

Supplementary Information

Integrating Cobalt Phosphide and Cobalt Nitride-Embedded Nitrogen-Rich Nanocarbon: High-Performance Bifunctional Electrocatalysts for Oxygen Reduction and Evolution

Xing Zhong,^a Yu Jiang,^a Xianlang Chen,^a Lei Wang,^a Guilin Zhuang,^a Xiaonian Li^a
and Jian-guo Wang^{*a}

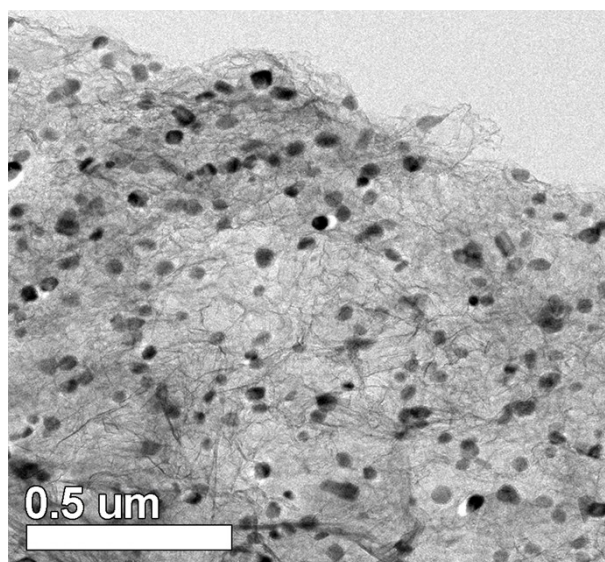


Fig. S1 TEM image of CoNP@NC/NG-700, Scale bar is 0.5 μm.

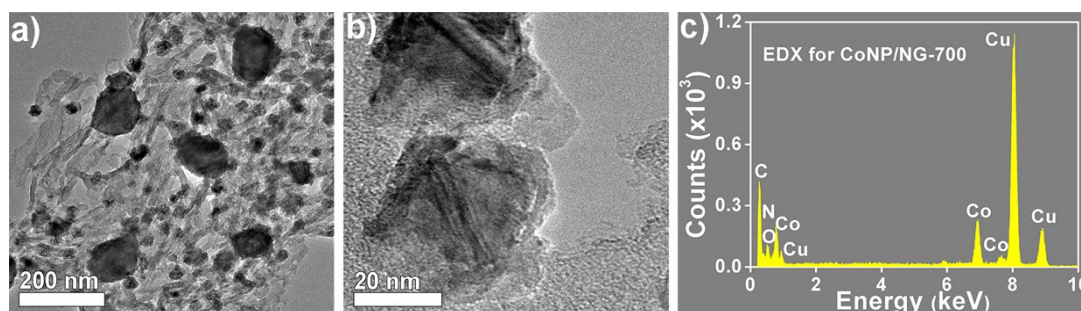


Fig. S2 (a) TEM image of CoNP/NG-700, Scale bar is 200 nm; (b) TEM image of CoNP/NG-700, Scale bar is 20 nm (c) EDX spectrum of a CoNP nanoparticle in CoNP/NG-700.

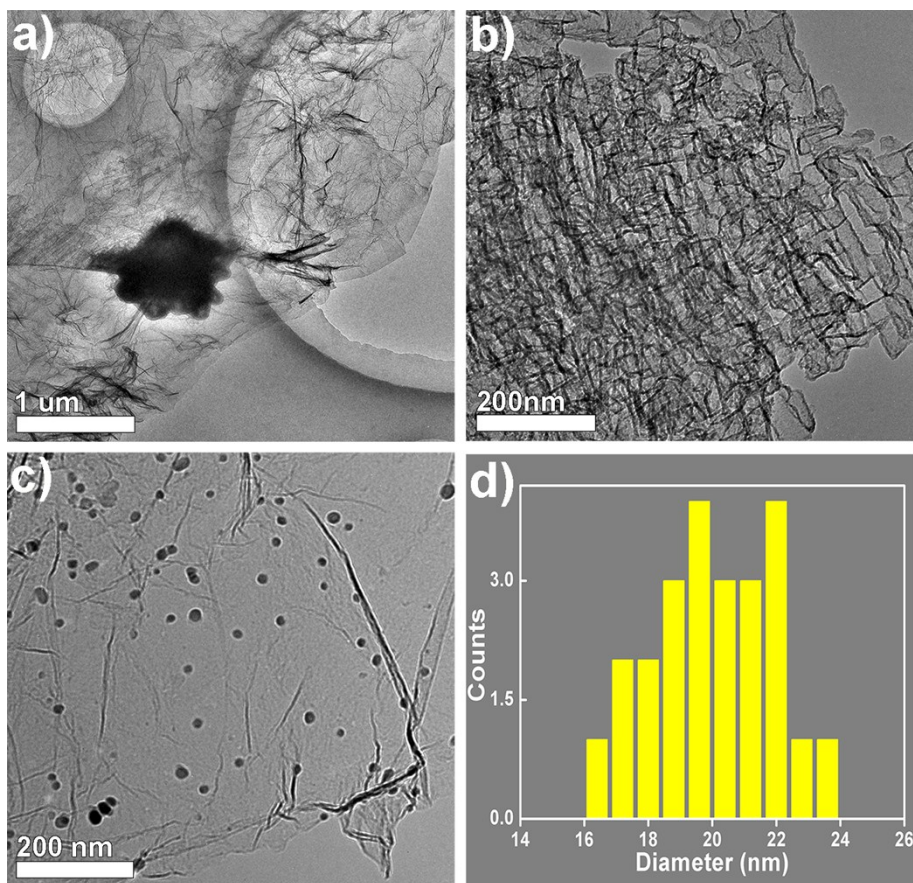


Fig. S3 (a) TEM image of CoNP@NC/NG-600, Scale bar is 1 μm; (b) TEM image of CoNP@NC/NG-800, Scale bar is 200 nm; (c) TEM image of CoNP@NC/NG-800, Scale bar is 200 nm (d) Particle size distribution of CoNP@NC/NG-800.

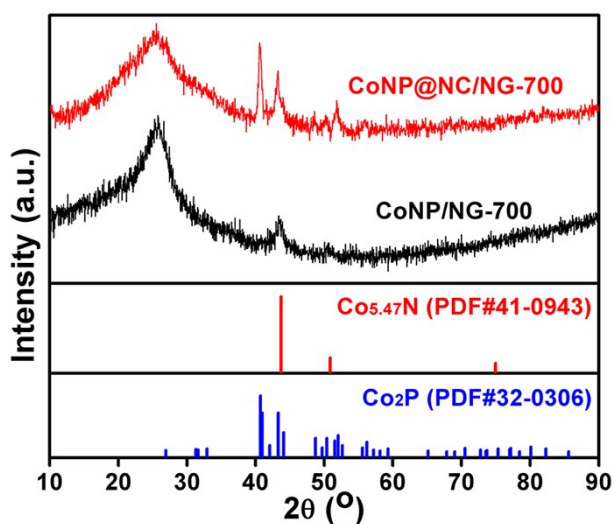


Fig. S4 XRD result of CoNP@NC/NG-700 and CoNP/NG-700.

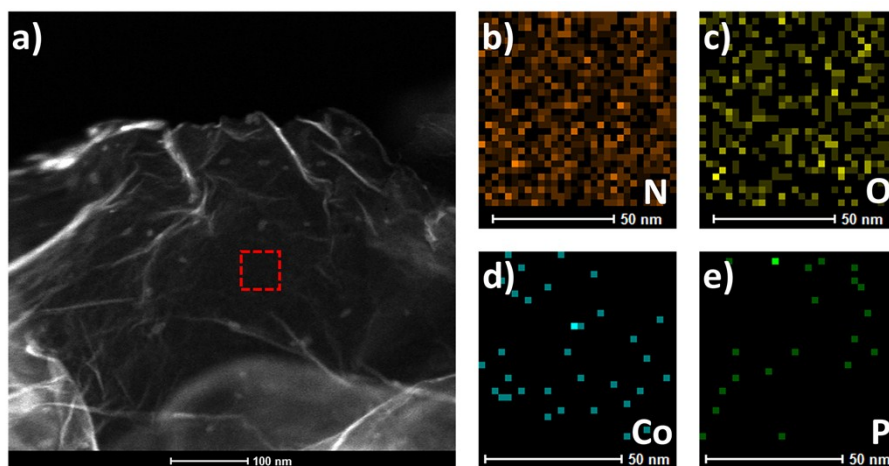


Fig. S5 (a) The TEM image of CoNP@NC/NG-700 with a scale bar of 100 nm, (b-e) The blank space EDS elemental mapping images of N, O, Co, and P.

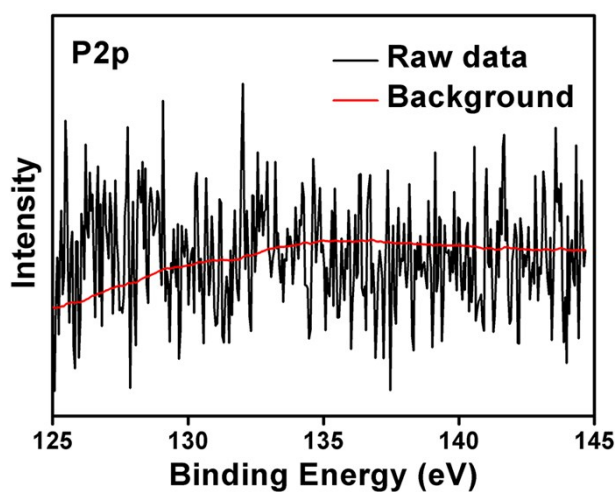


Fig. S6 XPS high-resolution scan of the P2p region of CoNP/NG-700.

Table S1. The calculated species concentrations (atomic %) of different atoms in CoNP@NC/NG-600, CoNP@NC/NG-700, CoNP@NC/NG-800 and CoNP/NG-700 based on XPS results.

Sample	C%	N%	O%	Co%	P%
CoNP@NC/NG-600	71.07	21.83	3.74	1.93	1.43
CoNP@NC/NG-700	77.01	9.74	8.83	1.98	2.44
CoNP@NC/NG-800	94.96	0.03	0.05	0.47	0.53
CoNP/NG-700	88.68	6.86	3.43	0.9	0.13

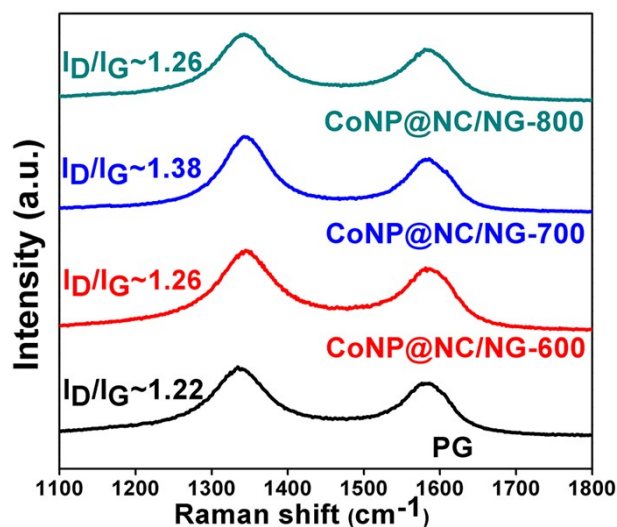


Fig. S7 Raman spectra measurements for PG and CoNP@NC/NG samples annealed at various temperature.

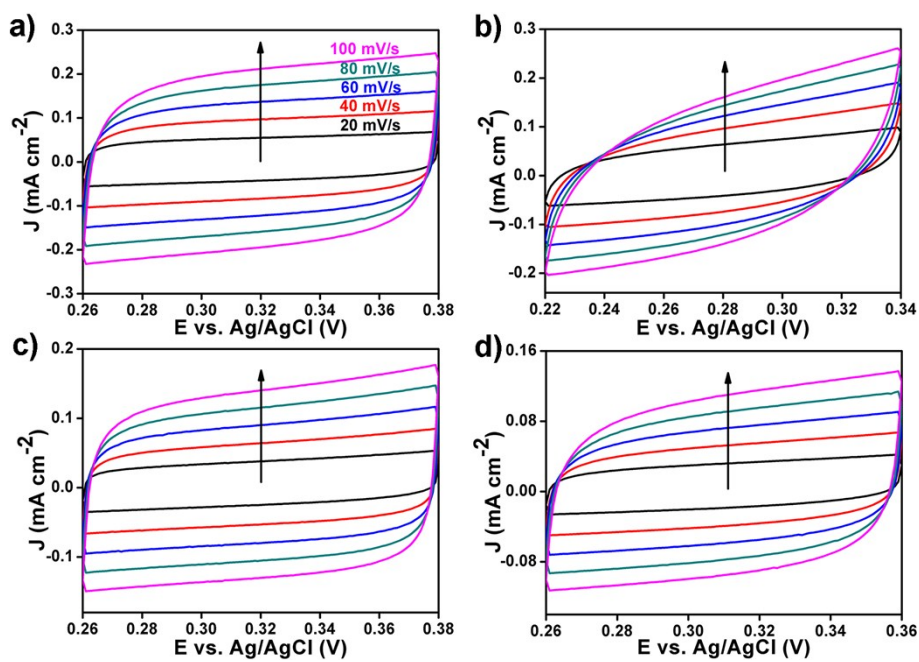


Fig. S8 Cyclic voltammetry results at various scan rate for (a) CoNP@NC/NG-700, (b) CoNP@NC/NG-600, (c) CoNP@NC/NG-800 and (d) CoNP@NC/NG-700.

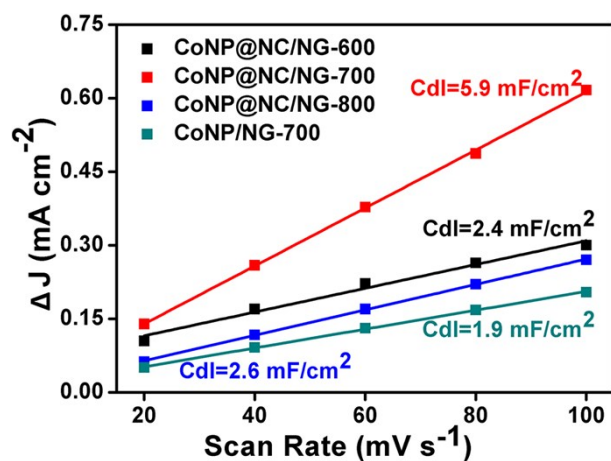


Fig. S9 Charging current density differences plotted against scan rates of CoNP@NC/NG-600, CoNP@NC/NG-700, CoNP@NC/NG-800 and CoNP/NG-700.

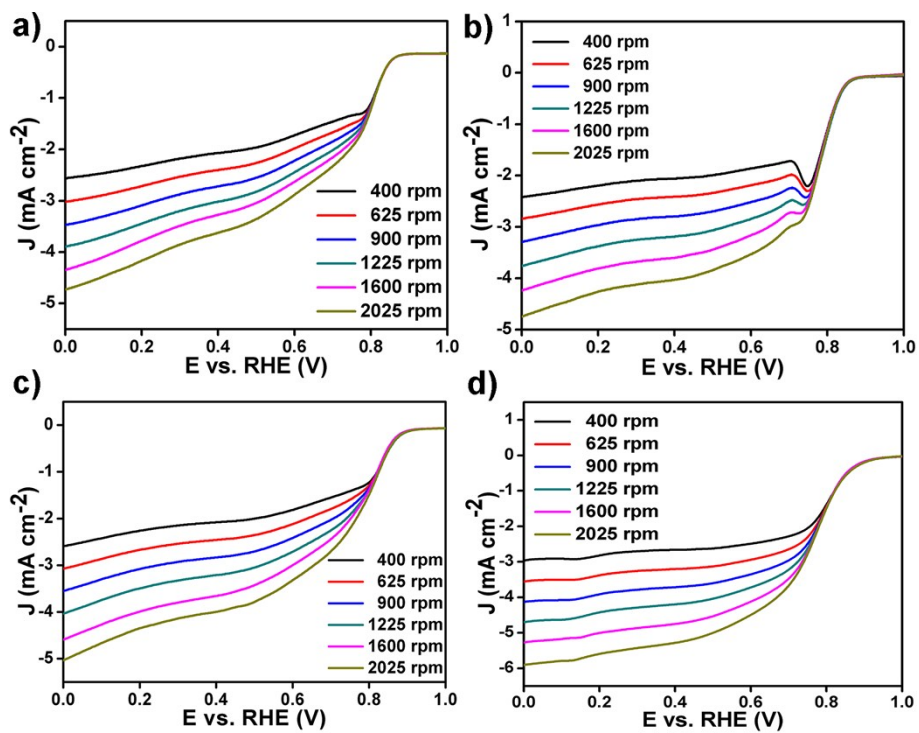


Fig. S10 A series of linear sweep voltammograms recorded from 400 to 2025 rpm for (a) CoNP@NC/NG-600, (b) CoNP@NC/NG-800, (c) CoNP/NG-700 and (d) Commercial 20 wt. % Pt/C.

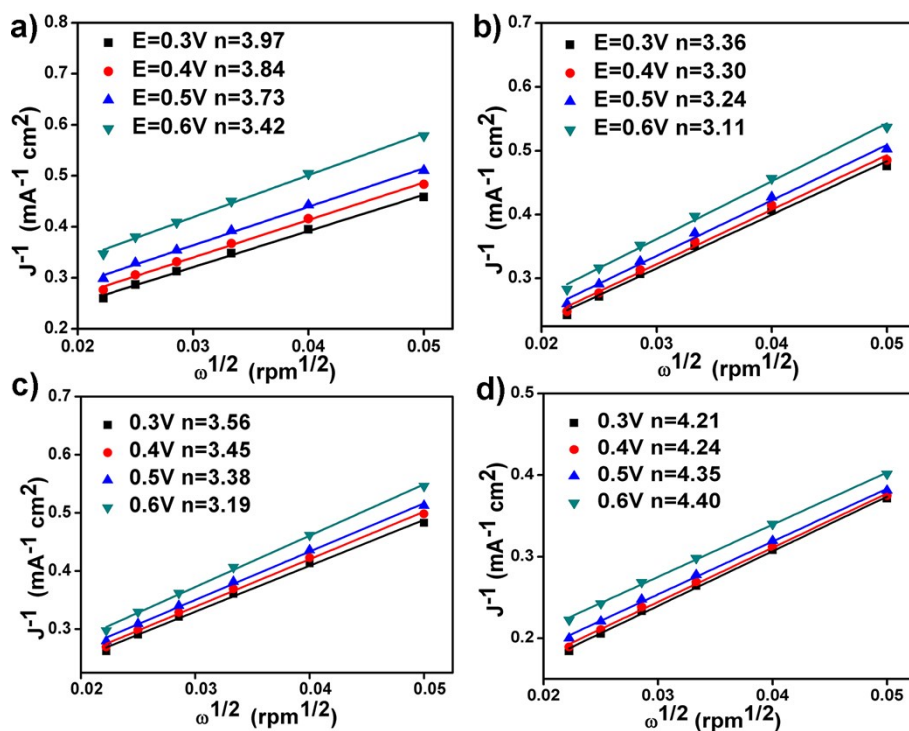


Fig. S11 The calculation results of overall electron transfer numbers for (a) CoNP@NC/NG-600, (b) CoNP@NC/NG-800, (c) CoNP/NG-700 and (d) Commercial 20 wt. % Pt/C.

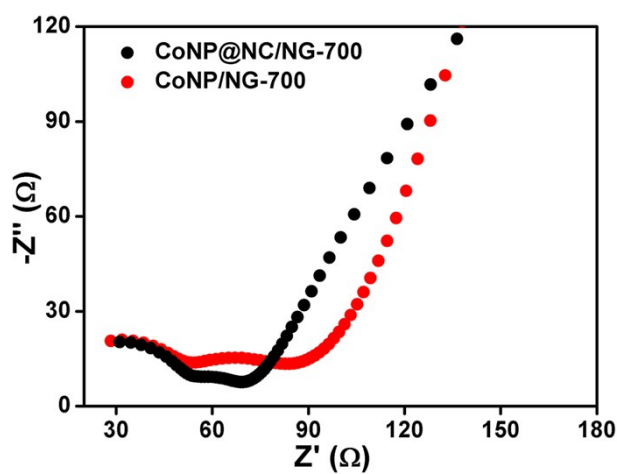


Fig. S12 EIS spectrum (recorded at 1.2 V vs. RHE) of CoNP@NC/NG-700 and CoNP/NG-700.

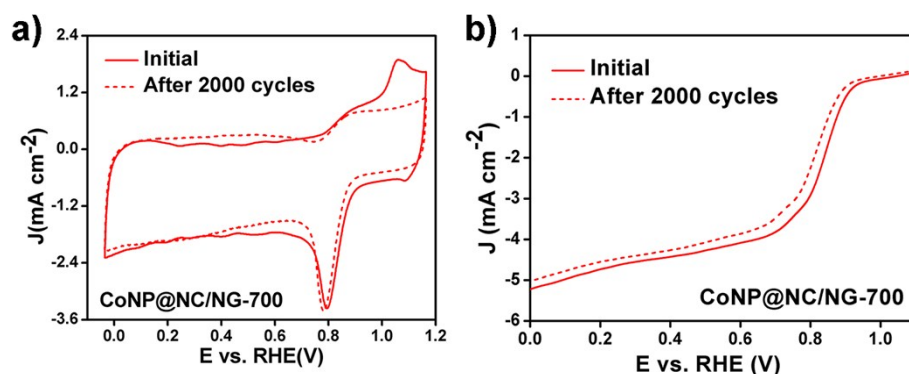


Fig. S13 (a) CVs and (b) LSVs of CoNP@NC/NG-700 before and after 2000 scan cycles between -1.0 to 0.2 V vs. Ag/AgCl.

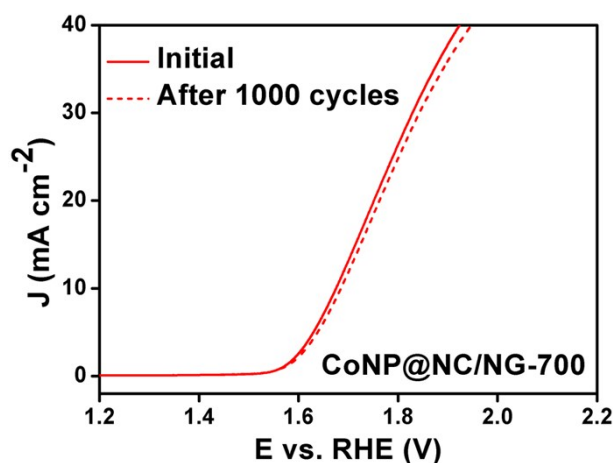


Fig. S14 LSVs of CoNP@NC/NG-700 before and after 1000 scan cycles between 0 to 1.2 V vs. Ag/AgCl.

Table S2: Catalytic activity of CoNP@NC/NG-700 compared to previous Co based materials from some other literatures with high catalytic activity in alkaline condition.

Materials	$E_{\text{onset,ORR}}$ (V)	E_{ORR} (V) at -3 mA cm^{-2}	E_{OER} (V) at 10 mA cm^{-2}	ΔE (V) $E_{\text{OER}} - E_{\text{ORR}}$	ref
CoNP@NC/NG-700	0.93	0.78	1.62	0.84	This work
20% Pt/C	0.93	0.74	1.95	1.21	Used in this work (Alfa Aesar)
20% Ru/C ¹		0.61	1.62	1.01	<i>J. Am. Chem. Soc.</i> 2010, 132, 13612-13614
20% Ir/C ¹		0.69	1.61	0.92	
Co/N-C-800 ²	0.83	0.74	1.60	0.86	<i>Nanoscale.</i> 2014, 6, 15080-15089
Co ₃ O ₄ /N-rmGO ³	0.88	0.85	1.54	0.69	<i>Nat. Mater.</i> 2011, 10, 780-786
NiCo ₂ S ₄ @N/S-rGO ⁴	0.85	0.72	1.70	0.98	<i>ACS Appl. Mater. Interfaces.</i> 2013, 5, 5002-5008

CNNT-ACN ⁵	0.93	/	1.68	/	<i>ACS Appl. Mater. Interfaces.</i> 2015, 7, 11991-12000
NiCo ₂ O ₄ /G ⁶	0.89	0.56	1.69	1.13	<i>J. Mater. Chem. A.</i> 2013, 1, 4754-4762
Co ₃ O ₄ /2.7Co ₂ MnO ₄ ⁷	0.90	0.68	1.77	1.09	<i>Nanoscale.</i> 2013, 5, 5312-5315
Ni _{0.6} Co _{2.4} O ₄ ⁸	0.88	0.80	1.76	0.96	<i>Chem. Commun.</i> 2015, 51, 9511-9514
N-graphene/CNT ⁹	0.88	0.69	1.65	0.96	<i>Angew. Chem., Int. Ed.</i> 2014, 53, 6496-6500
CCH-2/C ¹⁰	0.93	0.82	1.74	0.92	<i>Chem. Commun.</i> 2014, 50, 15529-15532
CoxSy@C-1000 ¹¹	0.92	/	1.70	/	<i>Nanoscale.</i> 2015, 7, 20674-20684

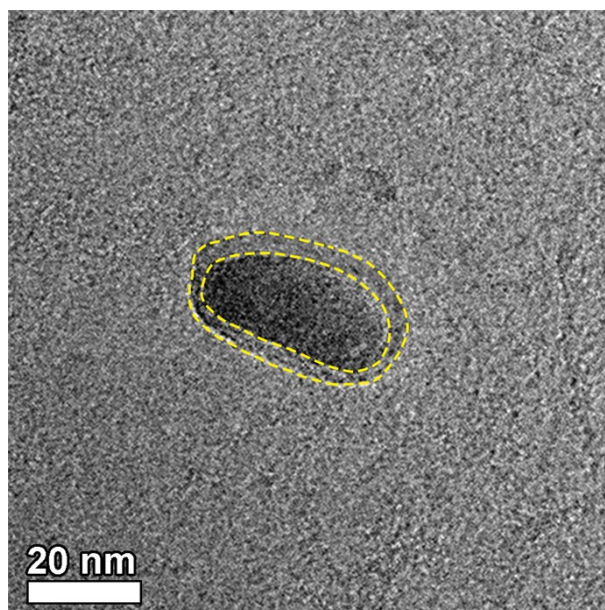


Fig S15 TEM image of CoNP@NC/NG-700 after 1000 scan cycles between 0 to 1.2 V vs. Ag/AgCl.

References

1. Y. Gorlin and T. F. Jaramillo, *J Am Chem Soc*, 2010, **132**, 13612-13614.
2. Y. H. Su, Y. H. Zhu, H. L. Jiang, J. H. Shen, X. L. Yang, W. J. Zou, J. D. Chen and C. Z. Li, *Nanoscale*, 2014, **6**, 15080-15089.
3. Y. Y. Liang, Y. G. Li, H. L. Wang, J. G. Zhou, J. Wang, T. Regier and H. J. Dai, *Nat Mater*, 2011, **10**, 780-786.
4. Q. Liu, J. T. Jin and J. Y. Zhang, *Acs Appl Mater Inter*, 2013, **5**, 5002-5008.
5. R. M. Yadav, J. J. Wu, R. Kochandra, L. L. Ma, C. S. Tiwary, L. H. Ge, G. L. Ye, R. Vajtai, J. Lou and P. M. Ajayan, *Acs Appl Mater Inter*, 2015, **7**, 11991-12000.

6. D. U. Lee, B. J. Kim and Z. W. Chen, *J Mater Chem A*, 2013, **1**, 4754-4762.
7. D. D. Wang, X. Chen, D. G. Evans and W. S. Yang, *Nanoscale*, 2013, **5**, 5312-5315.
8. T. N. Lambert, J. A. Vigil, S. E. White, D. J. Davis, S. J. Limmer, P. D. Burton, E. N. Coker, T. E. Beechem and M. T. Brumbach, *Chem Commun*, 2015, **51**, 9511-9514.
9. Z. H. Wen, S. Q. Ci, Y. Hou and J. H. Chen, *Angew Chem Int Edit*, 2014, **53**, 6496-6500.
10. Y. Wang, W. Ding, S. G. Chen, Y. Nie, K. Xiong and Z. D. Wei, *Chem Commun*, 2014, **50**, 15529-15532.
11. B. L. Chen, R. Li, G. P. Ma, X. L. Gou, Y. Q. Zhu and Y. D. Xia, *Nanoscale*, 2015, **7**, 20674-20684.