

Architecture of CoN_x single clusters on nanocarbon as excellent oxygen reduction catalysts with high-efficient atomic utilization

Ting He,^a Hui Xue,^a Xiaojuan Wang,^{a,b} Shuanghua He,^c Yulai Lei,^a Yuyuan Zhang,^a Rujuan Shen,^c Yi Zhang,^{*,a} and Juan Xiang,^{*,a}

^aCollege of Chemistry and Chemical Engineering Central South University 932 Lushan South Road Yuelu District, Changsha, Hunan, China

^bCollege of Chemistry and Chemical Engineering, University of South China Hengyang, Hunan, China

^cSchool of Mechanical Engineering, Hefei University of Technology, Hefei 230009, China

^dState Key Laboratory of Power Metallurgy Central South University 932 Lushan South Road Yuelu District, Changsha, Hunan, China

Email: yzhangcsu@csu.edu.cn; xiangj@csu.edu.cn

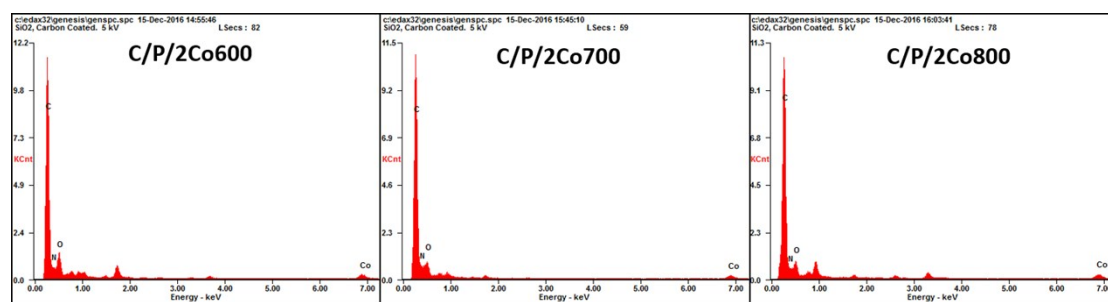


Fig. S1 EDS analysis of C/P/2Co600, C/P/2Co700 and C/P/2Co800 catalysts, respectively.

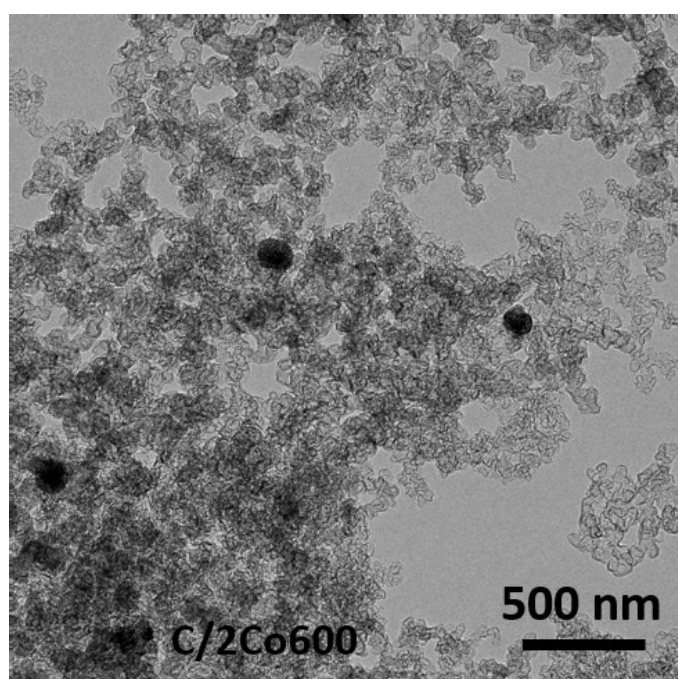


Fig. S2 The TEM image of C/2Co600. Some large cobalt oxide nanoparticles distribute in carbon supports.

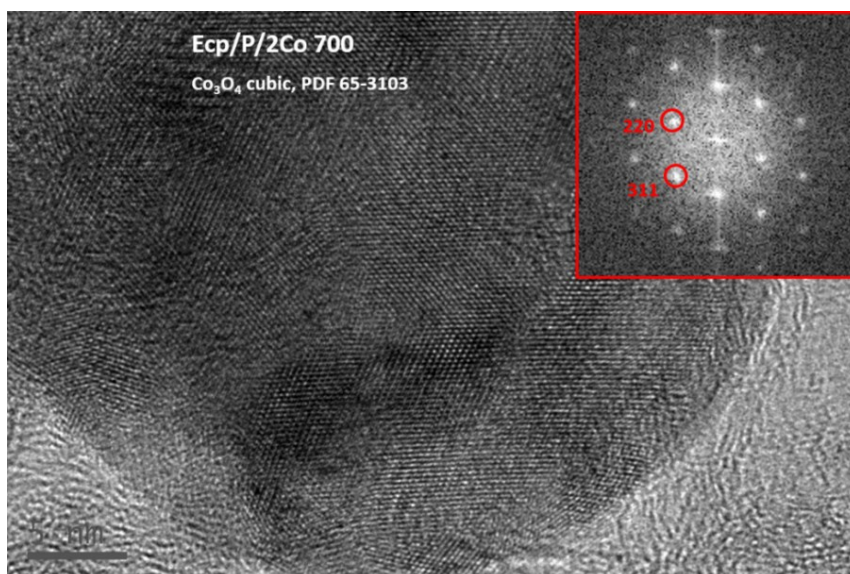


Fig. S3 The HRTEM image of C/P/2Co700 and corresponding FFT image, which clearly indicate the Co₃O₄ nanoparticles with a cubic crystal system (PDF 65-3103).

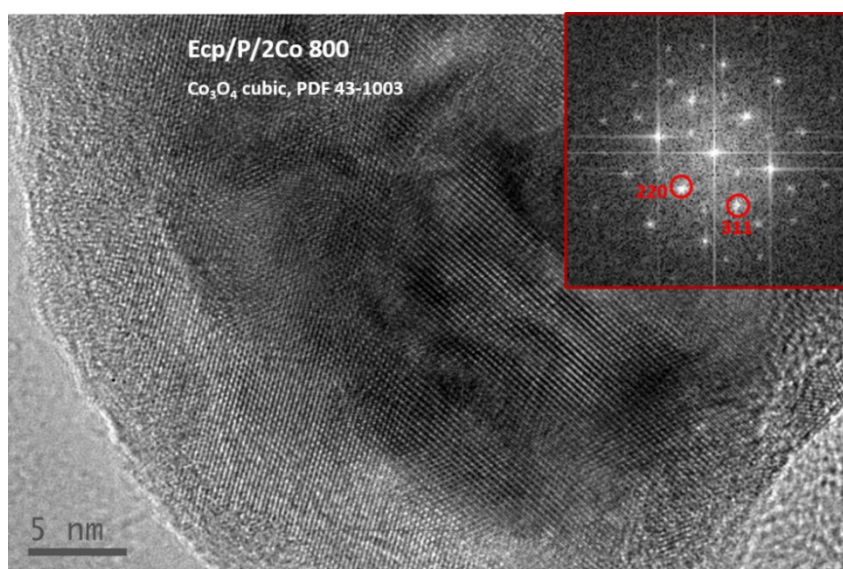


Fig. S4 The HRTEM image of C/P/2Co800 and corresponding FFT image, which clearly indicate the Co₃O₄ nanoparticles with a cubic crystal system (PDF 43-1003).

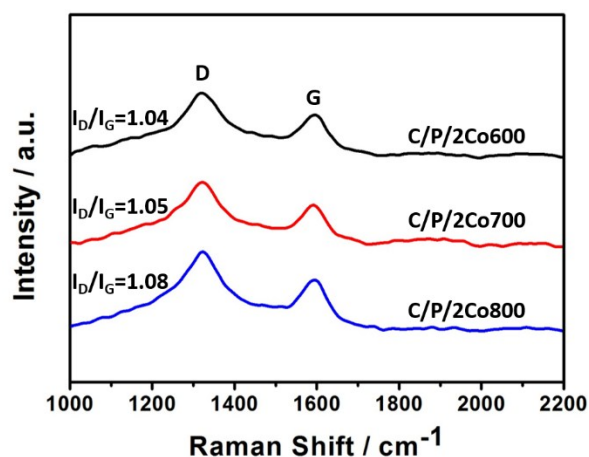


Fig. S5 The Raman spectra of C/P/2Co600-800.

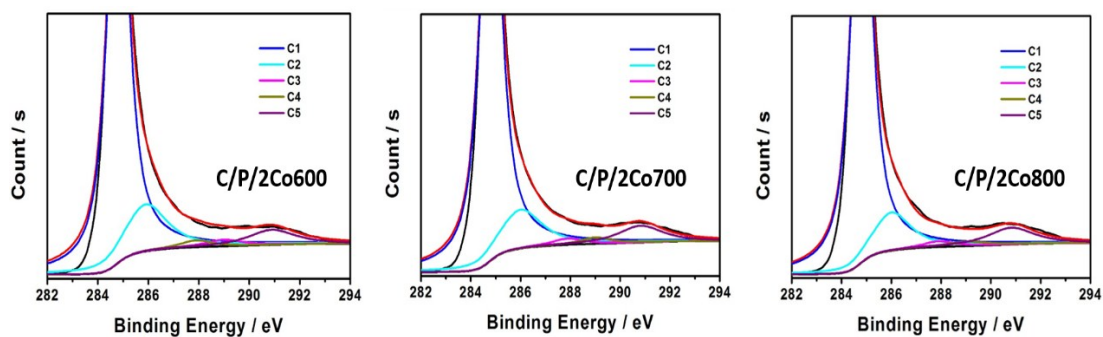


Fig. S6 Peak assignments for the C(s) of C/P/2Co (600-800) catalysts.

Table S1 Percentages of elements for C/P/Co(600-800) catalysts from XPS.

Elements	C/P/2Co600 (At %)	C/P/2Co700 (At %)	C/P/2Co800 (At %)
C	94.93	95.72	96.66
O	2.7	2.38	1.99
N	1.95	1.5	0.97
Co	0.42	0.39	0.38

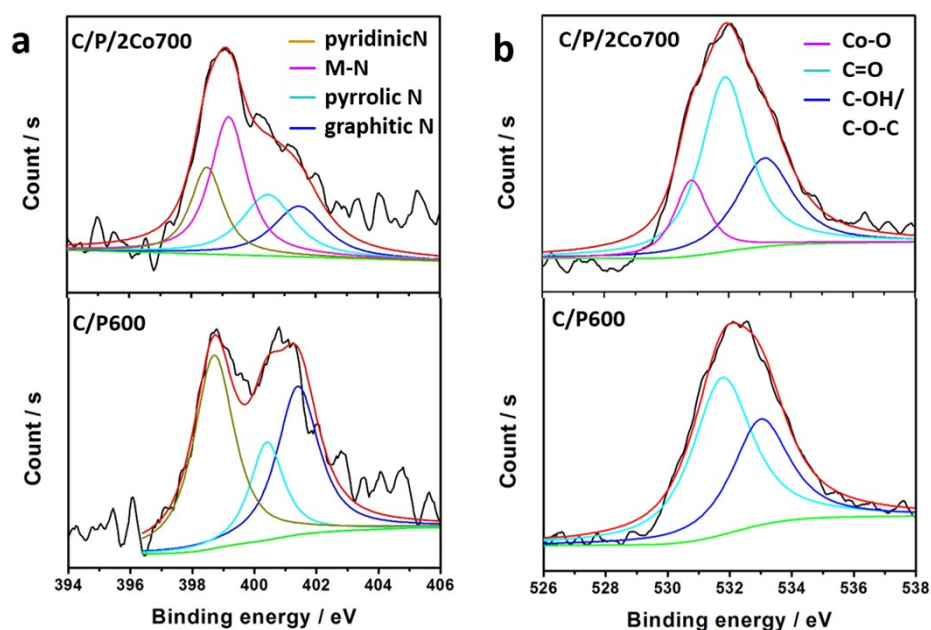


Fig. S7 XPS analysis of C/P/2Co700 and C/P600. (a) XPS spectra for N 1s. (b) XPS spectra for O 1s.

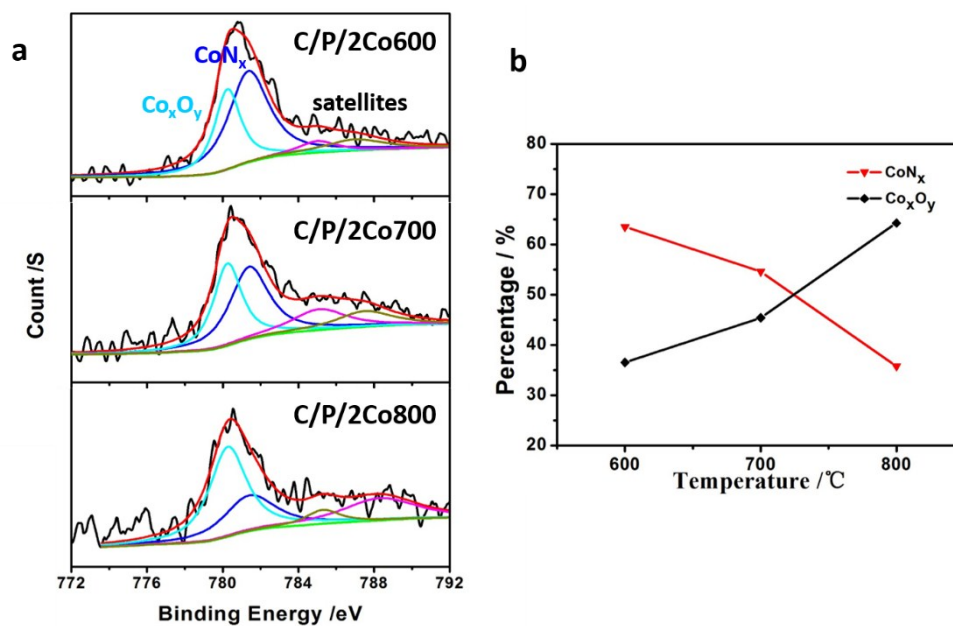


Fig. S8 (a) XPS analysis of C/P/2Co600, C/P/2Co700 and C/P/2Co800 catalysts for Co 2p. (b) The variation tendency of CoN_x and Co_xO_y contents in C/P/2Co(600-800) catalysts.

Table S2 The percentages of CoN_x and Co_xO_y in C/P/2Co(600-800) catalysts.

Catalysts	$\text{CoN}_x\%$	$\text{Co}_x\text{O}_y\%$	N/O
C/P/2Co600	63.48	36.52	1.74
C/P/2Co700	54.57	45.43	1.20
C/P/2Co800	35.75	64.25	0.56

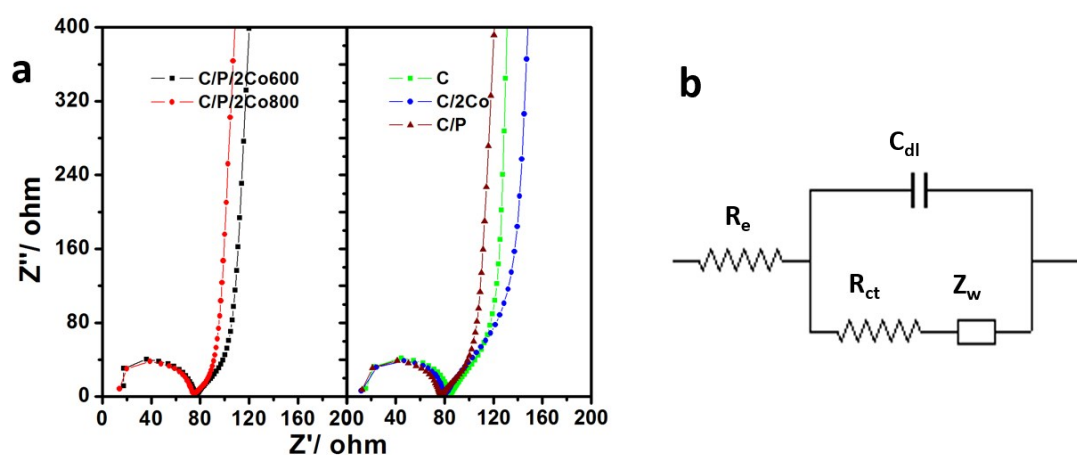


Fig. S9 (a) Impedance spectroscopies of five control catalysts and (b) the corresponding equivalent-circuit diagram.

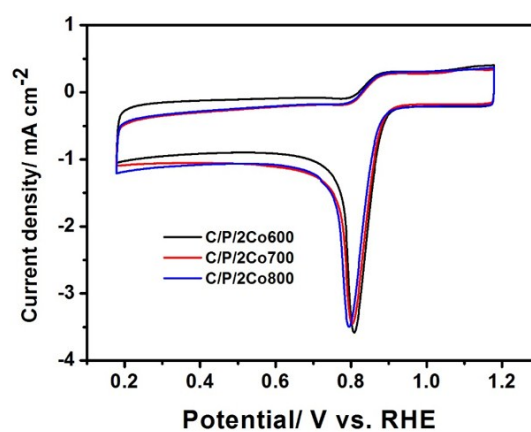


Fig. S10 The CV curves of C/P/2Co600, C/P/2Co700 and C/P/2Co800 catalysts.

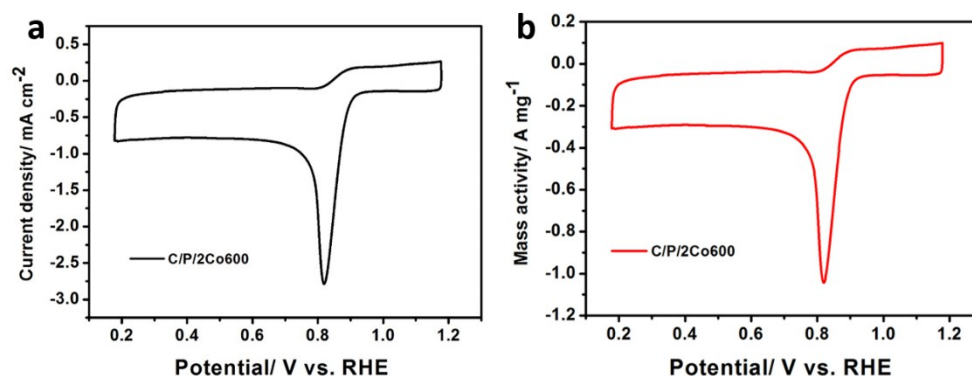


Fig. S11 The CV curve and mass active of C/P/2Co600 at 20 mV S⁻¹ with the loading mass of 127.4 $\mu\text{g cm}^{-2}$.

Table S3 The calculation detail of mass active (ampere per milligram of cobalt).

Items	Calculation details
Total mass on the electrode	$1 \text{ mg mL}^{-1} \times 6 \times 10^{-3} \text{ mL} = 6 \times 10^{-3} \text{ mg}$
Percentage of Co atoms	2.1 wt% (0.4 at%)
Mass of Co atoms	$2.1\% \times 6 \times 10^{-3} \text{ mg} = 1.26 \times 10^{-4} \text{ mg}$
Mass active ($\text{A mg}_{\text{Co}}^{-1}$)	Current/ $1.26 \times 10^{-4} \text{ mg}$

Table S4 The ORR catalytic performance of C/P/2Co600 and recently developed TM–N/C materials.

Materials	half-wave potentials (0.1 M KOH)	Ref.
C/P/2Co600 single cluster catalyst	0.846 V	This paper
NiCoMnO ₄ /N-doped graphene	0.750 V	1
Fe ₂ N@N-doped porous carbon	0.803 V	2
CoFe/N-doped carbon nanotubes	0.840 V	3
Porous Co–Nx/C catalysts	0.830 V	4
Co ₃ (PO ₄) ₂ C–N/rGOA	0.837 V	5
N-doping Single Cobalt Atoms catalysts	0.881 V	6

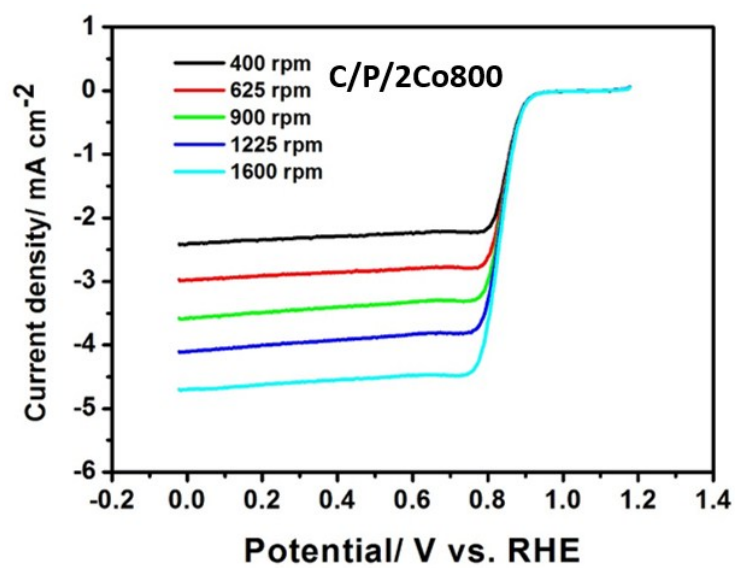


Fig. S12 Polarization curves of C/2Co600 catalysts at different rotation rate in O₂-saturated KOH.

Table S5 Average electron transfer numbers (E) for different materials.

Potential/V	E for Pt/C	E for C/P/2Co600	E for C/P/2Co800	E for C600
0.702	3.77	3.62	3.12	2.08
0.600	3.89	3.71	3.22	2.20
0.502	3.85	3.73	3.23	2.31
0.400	3.89	3.79	3.28	2.46
0.301	3.90	3.86	3.33	2.64
0.202	3.86	3.93	3.36	2.97
0.100	3.90	4.00	3.42	3.38
0.002	4.00	4.00	3.50	3.48
Average E value	3.88	3.83	3.31	2.69

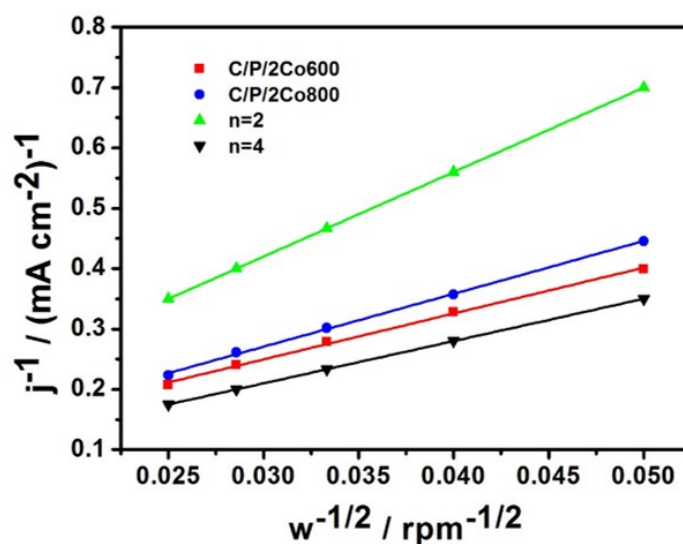


Fig. S13 Koutecky-Levich plots of C/P/2Co600 and C/P/2Co800 at 0.6 V.

References

- 1 A. Pendashteh, J. Palma, M. Anderson and R. Marcilla, *Appl. Catal. B* 2017, **201**, 241-252.
- 2 X. Huang, Z. Yang, B. Dong, Y. Wang, T. Tang and Y. Hou, *Nanoscale*, 2017, **9**, DOI: 10.1039/C7NR00988G.
- 3 P. Cai, Y. Hong, S. Ci and Z. Wen, *Nanoscale*, 2016, **8**, 20048-20055.
- 4 J. Wei, Y. Hu, Z. Wu, Y. Liang, S. Leong, B. Kong, X. Zhang, D. Zhao, G. P. Simon and H. Wang, *J. Mater. Chem. A*, 2015, **3**, 16867-16873.
- 5 T. Zhou, Y. Du, S. Yin, X. Tian, H. Yang, X. Wang, B. Liu, H. Zheng, S. Qiao and R. Xu, *Energy Environ. Sci*, 2016, **9**, 2563-2570.

- 6 P. Yin, T. Yao, Y. Wu, L. Zheng, Y. Lin, W. Liu, H. Ju, J. Zhu, X. Hong, Z. Deng, G. Zhou, S. Wei and Y. Li, *Angew. Chem. Int. Ed.*, 2016, **55**, 10800-10805.