. (a) Raman and (b) XPS survey spectrum of the rGO.

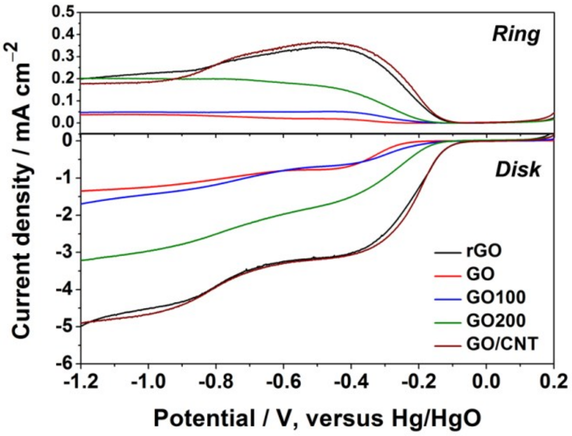

Figure S3. LSV-RRDE of rGO, GO and its thermally treated derivatives at 100 °C and 200 °C, and GO/CNT composite, measured at 10 mV s^{-1} and 1600 rpm in O_2-saturated 0.1 M KOH electrolyte.

This study (Figure S3) was conducted to illustrate the effect of conductivity in a qualitative manner based on the oxygen content. High oxygen content must be associated with poor conductivity. For example, GO and GO100 have an oxygen content of ~29 at.% (Table S1); the Faradaic current density were both very poor. When the oxygen content is reduced to 19 at.% for GO200, the current density gets better, and even better for rGO, which has an oxygen content at 9.1 at.%. In order to keep the oxygen content and distribution native, we made blends with purified CNT as conductive filler and an optimized blend composition is 20 wt.%. The 20 wt.% of active insulating material was determined by comparative experiment using different GO content at 0, 10, 20, 30, 50 wt.%. The same optimal active content was also found for Mn_3O_4/CNT blend (*ChemSusChem*, **2015**, *8*, 3331-3339).

Table S1. Composition analysis of samples based on XPS survey evaluation.

Samples	Composition (at. %)		
	C	N	O

rGO	90.89	NA	9.11
GO	70.08	NA	29.92
GO100	71.69	NA	28.31
GO200	81.00	NA	19.00
H_2-rGO-800	98.10	NA	1.90
N-rGO-400	91.82	2.17	6.00
N-rGO-800	93.16	4.59	2.25
GONR	69.40	NA	30.60
N-rGO-800-HNO_3	87.51	4.75	7.74

Table S2. The FWHM values for the D band in Raman spectra for rGO samples.

Samples	**I_D/I_G ratio** (based on direct reading)	**FWHM values of the D band (cm^{-1})**
rGO	0.80 ±0.02	125.2 ±5.1
H_2-rGO-800	0.75 ±0.02	190.4 ±6.7
N-rGO-400	0.95 ±0.01	119.1 ±3.2
N-rGO-800	1.00 ±0.01	93.1 ±1.9

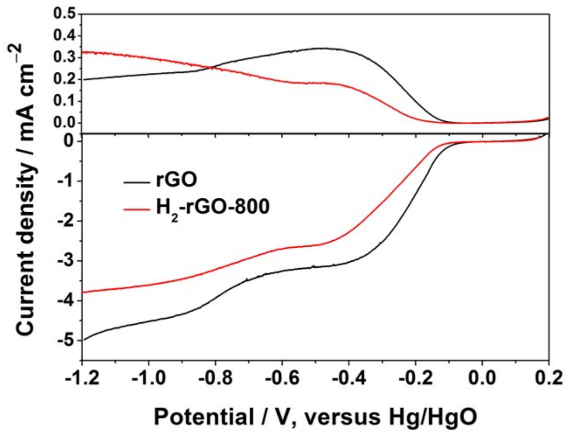

Figure S4. The LSV-RRDE profiles of rGO and H_2-treated rGO at 800 °C.

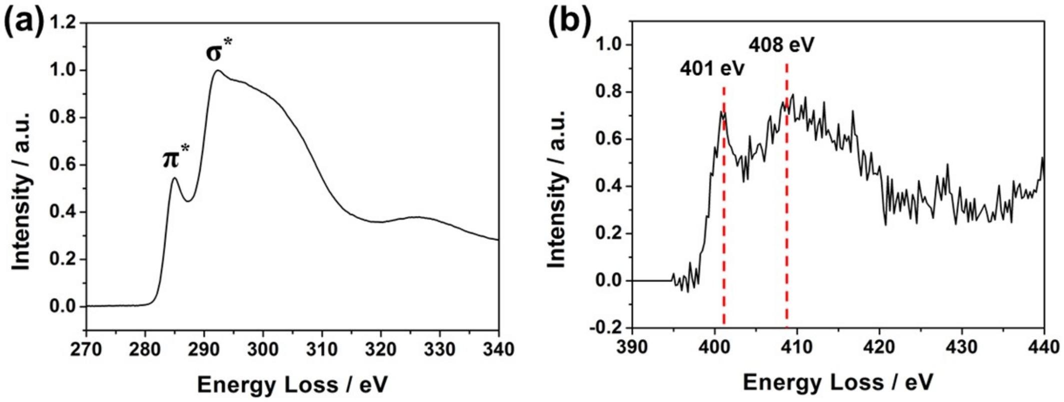

Figure S5. EELS spectra collected at a basal plane of N-rGO-800: (a) C *K*-edge and (b) N *K*-edge.

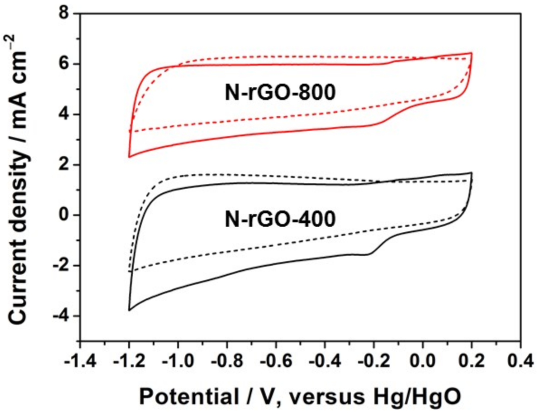

Figure S6. The CV profiles of NrGO-400 and NrGO-800 in N_2-deaerated and O2-saturated 0.1 M KOH electrolyte.

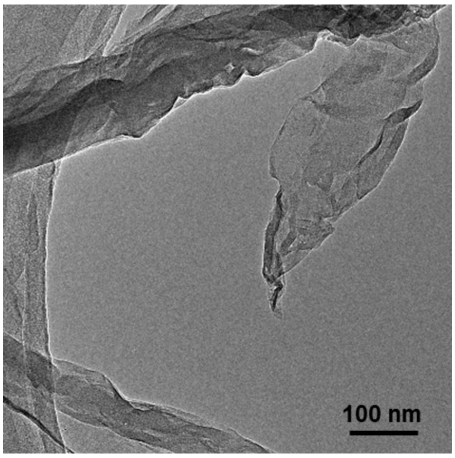

Figure S7. A TEM micrograph of the as-prepared GONR.

Table S3. A collection of ORR activity indices of samples based on LSV-RRDE.

Sample	**E_{onset} (V, versus Hg/HgO)**	**% j_{Levich} (4e)**		**mass activity (mA mg^{-1}_{total})**	
		@ –0.6 V	**@ –1.1 V**	**@ –0.6 V**	**@ –1.1 V**
CNT	–0.161	50.7%	75.0%	6.03	8.93
GONR	–0.155	17.6%	32.8%	2.09	3.90
GONR/CNT	–0.093	54.0%	87.4%	6.43	10.40
rGO	–0.100	57.1%	82.3%	6.79	9.79
N-rGO-800	–0.022	67.1%	68.6%	7.98	8.16
GONR/N-rGO-800	–0.014	65.4%	99.6%	7.78	11.85
20% Pt/C	–0.006	76.8%	N/A*	9.14	N/A*

* not directly measurable due to the occurrence of hydrogen evolution reaction.

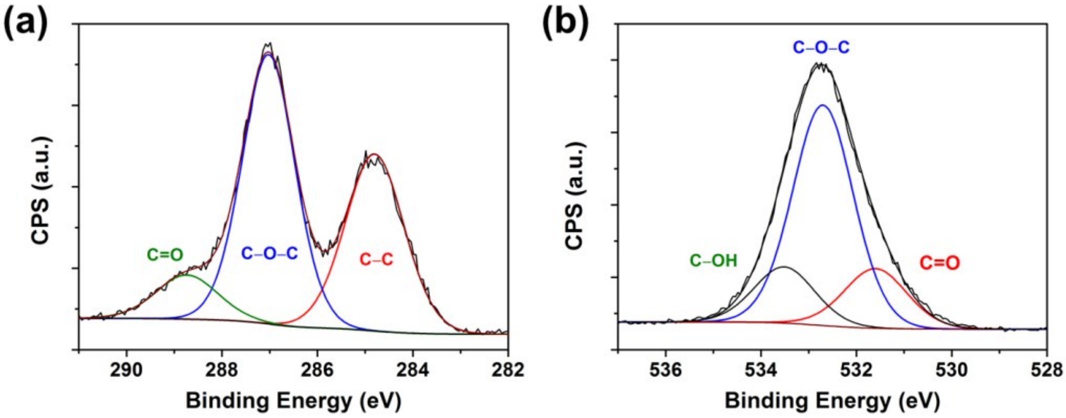

Figure S8. High-resolution XPS (a) C *1s* and (b) O *1s* spectra of GONR.

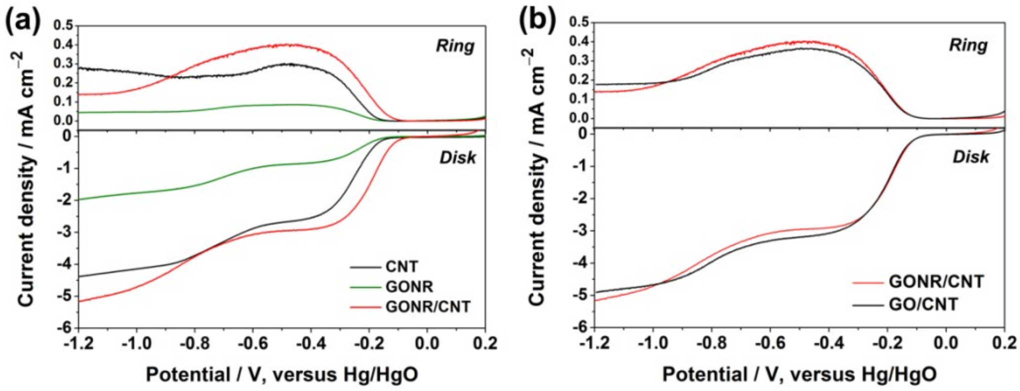

Figure S9. LSV-RRDE profiles of (a) CNT, GONR and GONR/CNT composite and (b) GO/CNT and GONR/CNT composites in O_2-saturated 0.1 M KOH for demonstrating their differences. GONR by itself is shown here for clarification.

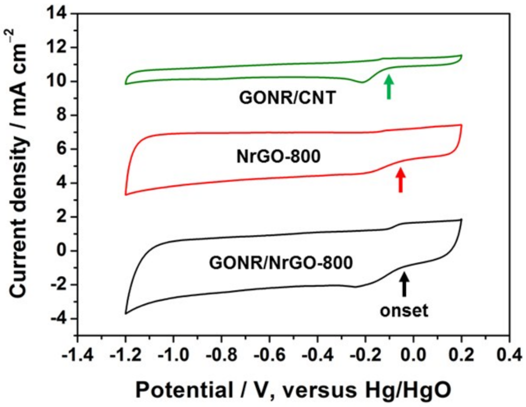

Figure S10. CV profiles (50 mV s^{-1}) of GONR/CNT, NrGO-800 and their composite collected in O_2-saturated 0.1 M KOH electrolyte.

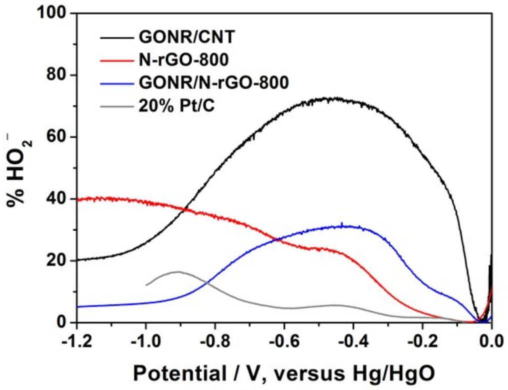

Figure S11. The %HO_2^- profiles for GONR/N-rGO-800 and its constituents along the

ORR potential in O_2-saturated 0.1 M KOH, based on the LSV-RRDE results.

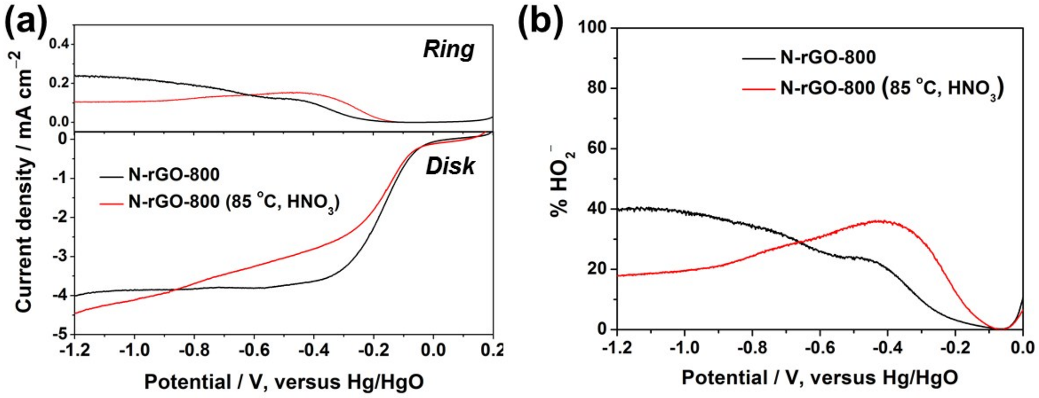

Figure S12. (a) LSV-RRDE and (b) the %HO_2^- profiles of acid-treated N-rGO-800 at 85 °C for overnight, compared to N-rGO-800, in O_2-saturated 0.1 M KOH.