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## Supporting Information

### **Graphene/Nitrogen-Doped Porous Carbon Sandwiches for Metal-Free Oxygen Reduction Reaction: Conductivity versus Active Sites**

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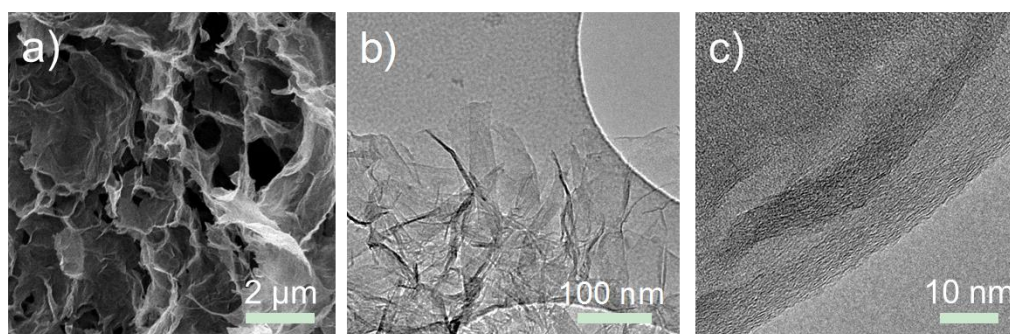
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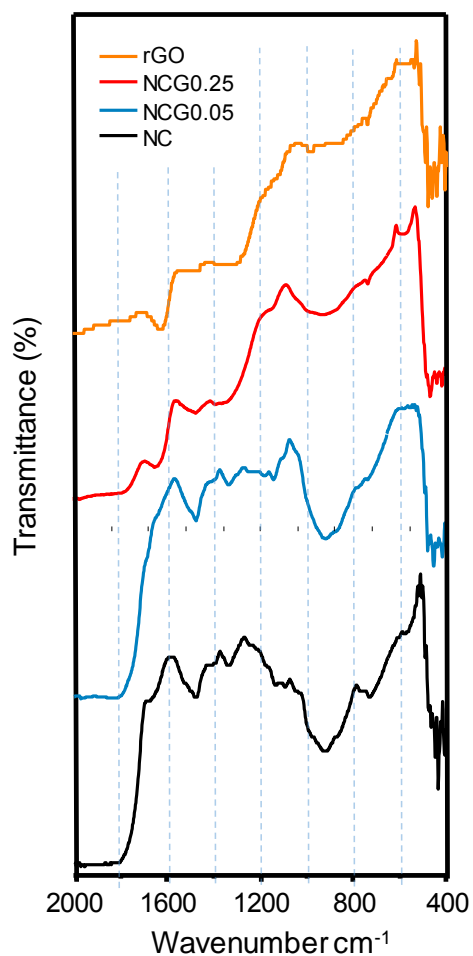
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## Supplementary figures



**Fig. S1** (a) SEM image and (b, c) TEM images of rGO obtained after HTC and high-temperature annealing.



**Fig. S2** FTIR spectra of NC, NCG0.05, NCG0.25 and rGO

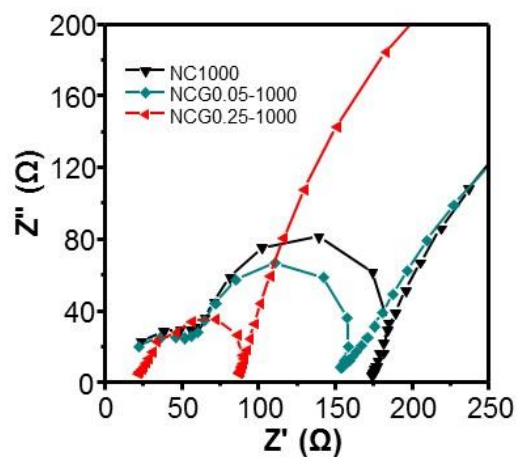


Fig. S3 Electrical conductivity of different samples measured by the impedance

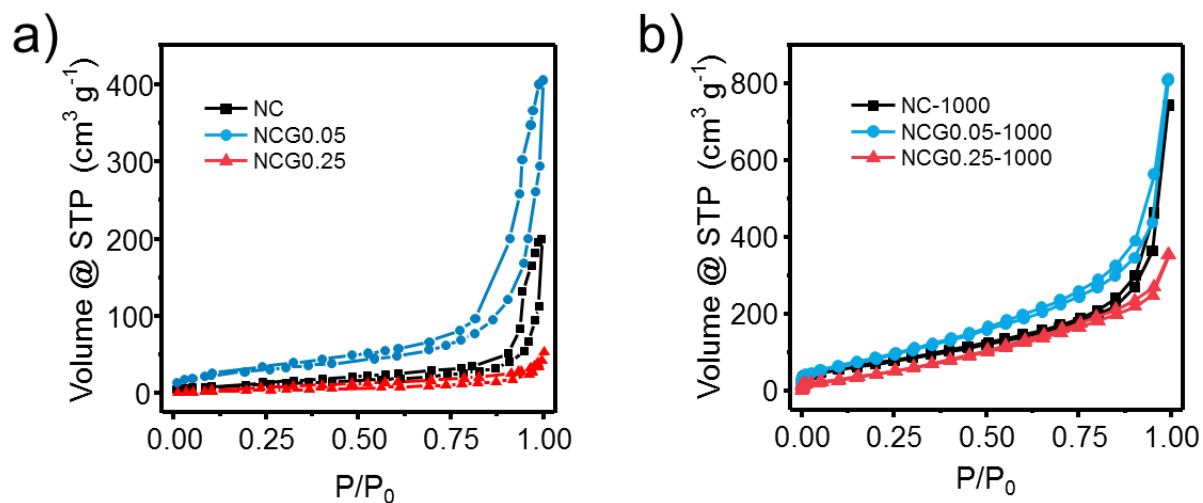


Fig. S4 The N<sub>2</sub> sorption isotherms of samples obtained after (a) HTC and (b) high-temperature annealing.

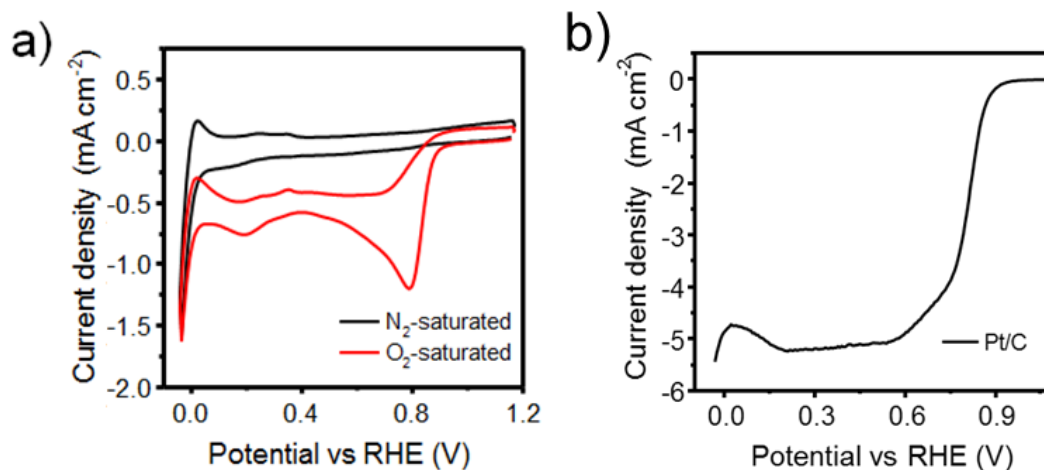


Fig. S5 (a) CV and (b) LSV curves of Pt/C catalyst.

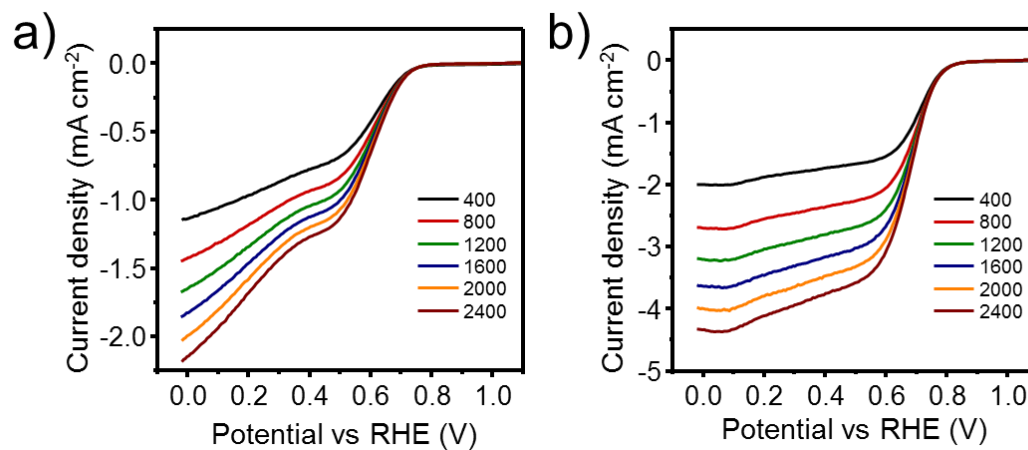
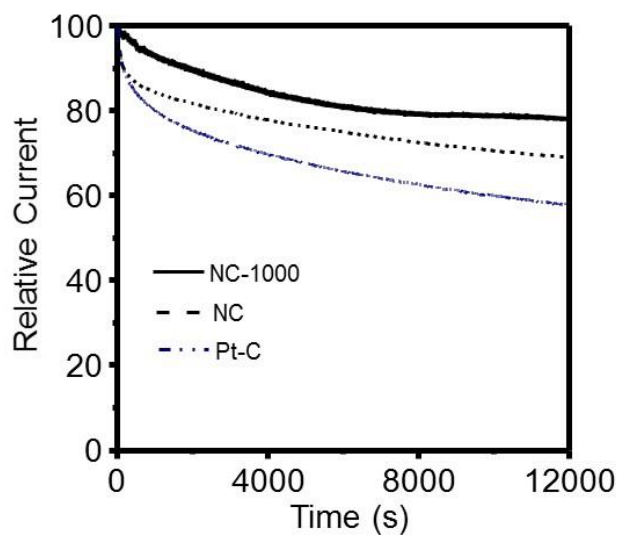
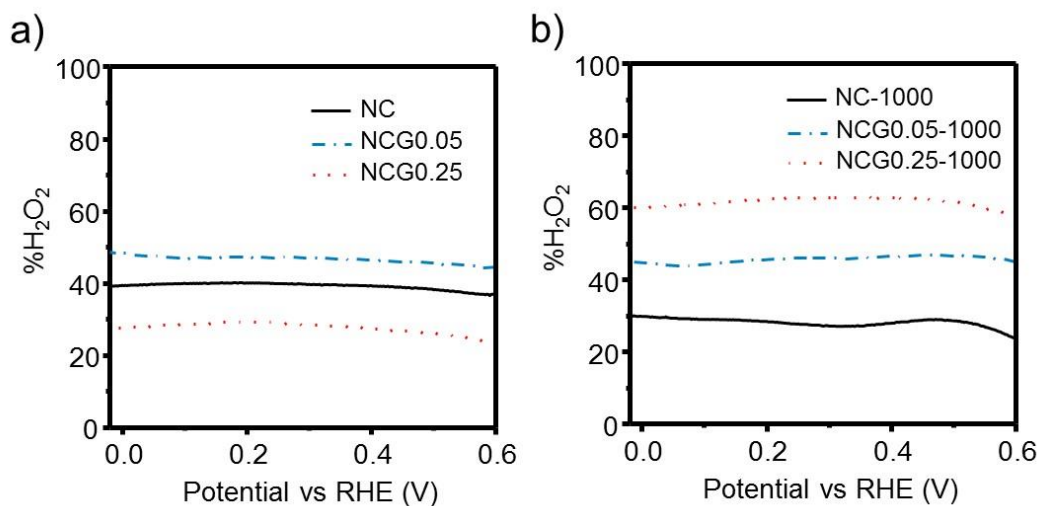


Fig. S6 LSV curves of (a) NCG0.25 and (b) NC-1000 at different rotating speeds of 400, 800, 1200, 1600, 2000, and 2400 rpm, respectively.



**Fig. S7** Current–time chronoamperometric responses of NC-1000, NC and Pt-C measured at peak potential in CV curves as shown in Fig. 4a.



**Fig. S8** Peroxide yields of (a) NC, NCG0.05, NCG0.25 and (b) NC-1000, NCG0.05-1000, NCG0.25-1000 in 0.1M KOH at rotating speed of 1600 rpm.



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## Supplementary tables

Table S1 Mass record of different samples during fabrication.

	GO (mg)	Chitosan (mg)	Monocomponent-calculated yield (mg) <sup>[a]</sup>			Experimental yield (mg)
			rGO	HTC- chitosan	Product	
GO	60	0	25.9	0	25.9	25.9
NC	0	1200	0	372.0	372.0	372.0
NCG0.25	60	180	25.9	55.8	81.7	122.6
NCG0.05	60	1200	25.9	372.0	397.9	672.4

a) The monocomponent-calculated yield was calculated based on the yield of chitosan and GO in monocomponent HTC systems. Experimental yield refers to the mass of product obtained in the actual experiment.



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**Table S2** XPS results of different samples.

Sample	Atom Species (at. %)						
	C	O	N	Pyridinic-N	Pyrrolic-N	Quaternary-N	Oxidized-N
NC	75.16	21.39	3.45	1.27	1.38	0.79	-
NCG0.05	76.13	18.22	5.65	1.49	2.97	1.19	-
NCG0.25	80.97	15.01	4.02	1.08	2.15	0.79	-
NC-1000	90.87	7.45	1.68	0.47	-	0.97	0.24
NCG0.05-1000	96.48	2.04	1.48	0.26	-	0.98	0.23
NCG0.25-1000	94.39	4.39	1.22	0.17	-	0.84	0.21



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**Table S3** Specific surface area and total pore volume of different samples.

Sample	NC	NCG0.05	NCG0.25	NC-1000	NCG0.05-1000	NCG0.25-1000
SSA (m <sup>2</sup> g <sup>-1</sup> )	36	99	25	278.9	339	223
Pore volume (cm <sup>3</sup> g <sup>-1</sup> )	0.1	0.34	0.06	0.81	0.91	0.43

**Table S4** The ORR peak potential and peak current density in CV curves as shown in Fig. 4a.

Sample	Peak potential vs RHE (mV)	Peak current density (mA cm <sup>-2</sup> )
NC	510	0.517
NCG0.05	506	0.384
NCG0.25	575	0.362
NC-1000	690	1.055
NCG0.05-1000	609	0.935
NCG0.25-1000	563	0.899





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**Table S5** ORR activity observed from the LSV curves in Fig. 4b.

	NC	NCG0.05	NCG0.25	NC- 1000	NCG0.05 -1000	NCG0.25 -1000
Onset potential* (mV)	832	839	922	993	987	844
Saturated current density (mA cm <sup>-2</sup> )	1.57	1.75	1.85	3.61	3.39	3.15
Half wave potential (mV)	340	357	524	666	600	363

\* The onset potential is determined as the potential required for a current density of  $-2 \mu\text{A cm}^{-2}$  (vs. RHE)