Electronic Supplementary Information

N,P-co-doped 3D Graphene/Cobalt-Embedded Electrocatalyst for Oxygen Reduction Reaction

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Table S1 Related atom contents of the samples determined by XPS analysis.

	Co Content (%)	N Content (%)	P Content (%)
Co/N,P-GAs-800	0.37	2.86	0.14
Co/N,P-GAs-900	0.29	2.93	0.12
Co/N,P-GAs-1000	0.23	1.63	0.11
N-GAs-900	0	1.80	0

Table S2 Related N atom contents of the samples determined by XPS analysis.

Samples	N	Pyridinic N		Pyrrolic N		Graphitic N	
	Content (%)	B.E. (eV)	Content (%)	B.E. (eV)	Content (%)	B.E. (eV)	Content (%)
Co/N,P-GAs-900	2.93	398.2	0.79	399.3	0.82	401.1	1.32
N-GAs-900	1.80	398.2	0.49	399.3	0.32	401.1	0.99

Table S3 Relative surface concentrations of nitrogen species obtained by fitting high-resolution N1s XPS spectra of samples.

Samples	pyridinic-N	pyrrolic-N	graphitic-N
Co/N,P-GAs-800	29.68	28.71	41.61
Co/N,P-GAs-900	27.19	27.82	44.99
Co/N,P-GAs-1000	22.52	26.78	50.70

Table S4 Relative surface concentrations of phosphorus species obtained by fitting high-resolution P 2p XPS spectra of samples.

Samples	P-C	P-N	C-O-PO_3
Co/N,P-GAs-800	60.71	24.41	14.88
Co/N,P-GAs-900	33.99	34.99	31.02
Co/N,P-GAs-1000	57.73	13.41	28.86

Table S5 The comparison of the ORR performance of different catalysts in 0.1 M KOH electrolyte.

Electrocalyst	$\triangle E_{onset}^{a,c}$(V)	$\triangle E_{1/2}^{a,c}$(V)	$j_L^{b,c}$(mA cm^{-2})	Loading (μg cm^{-2})	Reference electrode	Ref.
Co/N,P-GAs-900	-0.03	-0.02	5.22	280	SCE	This Work
$N\text{-}G_{750}$	~-0.11	~-0.17	4.27	Not given	Ag/AgCl	1
N-doped GNR aerogel	0.01	-0.06	2.2	Not given	Ag/AgCl	2
CNPS-900	-0.192	-0.056	3.01	159	SCE	3
B,N-graphene	-0.11	-0.13	5.2	280	RHE	4
GNSP-31	0.030	0.025	6.39	Not given	Ag/AgCl	5
PSNG1:10	-0.052	0.015	5.05	280	SCE	6
Co_3O_4/rmGO	~-0.93	-0.07	~5.00	Not given	RHE	7
$NiCo_2O_4$-G	~-0.12	~-0.11	~-4.10	407	SCE	8
TTF-700-96	-0.14	-0.07	5.0	300	RHE	9
$CoFe_2O_4$/rGO	-0.136	-0.08	~-6.40	1006	Ag/AgCl	10

[a] Represents the difference in onset potential or half-wave potential between the various catalysts and Pt/C.

[b] Represents the diffusion-limited current density of the various catalysts at a rotation speed of 1600 rpm.

[c] The onset potential (E_{onset}), half-wave potential ($E_{1/2}$) and diffusion limited current density (j_L) were obtained from the corresponding literatures and the corresponding figures in the present study.

Refrence:

[1] Hou Z, Jin Y, Xi X, Huang T, Wu D, Xu P, Liu R (2017) Hierarchically porous nitrogen-doped graphene aerogels as efficient metal-free oxygen reduction catalysts J Colloid Interf Sci 488317-321.

[2] Gong YJ, Fei HL, Zou XL, Zhou W, Yang SB, Ye GL, Liu Z, Peng ZW, Lou J, Vajtai R, Yakobson BI, Tour JM, Ajayan PM (2015) Boron- and Nitrogen-Substituted

Graphene Nanoribbons as Efficient Catalysts for Oxygen Reduction Reaction. Chem. Mater 27: 1181-1186.

[3] Dou S, Shen A, Ma Z L, Wu J H, Tao L, Wang S Y (2015) N-, P- and S-tridoped graphene as metal-free electrocatalyst for oxygen reduction reaction. J Electroanal. Chem 753: 21-27.

[4] Zhen Y, Jiao Y, Ge L, Jaroniec M, S Z Qiao (2013) Two-step boron and nitrogen doping in graphene for enhanced synergistic catalysis. Angew Chem Int Ed 52: 3110-3116.

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[7] Liang YY, Li YG, Wang HL, Zhou JG, Wang J, Regier T, Dai H J (2011) Co_3O_4 nanocrystals on graphene as a synergistic catalyst for oxygen reduction reaction. Nat Mater 10: 780-786.

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[9] L Hao, S Zhang, R Liu, J Ning, G Zhang, L Zhi (2015) Bottom-up construction of triazine-based frameworks as metal-free electrocatalysts for oxygen reduction reaction. Adv Mater 27: 3190-3195.

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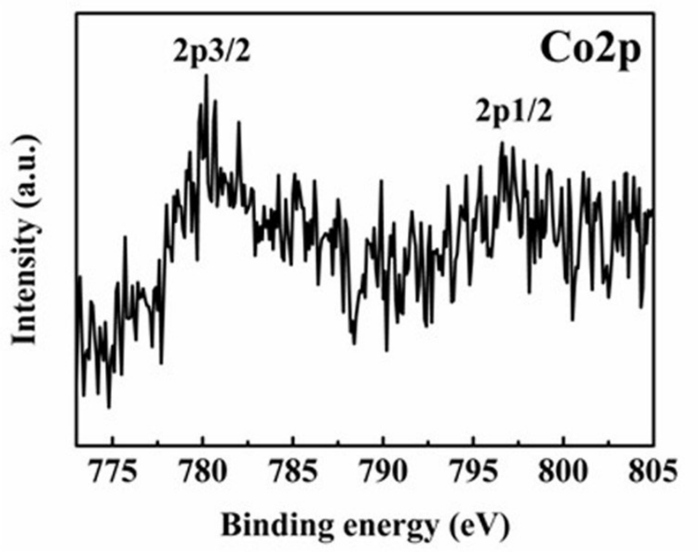

Fig. S1 High resolution Co 2p spectrum of Co/N,P-GAs-900.

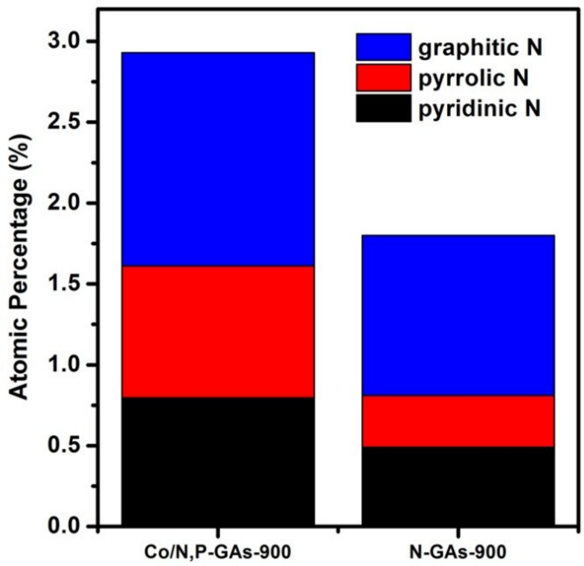

Fig. S2 The atomic percentages of deconvoluted N 1s peaks of Co/N,P-GAs-900 and N-GAs-900.

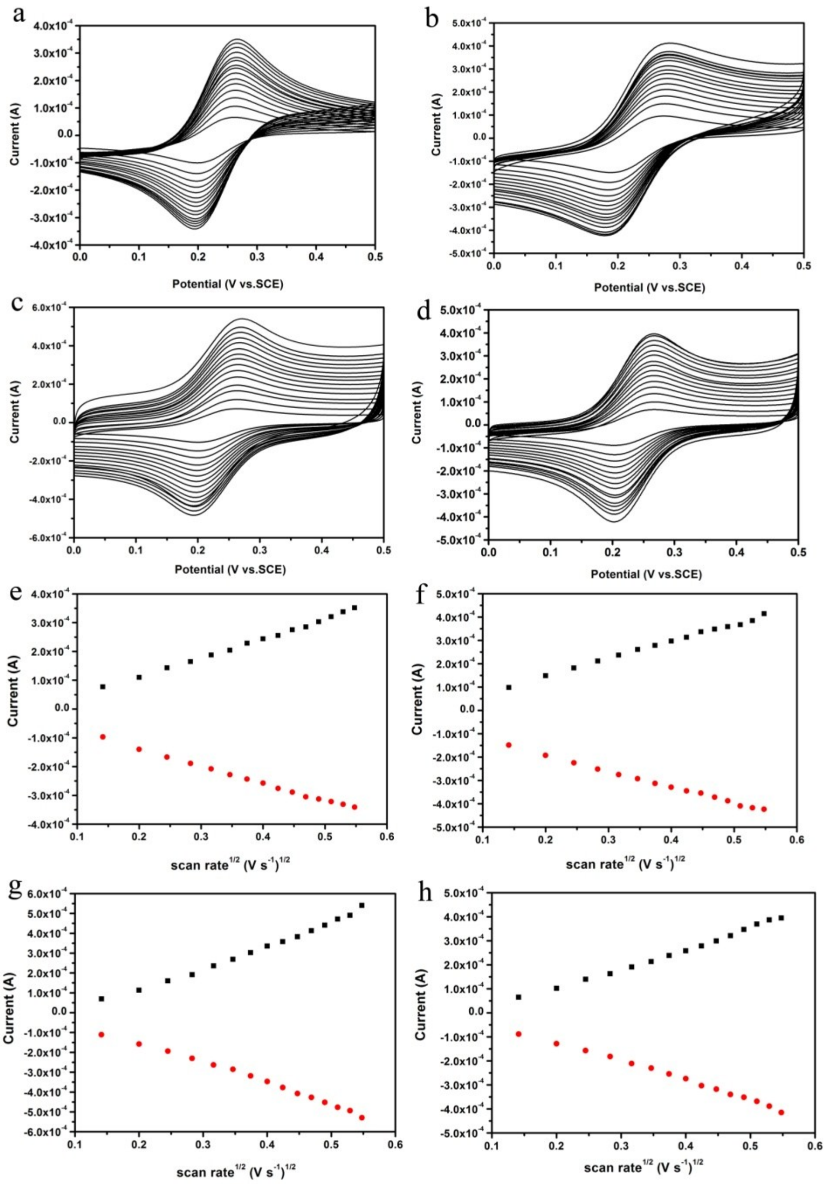

Fig. S3 CV curves of bare GC electrode (a) Co/N,P-GAs-800 (b), Co/N,P-GAs-900 (c) and Co/N,P-GAs-1000 (d) in 5 mM $Fe(CN)_6^{3-/4-}$/1 M KCl at various scan rates from 20 to 300 mV s^{-1}; plots of i_p *vs.*$v^{1/2}$ for bare GC electrode (e) Co/N,P-GAs-800 (f), Co/N,P-GAs-900 (g) and Co/N,P-GAs-1000 (h).

The electrochemically assessible surface area can be estimated according to the Randles-Sevcik equation given below:

$$i_\mathrm{p} = 2.99 \times 10^5 n\mathrm{ACD}^{1/2}v^{1/2}$$

Where i_p is the peak current, D and C are the diffusion coefficient and bulk concentration of the redox probe (5 mM $K_3[Fe(CN)_6]$), respectively. *n* is the number of electrons transferred (n = 1), v is the scan rate and A is the electrochemically assessible surface area. Consequently, the electrochemically assessible surface areas of Co/N,P-GAs-800, Co/N,P-GAs-900 and Co/N,P-GAs-1000 were estimated according to the slope of the straight line of i_p versus $v^{1/2}$.

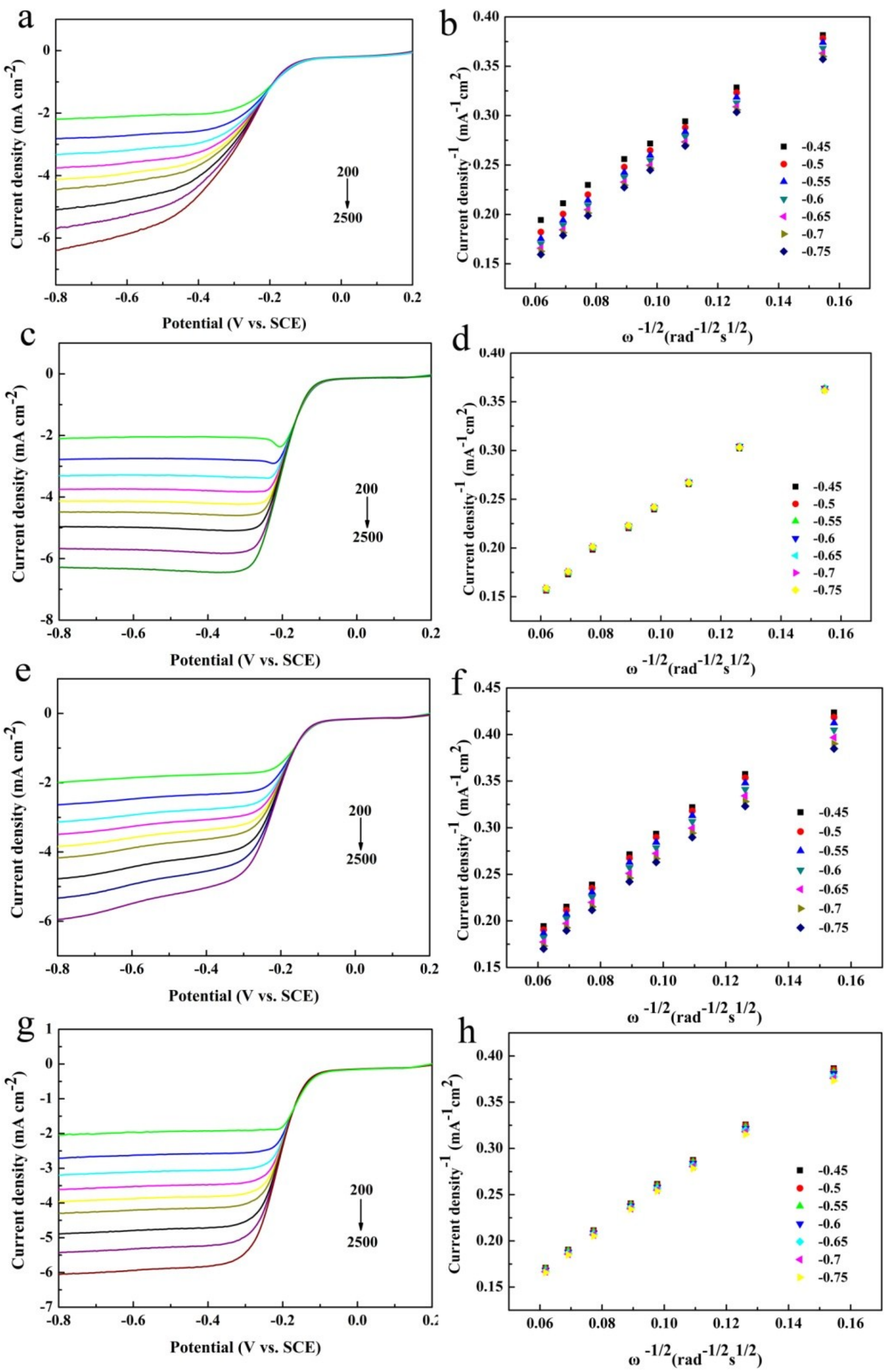

Fig. S4 LSV curves of (a) N-GA-900, (c) Co/N-GA-900, (e) Co/N,P-GA-800 and (g) Co/N,P-GA-1000 in an O_2-saturated 0.1 M KOH electrolyte at 1600 rpm with a scan rate of 10 mV s^{-1}; The corresponding Kouteckey-Levich plots of (b) N-GA-900, (d) Co/N-GA-900, (f) Co/N,P-GA-800 and (h) Co/N,P-GA-1000.

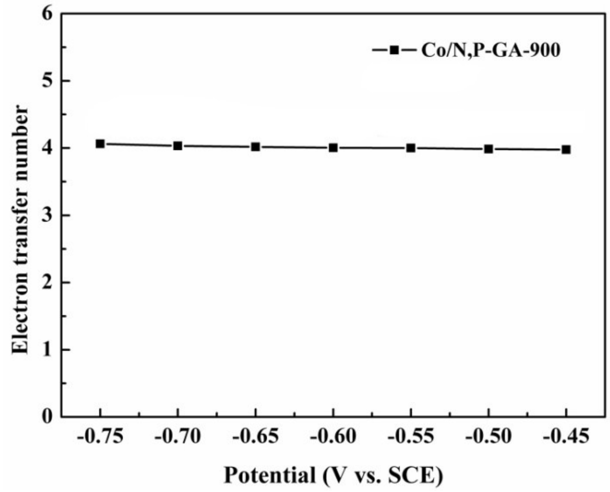

Fig. S5 The electron transfer number (n) of the Co/N,P-GAs-900 according to the K-L plots.

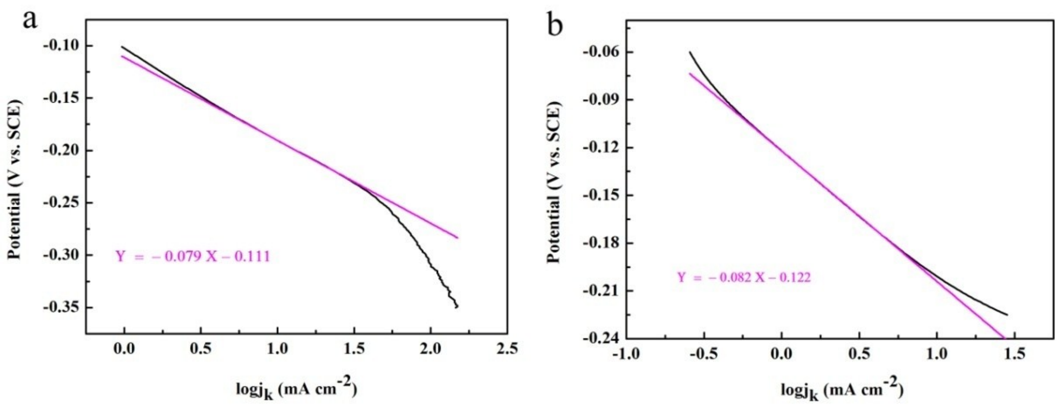

Fig. S6 Tafel plots obtained from the LSV measurements on the (a) Co/N,P-GAs-900 and (b) Pt/C at the rotation speed of 1600 rpm, respectively.