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

Supporting Information

B, N- and P, N-doped Graphene as Highly Active Catalysts for Oxygen Reduction Reactions in Acidic Media

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1. Equations

1.1 Calculation of kinetic current

$$\frac{1}{I} = \frac{1}{I_k} + \frac{1}{I_d}$$

I: current from disk electrode, I_k: kinetic current, and I_d: diffusion current.

1.2 Calculation of H_2O_2 yield and number of electrons transferred

$$H_2O_2\ (\%) = 200 \times \frac{I_R/n}{I_R/n + I_D}$$

$$\mathrm{N} = 4 \times \frac{I_D}{I_R/n + I_D}$$

I_R: current from ring disk electrode, I_D: current from disk electrode, n: collection efficient, and N: number of electrons transfered.

2. Tables

Table S1. Compositions of the prepared graphene-based catalysts obtained from EA and ICP analysis.

	C[a]	H[a]	O[a]	N[a]	B[b]	P[b]	Co+Fe[b]	N/C[c]	B/C[c]	P/C[c]
NGr	86.9	6.6	0.3	5.9	-	-	0.3	6.8	-	-
BNGr	82.6	7.8	0.8	6.9	1.5	-	0.3	8.4	1.9	-
PNGr	85.8	7.0	1.4	5.1	-	0.4	0.3	5.9	-	0.5

[a] Compositions obtained from EA analysis (at. %) [b] Compositions obtained from ICP analysis (at. %) [c] Doping concentrations (%)

Table S2. Proportion of various N-doping types among pyridinic-N (N1), graphitic-N (N2), and pyridinic-oxide (N3) in the prepared catalysts obtained from the XPS results. The values in parenthesis for BNGr indicate the proportions of all N-doping type including BN (N0).

%	N0	N1	N2	N3
NGr	-	53.8	29.8	16.4
BNGr	- (40.6)	77.9 (46.3)	18.2 (10.8)	3.9 (2.3)
PNGr	-	64.4	28.6	7.0

Table S3. Proportion of B-doping and P-doping types in the BNGr and PNGr, respectively.

B (%)[a]			P (%)[b]		
B1	B2	B3	P1	P2	P3
25.0	48.9	26.1	16.2	77.6	6.2

[a] B1 (190.3 eV): BN, B2 (191 eV): BC_3, B3 (192 eV): Partially oxidized carbon (BN_3, BCO_2, and BC_2O). [b] P1(129.4 eV): Me_xP (Me=Co or Fe; x=1~2), P2 (132.9 eV): P-O, P3 (135 eV): P-C.

3. Figures

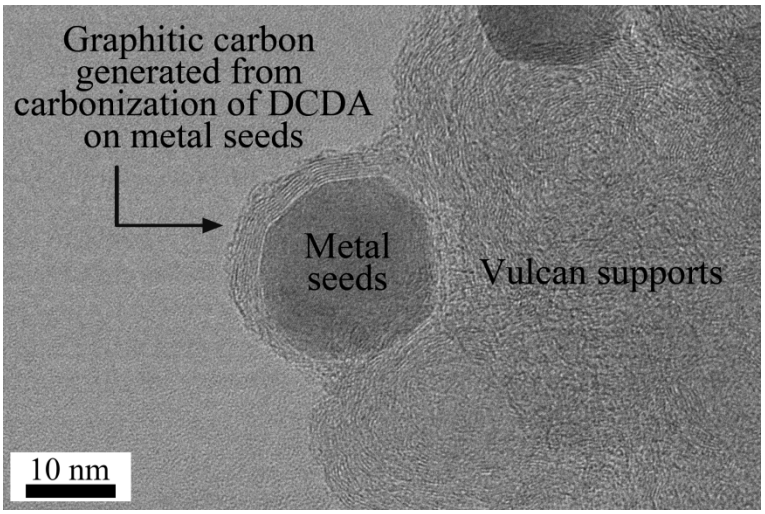

Fig. S1 Newly generated graphite materials *via* carbonization of DCDA on metal seeds.[1]

[1] C. H. Choi, S. H. Park, S. I. Woo, *Int J Hydrogen Energ* **2012**, *37*, 4563-4570.

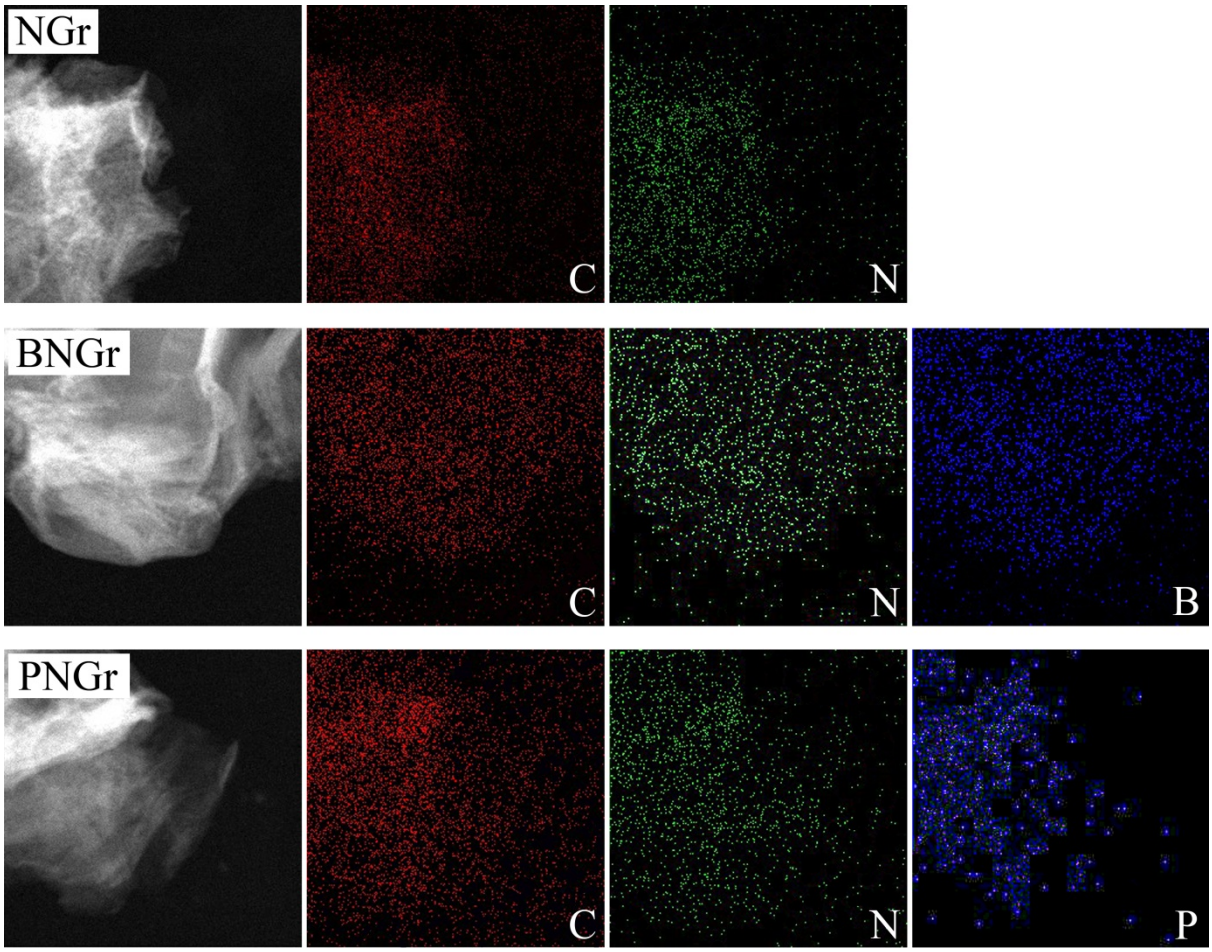

Fig. S2 EDS mapping images of NGr, BNGr, and PNGr**.**

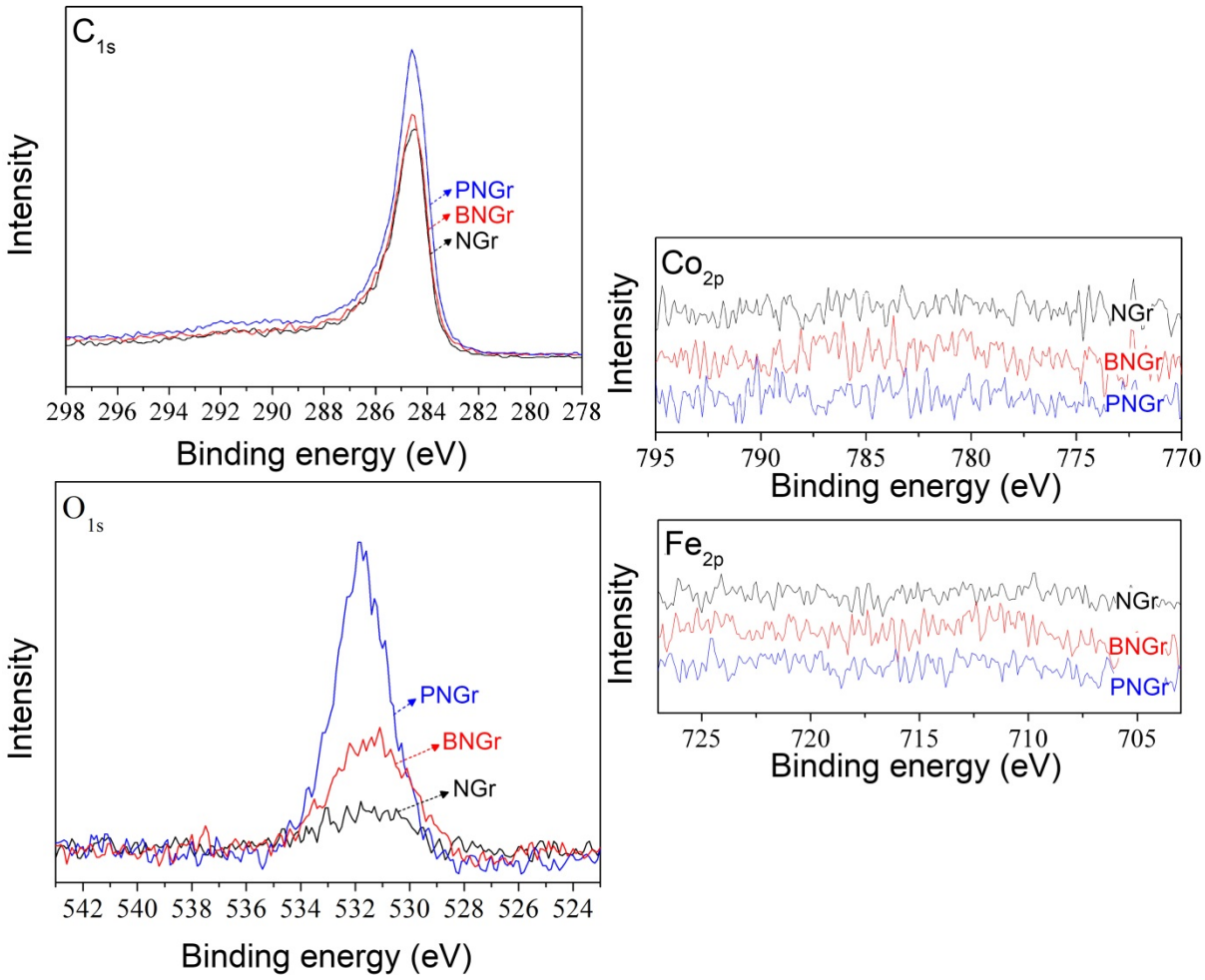

Fig. S3 XPS results for C_{1s}, O_{1s}, Co_{2p}, and Fe_{2p} in the prepared catalysts.

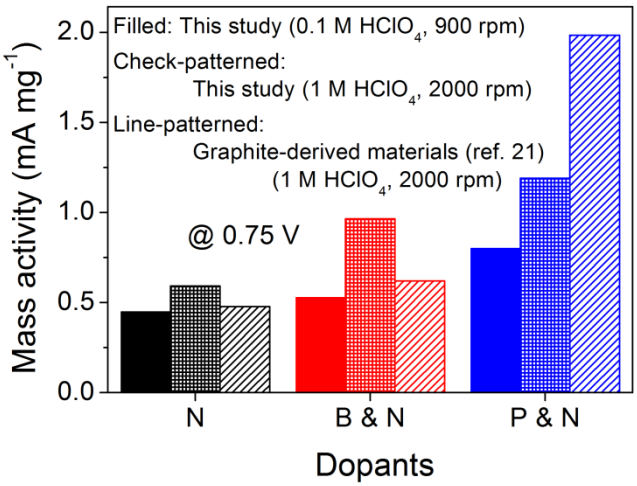

Fig. S4 Mass activities calculated at 0.75 V for the graphene- and graphite-derived catalysts. The mass activities for the graphite-derived catalysts were calculated from our previous works (ref. 21). Moreover, for more valid comparison, the mass activity of the graphene-derived catalysts were obtained at the same conditions with ref. 21 and was indicated by check-pattered bar.

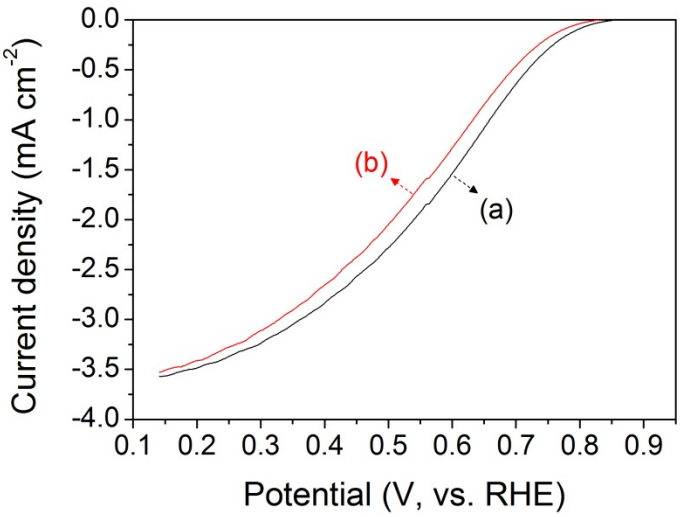

Fig. S5 LSV results of the NGr (a) before and (b) after acid-leaching steps in oxygen saturated 0.1M $HClO_4$.

As shown in Table S1, NGr has ~0.3 at.% metal residues, which is corresponded to ~1.3 wt.%. However, most of the metal residue was eliminated (< 0.2 wt. %) after the additional secondary acid leaching step.

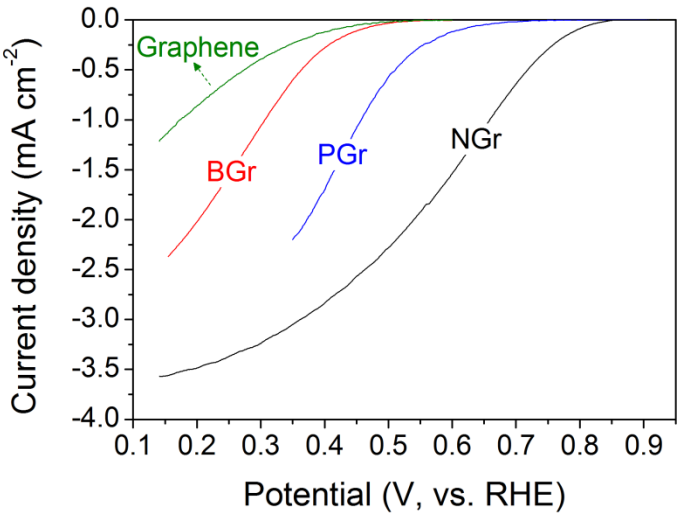

Fig. S6 LSV results of bare graphene, BGr, PGr, and NGr in oxygen saturated 0.1M $HClO_4$.