

Porous Cobalt, Nitrogen-Codoped Carbon Nanostructures from Carbon Quantum Dots and VB12 and Their Catalytic Properties for Oxygen Reduction

Supporting Information

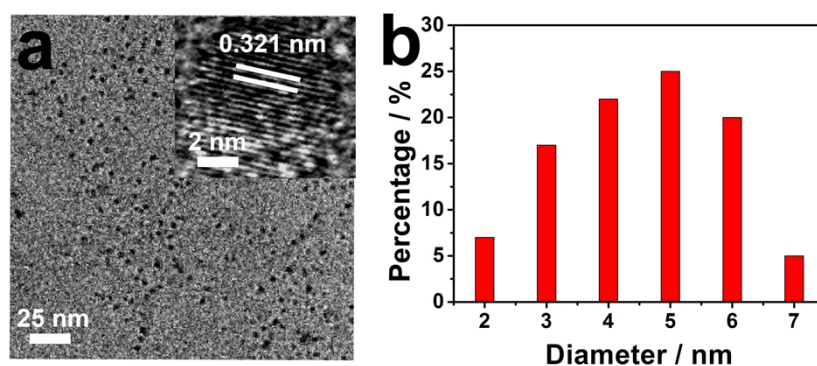


Fig. S1 (a) TEM image of CQDs. Inset is the HRTEM image of a single CQDs. (b) The particle size distribution of CQDs.

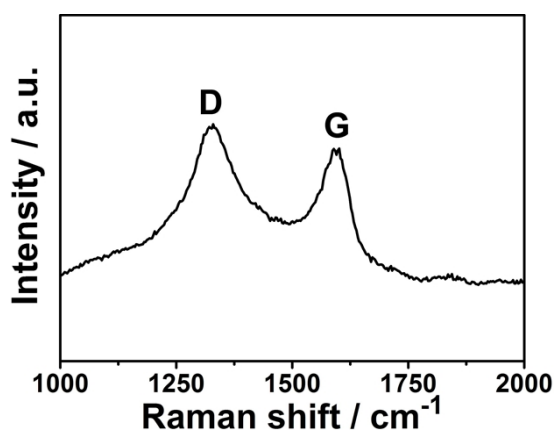


Fig. S2 Raman spectrum of CQDs.

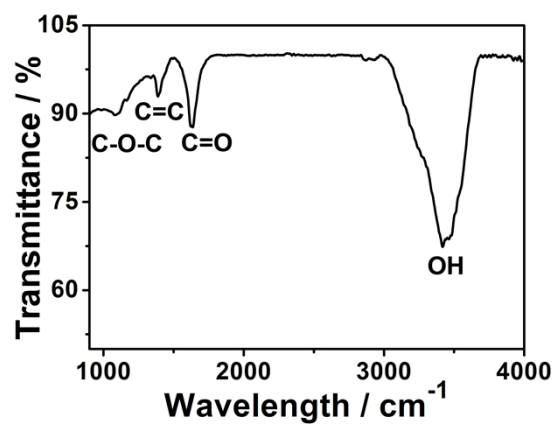


Fig. S3 FTIR spectrum of CQDs.

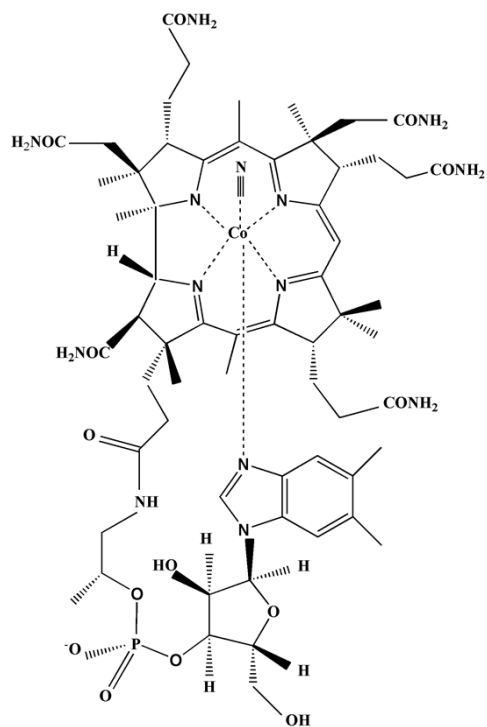


Fig. S4 The molecular structure of VB12.

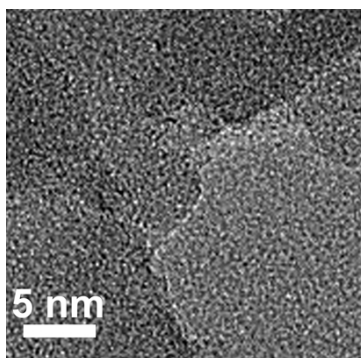


Fig. S5 TEM image of pyrolyzed VB12 at 700 °C for 4h.

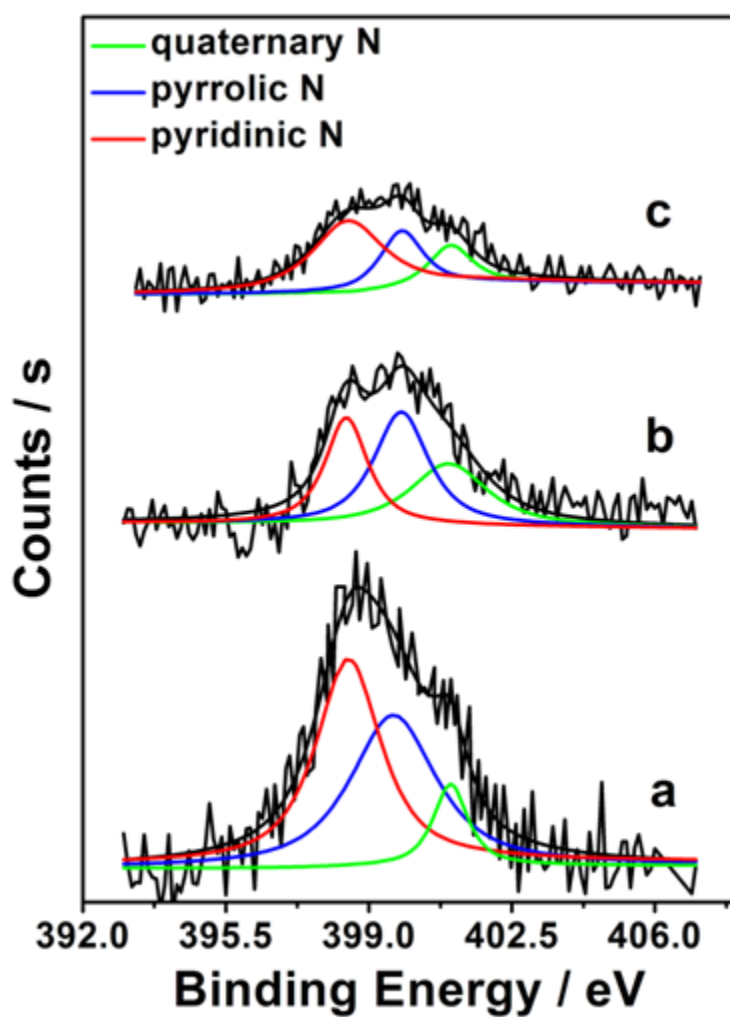


Fig. S6 The high resolution N1s spectrum of (a) $\text{Co}_{1.23}/\text{N}_{3.05}/\text{C-500}$, (b) $\text{Co}_{1.12}/\text{N}_{2.92}/\text{C-700}$ and (c) $\text{Co}_{1.03}/\text{N}_{2.79}/\text{C-900}$.

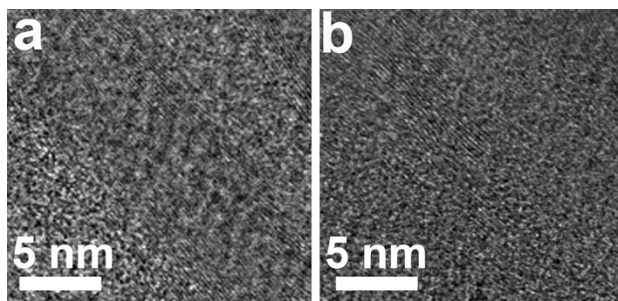


Fig. S7 TEM images of (a) $\text{Co}_{1.23}/\text{N}_{3.05}/\text{C-500}$ and (b) $\text{Co}_{1.03}/\text{N}_{2.79}/\text{C-900}$.

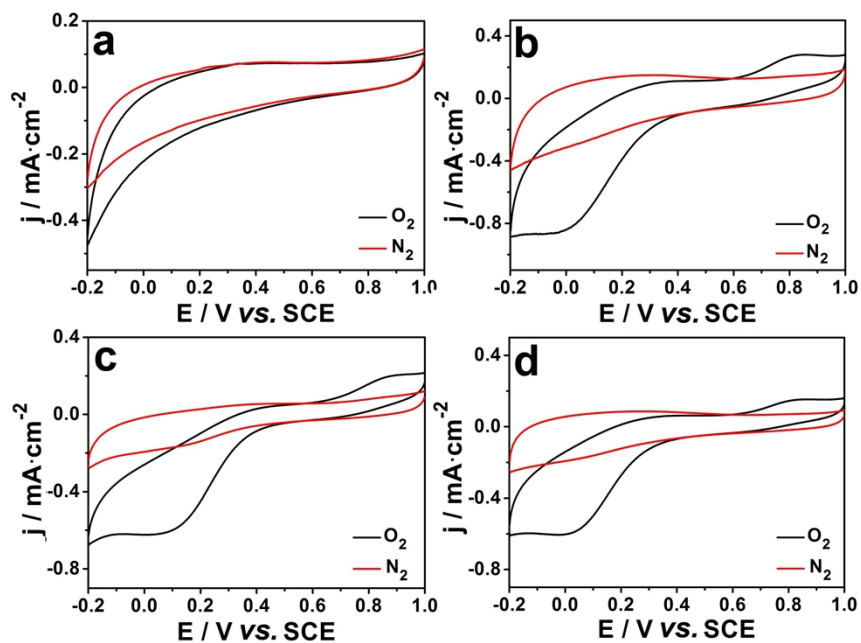


Fig. S8 CVs of (a) $\text{Co}_0/\text{N}_0/\text{C}$, (b) $\text{Co}_{0.68}/\text{N}_{1.22}/\text{C}$, (c) $\text{Co}_{1.87}/\text{N}_{5.02}/\text{C}$ and (d) $\text{Co}_{3.68}/\text{N}_{5.88}/\text{C}$ in 0.1 M HClO_4 solution saturated with N_2 (red line) and O_2 (black line) at a scan rate of $50 \text{ mV} \cdot \text{s}^{-1}$.

Table S1 Finely tuned contents for Co and N.

Entry	CQDs:VB12 [mg/mg]	Raw materials:Products for Co concentration	Raw materials:Products for N concentration
1	1:0	0:0	0:0
2	9:1	0.435:0.68	1.45:1.22
3	4:1	0.87:1.12	2.89:2.92
4	1:1	2.175:1.87	7.23:5.02
5	0:1	4.35:3.68	14.46:5.88

Table S2 Deconvolution results (at%) for N 1s high-resolution spectra. Compared with other samples, the Co_{1.12}/N_{2.92}/C-700 possesses the highest levels of quaternary nitrogen content.

Sample	Pyridinic (398.5 eV)	Pyrrolic (399.8 eV)	Quaternary (401 eV)
Co _{1.23} /N _{3.05} /C-500	1.8	1.6	0.9
Co _{1.12} /N _{2.92} /C-700	1.2	1.7	1.3
Co _{1.03} /N _{2.79} /C-900	1.7	0.8	0.5
Co ₀ /N ₀ /C-700	---	---	---
Co _{0.68} /N _{1.22} /C-700	0.6	0.5	0.8
Co _{1.87} /N _{5.02} /C-700	1.8	1.9	1.1
Co _{3.68} /N _{5.88} /C-700	2.3	2.1	1.1

Table S3 The Co, N concentrations and BET area of the samples prepared at 500 and 900 °C.

Entry	Temperature [°C]	Co concentration [%]	N concentration [%]	BET area [m ² ·g ⁻¹]
1	500	1.23	3.05	137.51
2	900	1.03	2.79	142.38

Table S4 The peak current density of ORR in 0.1 M KOH and HClO₄ solution saturated with O₂ at the scan rate of 50 mV·s⁻¹.

Sample	Peak current density (mA·cm ⁻¹)	
	Alkaline	Acid
Co ₀ /N ₀ /C	0.46	—
Co _{0.68} /N _{1.22} /C	0.39	0.87
Co _{1.12} /N _{2.92} /C	0.57	1.11
Co _{1.87} /N _{5.02} /C	0.55	0.64
Co _{3.68} /N _{5.88} /C	0.23	0.61

Table S5 Various electrocatalysts for oxygen reduction reaction.

Electrocatalyst	Peak potential (vs. RHE)	Pyrolysis temperature	Literature
	[V]	[°C]	
Co-N-GN	0.781	---	S1
Co/N/rGO(NH ₃)	0.626	850	S2
Co/N/C	0.756	800	S3
N-CoO	0.486	---	S4
700°C/GC	0.776	700	S5
Co-N-C	0.766	900	S6
Co-PPy/BP	0.809	---	S7
Co/N/C	0.844	700	Our work

References

- S1 S. Jiang, C. Zhu, S. Dong, *J. Mater. Chem. A*, 2013, **1**, 3593.
- S2 K. Niu, B. Yang, J. Cui, J. Jin, X. Fu, Q. Zhao, J. Zhang, *J. Power Sources*, 2013, **243**, 65.
- S3 L. Wang, L. Zhang, L. Bai, L. Han, S. Dong, *Electrochem. Commun.*, 2013, **34**, 68.
- S4 H. Yu, Y. Li, X. Li, L. Fan, S. Yang, *Chem. Eur. J.*, 2014, **20**, 3457.
- S5 A. Pacuła, K. Ikeda, T. Masuda, K. Uosaki, *J. Power Sources*, 2012, **220**, 20.
- S6 Y. Zhai, C. Zhu, E. Wang, S. Dong, *Nanoscale*, 2014, **6**, 2964.
- S7 Z. Li, Z. Liu, K. Zhu, Z. Li, B. Liu, *J. Power Sources*, 2012, **219**, 163.