

Supporting Information for

Cobalt-Nitrogen Complex on N-doped Three-Dimensional Graphene framework as Highly Efficient Electrocatalysts for Oxygen Reduction Reaction

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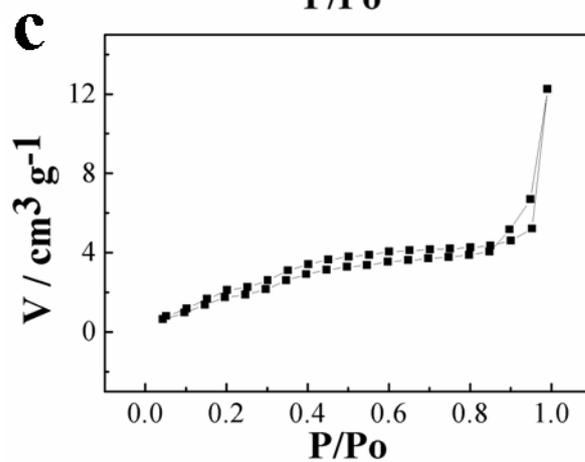
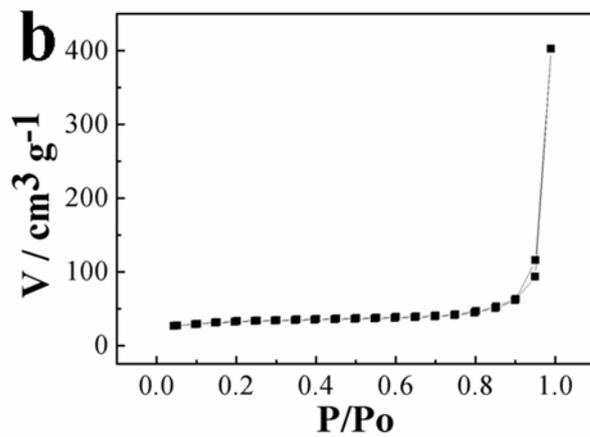
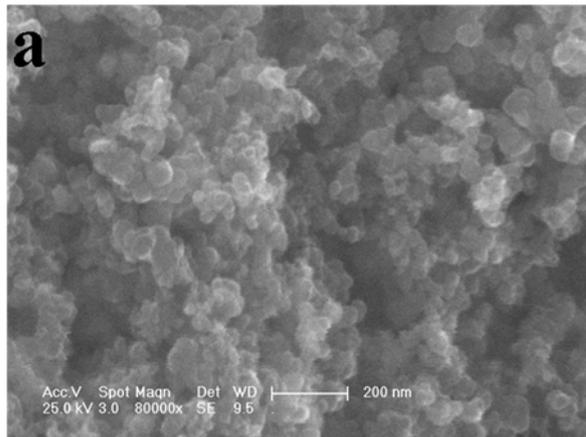


Figure S1. (a) SEM image of pyrolyzed VB12/C. (b) N₂ adsorption and desorption isotherms of pyrolyzed VB12/C. (c) N₂ adsorption and desorption isotherms of graphene prepared by a similar process as the g-VB12. The graphene prepared by this method has a BET surface area of 102 m² g⁻¹, close to that of some similar structure^{1,2}.

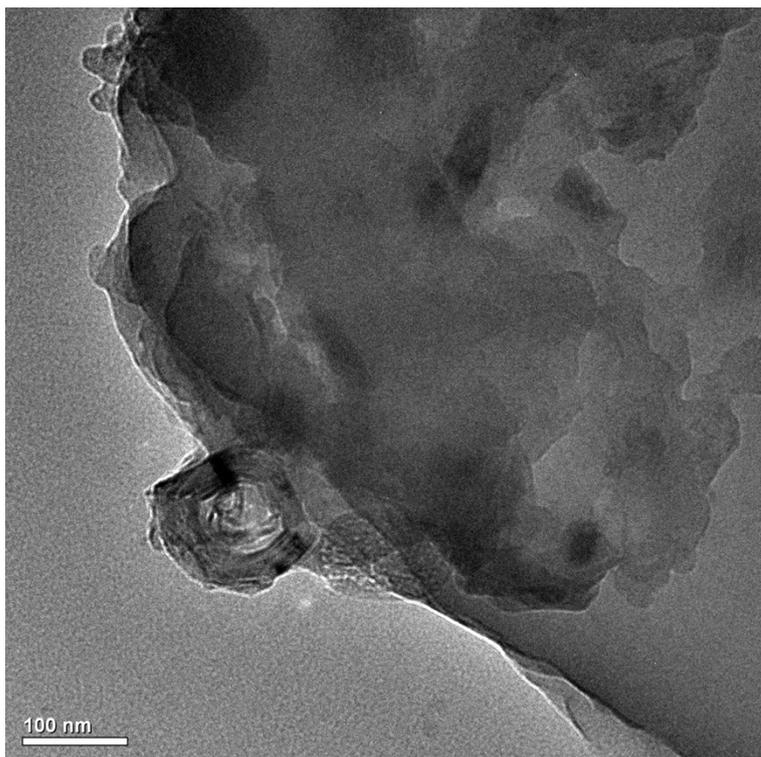


Figure S2. HRTEM image of g-VB12.

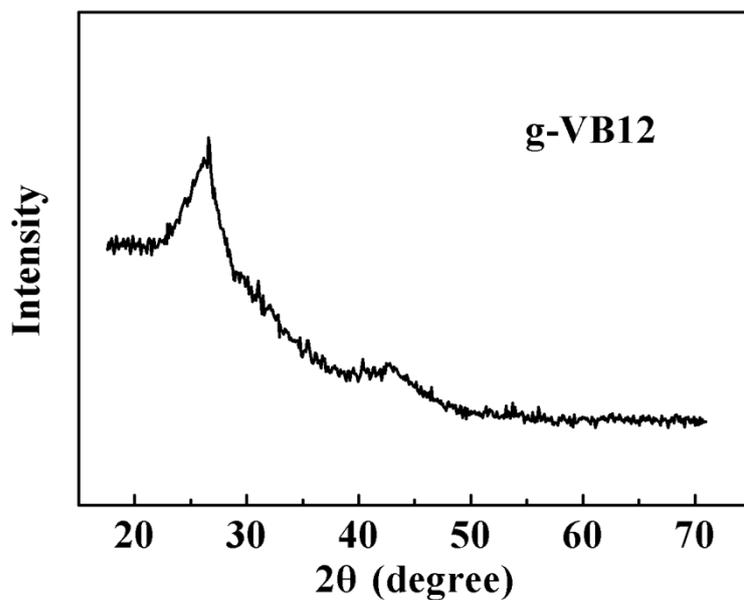


Figure S3. XRD pattern of g-VB12 catalyst. Only two obvious peaks centered at 26.2 and 42.7 are found, corresponding to the (002) and (100) planes of graphene materials. No information of crystalline Co/Co oxide phase was found, indicating that the Co element in the composite exists as coordinated state, not as nanocrystal phase.

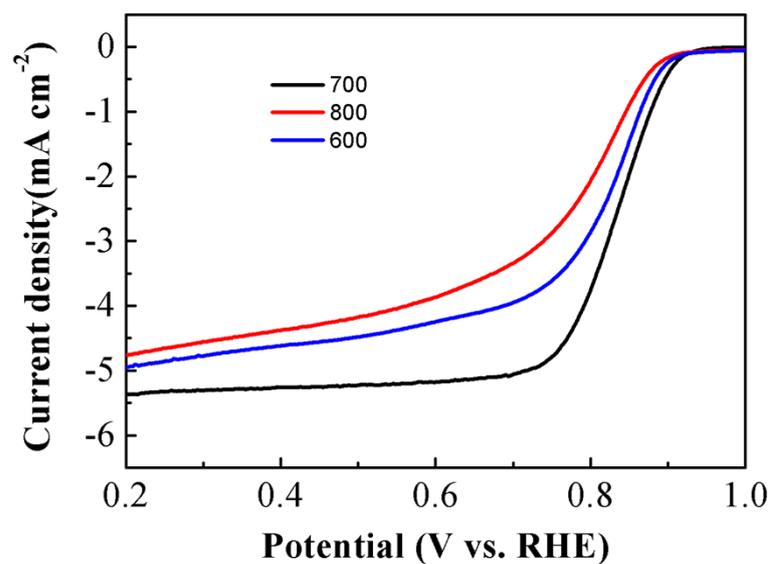


Figure S4. ORR polarization curves of g-VB12 catalyst in O₂-saturated 0.1 M KOH electrolyte as a function of the heat treatment temperature (°C).

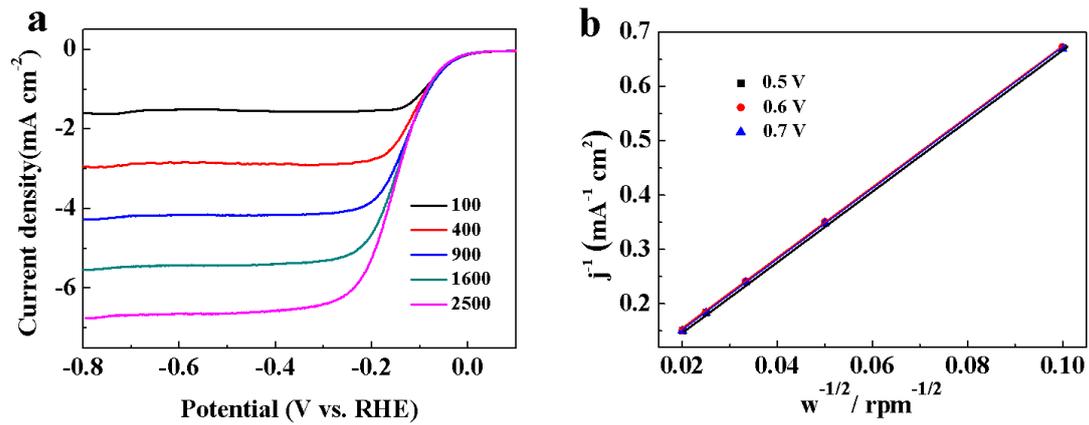


Figure S5. (a) ORR polarization curves for Pt/C catalyst at different rotation rates. (b) Koutecky-Levich plot for Pt/C catalyst at different potentials.

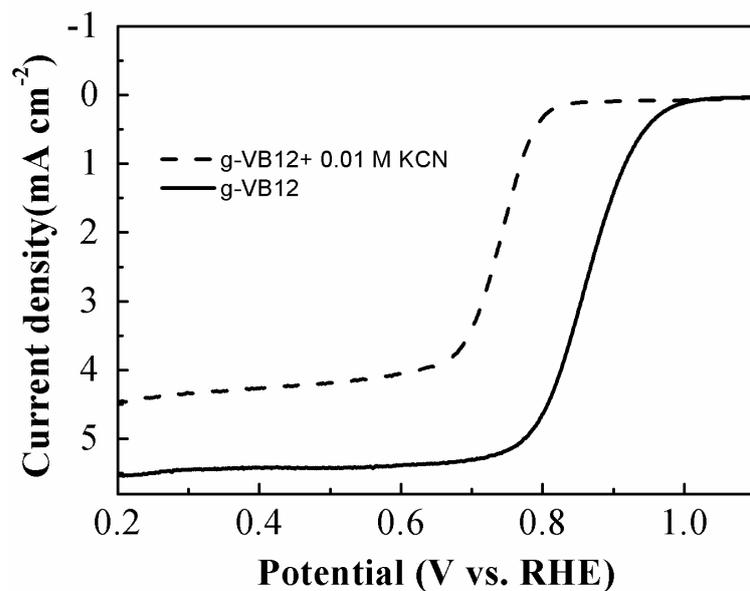


Figure S6. ORR polarization curves of g-VB12 catalyst in O₂-saturated 0.1 M KOH electrolyte with (dashed lines) and without (solid lines) 10 mM CN⁻.

Table S1 EDX analysis of g-VB12 and VB12/C¹

Sample	Elemental Content (atom %)				
	C	O	N	Co	N/Co
g-VB12	75.66	10.13	12.36	1.85	6.68
VB12/C	91.76	2.76	4.50	0.99	4.54

¹ The results of elemental content were obtained from average value of three parallel measurements. The information of trace fluorine (from the Nafion dispersion) and phosphorus were not monitored for they had no influence to the ORR electrocatalytic performance.

Table S2 Comparison of this work with previous top reports in the alkaline system

References	Materials	Onset potential	Half-wave potential	Electron transfer number
This study	Co-N-doped 3D mesoporous graphene	0.925 V	0.833 V	Above 3.92 (0.2 -0.8 V)
Nature Nanotech. 2012,7(6),394-400	Carbon nanotube-graphene complexes	>1.05 V	~0.87 V	
Nature Mater. 2011, 10(10), 780-786	Co ₃ O ₄ nanocrystals on N-doped graphene	0.88 V	0.83 V	3.9 (0.60-0.75 V)
Adv. Funct. Mater. 2012, 22(21), 4584-4591	MnO-mesoporous N-doped carbon	~0.94 V	0.81 V	3.84 (0.45-0.65 V)
J. Am. Chem. Soc. 2012, 134(38), 15849-15857	CoO/N-doped CNT	0.93 V	~0.85 V	3.8-3.9 (0.45-0.75 V)

- 1 Z.S. Wu, S.B. Yang, Y. Sun, K. Parvez, X.L. Feng, and K. Mullen, 3D Nitrogen-Doped Graphene Aerogel-Supported Fe₃O₄ Nanoparticles as Efficient Eletrocatalysts for the Oxygen Reduction Reaction. *J. Am. Chem. Soc.*, **2012** (22): 9082-9085.
- 2 R. Zhang, Y. Cao, P. Li, X. Zang, P. Sun, K. Wang, M. Zhong, J. Wei, D. Wu, F. Kang, and H. Zhu, Three-dimensional porous graphene sponges assembled with the combination of surfactant and freeze-drying. *Nano Research*, **2014** 1-11.