

Supporting Information

Synthesis of B-doped graphene quantum dots as metal-free electrocatalyst for oxygen reduction reaction

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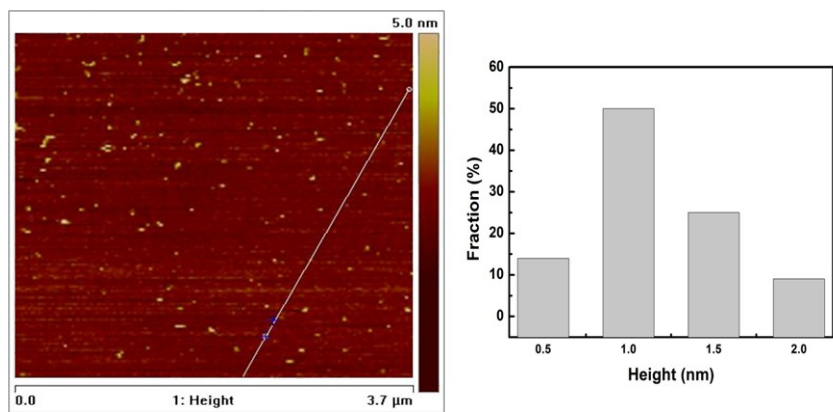


Fig. S1 AFM image of BGQD on mica substrate and its height distribution.

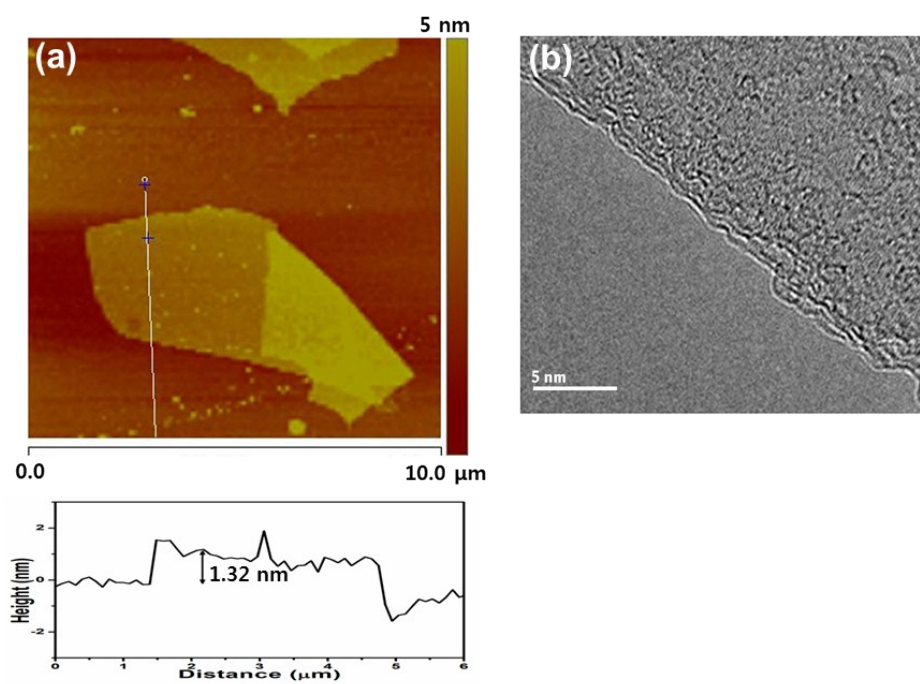


Fig. S2 AFM and TEM images of G-BGQD composite.

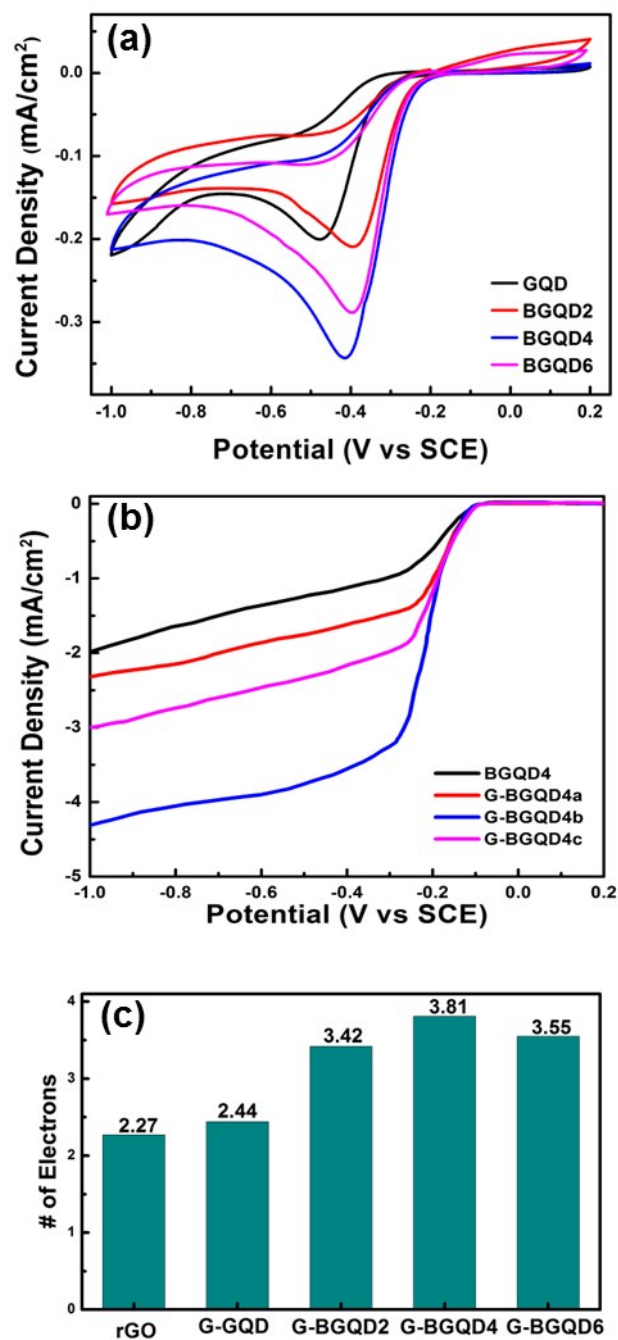


Fig. S3 (a) Cyclic voltammogram of different BGQD at a scan rate of 10 mV s^{-1} . (b) LSV curves of various concentrations of graphene in G-BGQD composites. The 40 mL GO solution of 0.2, 0.5 and 1.0 mg/mL was mixed with the 20 mL BGQD4 solution (0.03 mg/mL) for G-BGQD4a, G-BGQD4b and G-BGQD4c, respectively. (c) The electron transfer number (n) for different G-BGQD composites at -0.8 V.

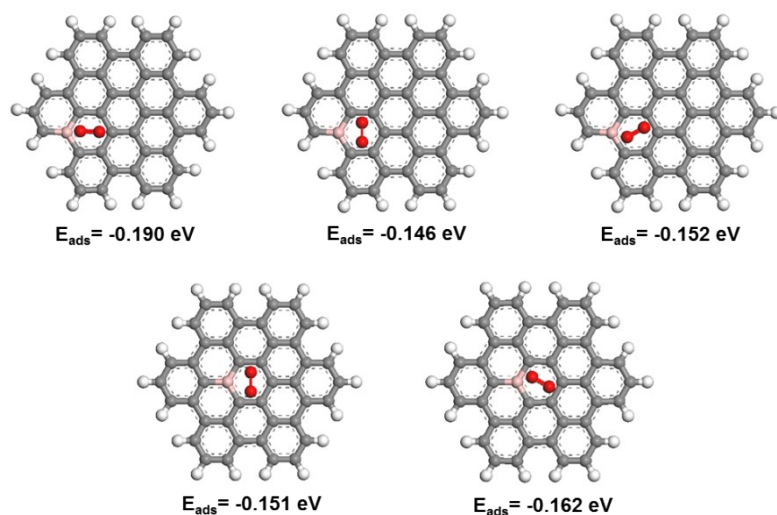


Fig. S4 Different optimized structures of O_2 adsorption on BC_3 bond structure in BGQD.

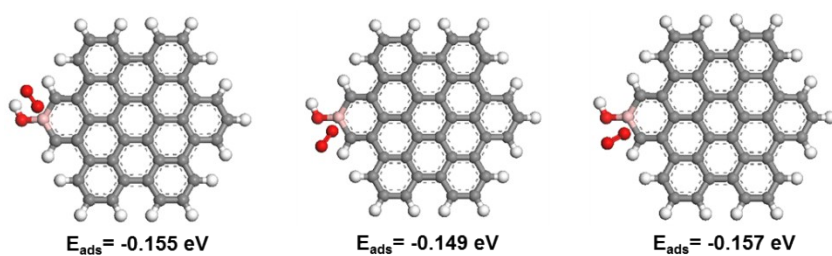


Fig. S5 Different optimized structures of O_2 adsorption on BC_2O bond structure in BGQD.

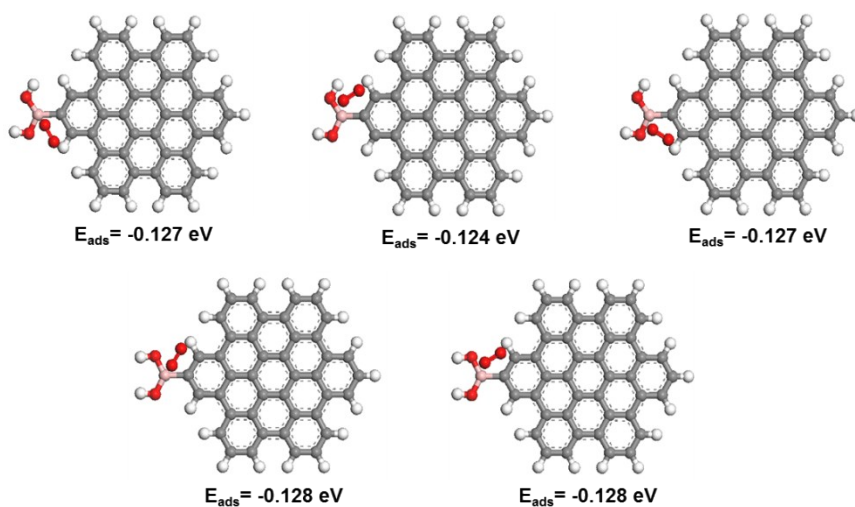


Fig. S6 Different optimized structures of O_2 adsorption on BCO_2 bond structure in BGQD.

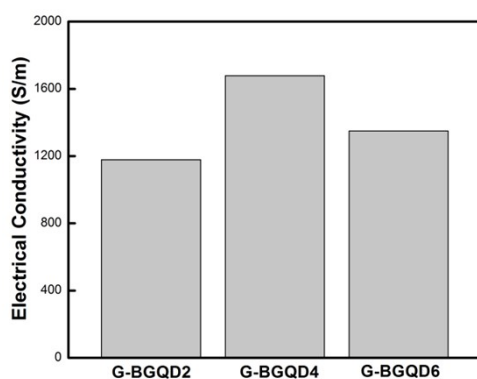
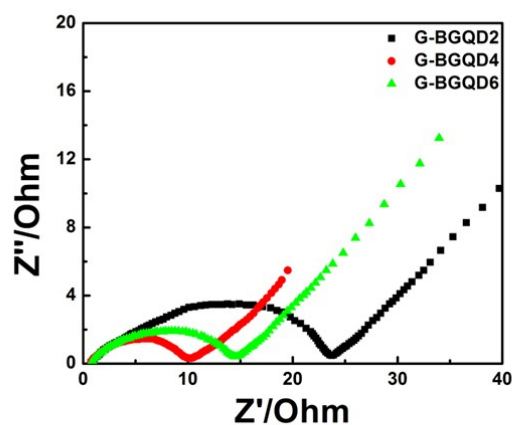


Fig. S7 The electric conductivity of different G-BGQD composites.



Sample	R_s (Ω)	R_{ct} (Ω)	CPE (μF)	Z_w (Ω^{-1})
G-BGQD2	0.996	23.62	13.5	0.135
G-BGQD4	0.758	9.236	15.38	0.0675
G-BGQD6	0.876	14.342	15.08	0.09

Fig. S8 Nyquist plots of different G-BGQD composites and the fitted parameters from the Nyquist plots. The inset (top) is the equivalent circuit used to fit the EIS spectra. In the circuit, the R_s represents the resistance of electrolyte solution, R_{ct} is charge-transfer resistance of catalyst, CPE is a constant phase element and Z_w is the Warburg diffusion impedance.

Table S1 Summary of the reported ORR performance of doped carbon materials

Catalyst	Synthesis method (precursors)	Doped carbon		Pt/C		Ref
		E_{onset} (V vs. Ag/AgCl)	# of electron	E_{onset} (V vs. Ag/AgCl)	# of electron	
G-BGQD	Hydrothermal reaction (glucose, boric acid)	-0.005	3.81	-0.035	3.91	<i>This work</i>
B-doped carbon	Thermal treatment (tetraphenylboron sodium)	-0.20	3.73	-0.05	-	s1
B-doped graphene	Thermal treatment (graphene oxide, boron oxide)	-0.05	3.7	> -0.05	-	s2
B-doped mesoporous carbon	Thermal treatment (sucrose, 4-hydroxyphenylboronic acid)	-0.16	3.86	-0.07	4	s3
B-N-doped GQDs	Thermal treatment (graphene oxide, boric acid, ammonia)	~0	3.93	~0	4	s4
B-N-doped graphene ribbon	Thermal treatment (graphene oxide, boric acid, ammonia)	0.1	3.89	~-0.5	3.91	s5
B-doped hollow carbon spheres	Hydrothermal, thermal treatment (resorcinol, 4-hydroxyphenylboronic acid)	-0.101	3.7	-0.09	3.9	s6
N-doped GQDs/graphene	Electrochemical reaction (graphene oxide, tetrabutylammonium perchlorate)	-0.16	3.6~4.4	-	-	s7
N-doped carbon nanoparticles/carbon nanofiber	Plasma, thermal treatment (2-cyanopyridine)	-0.14	3.2~3.5	-0.08	3.74~3.95	s8
N-doped carbon nanocages	Thermal treatment (Magnesium carbonate, pyridine)	-0.13	3.27	-0.03	3.92	s9
N-doped graphene	Oxidation, chemical treatment (graphite mesh, 4-aminobenzoic acid)	-0.13	3.2~3.5	-	-	s10

References

- [s1] G. Jo and S. Shanmugam, *Electrochem. Commun.*, 2012, 25, 101-104.
- [s2] Z. H. Sheng, H. L. Gao, W. J. Bao, F. B. Wang and X. H. Xia, *J. Mater. Chem.*, 2012, 22, 390-395.
- [s3] X. J. Bo and L. P. Guo, *Phys. Chem. Chem. Phys.*, 2013, 15, 2459-2465.
- [s4] H. Fei, R. Ye, G. Ye, Y. Gong, Z. Peng, X. Fan, E. L. G. Samuel, P. M. Ajayan and J. M. Tour, *ACS Nano*, 2014, 8, 10837-43
- [s5] Y. Gong, H. Fei, X. Zou, W. Zhou, S. Yang and G. Ye, et al. *Chem. Mater.*, 2015, 27, 1181-1186.
- [s6] H. J. Lu, Y. Li, L. Q. Zhang, H. N. Li, Z. X. Zhou, A. R. Liu, Y. J. Zhang and S. Q. Liu, *RSC Adv.* 2015, 5, 52126-52131.
- [s7] Y. Li, Y. Zhao, H. Cheng, Y. Hu, G. Shi, L. Dai and L. Qu, *J. Am. Chem. Soc.*, 2012, 134, 15-18.

[s8] G. Panomsuwan, N. Saito and T. Ishizaki, *ACS Appl. Mater. Interfaces*, 2016, 8, 6962-6971.

[s9] S. Chen, J. Bi, Y. Zhao, L. Yang, C. Zhang, Y. Ma, Q. Wu, X. Wang and Z. Hu, *Adv. Mater.*, 2012, 24, 5593-5597

[s10] I. Y. Jeon, D. Yu, S. Y. Bae, H. J. Choi, D. W. Chang, L. Dai and J. B. Baek, *Chem. Mater.*, 2011, 23, 3987-3992