

Supplementary information for

**Plasma Modified BiOCl/Sulfonated Graphene Microspheres as Efficient
Photoelectric Catalyst for Oxygen Evolution Reaction**

Miao Lv ^a, Shengming Jin ^a, Hui Wang ^a, Yumo Chen ^a, Ting Ma ^a, Kuixin Cui ^a, Junzhi Li ^a, Song
Wu ^a, Zhan Liu ^a, Yanru Guo ^b, Zhiliang Liu ^c, Xinghua Chang^{*a} and Xingguo Li^{*b}

^a Hunan Key Lab of Mineral Materials and Application, School of Minerals Processing and
Bioengineering, Central South University, Changsha 410083, PR China

^b Beijing National Laboratory for Molecular Sciences (BNLMS), The State Key Laboratory of Rare
Earth Materials Chemistry and Applications, College of Chemistry and Molecular Engineering,
Peking University, Beijing 100871, PR China

^c Key Laboratory of Superlight Materials and Surface Technology, Ministry of Education, College
of Material Science and Chemical Engineering, Harbin Engineering University, Harbin, 150001,
PR China

*Corresponding author: changxinghua@csu.edu.cn; xgli@pku.edu.cn

Metal element	Bi	Mn	Fe	Co	Ni
Atomic number	83	25	26	27	28
Valence electron configuration	$6s^2 6p^3$	$3d^5 4s^2$	$3d^6 4s^2$	$3d^7 4s^2$	$3d^8 4s^2$
radioactivity	Weak radioactivity, 1.9×10^{19} years	Some isotopes such as Mn-54 is radioactive	No radioactive	Some isotopes such as Co-60, Co-58 and Co-57 are radioactive	No radioactive
properties	Heaviest, most stable, most non-toxic	Ingestion cause neurological damage	Excessive ingestion cause iron poisoning	Expensive, cobalt and cobalt compounds cause cancer	The most common sensitizing metal

Table S1 Comparison of Bismuth with several transition metals

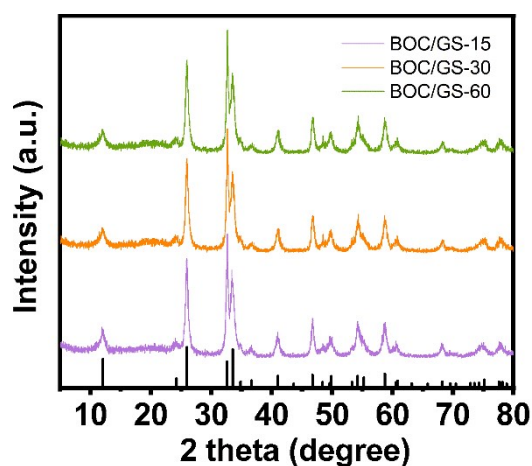


Figure S1. X-ray diffraction (XRD) patterns of BOC/GS-15, BOC/GS-30 and BOC/GS-60.

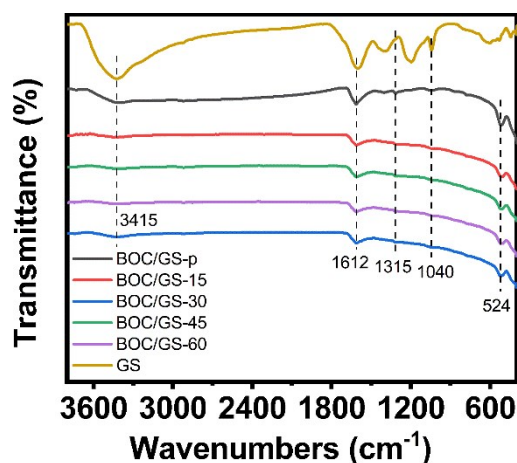


Figure S2. FTIR spectra of all samples.

Changes of functional groups on sulfonated graphene were identified by the FTIR spectrum in **Figure S2**. All the samples had absorption bands at 524, 1040, 1315, 1612 and 3415 cm^{-1} , which representing the Bi-O stretching vibration, $-\text{SO}_3$ stretching vibration, $\text{O}=\text{S}=\text{O}$ stretching vibration, $\text{C}=\text{C}$ of the unsaturated sp^2 hybrid and O-H stretching vibration in the sulfonic acid group ($-\text{SO}_3\text{H}$), were characteristic peaks of BiOCl and sulfonated graphene.¹⁻³ Therefore, the plasma treatment did not change the functional groups of GS.

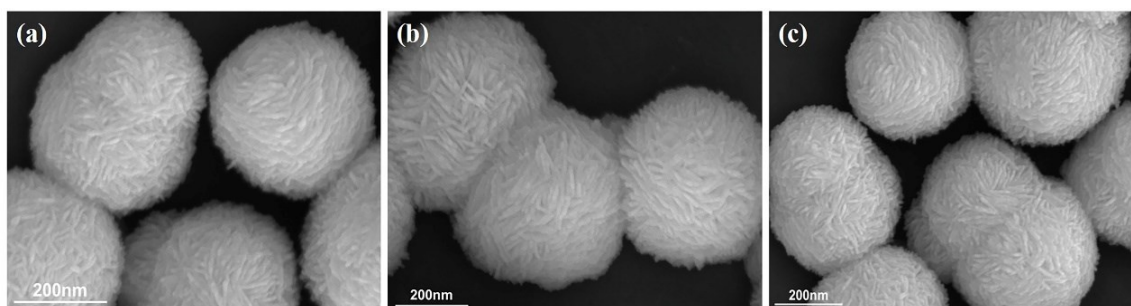


Figure S3. FESEM images of BOC/GS-15, BOC/GS-30 and BOC/GS-60.

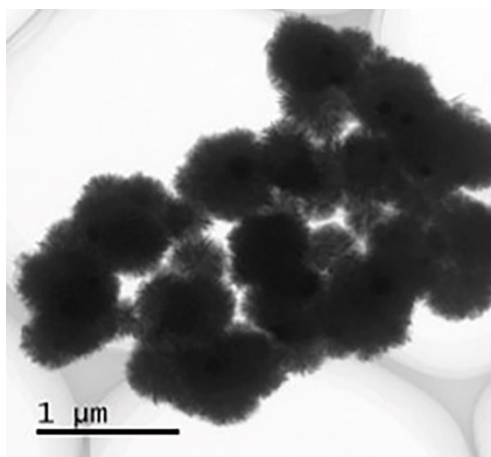


Figure S4. TEM image of BOC/GS-p.

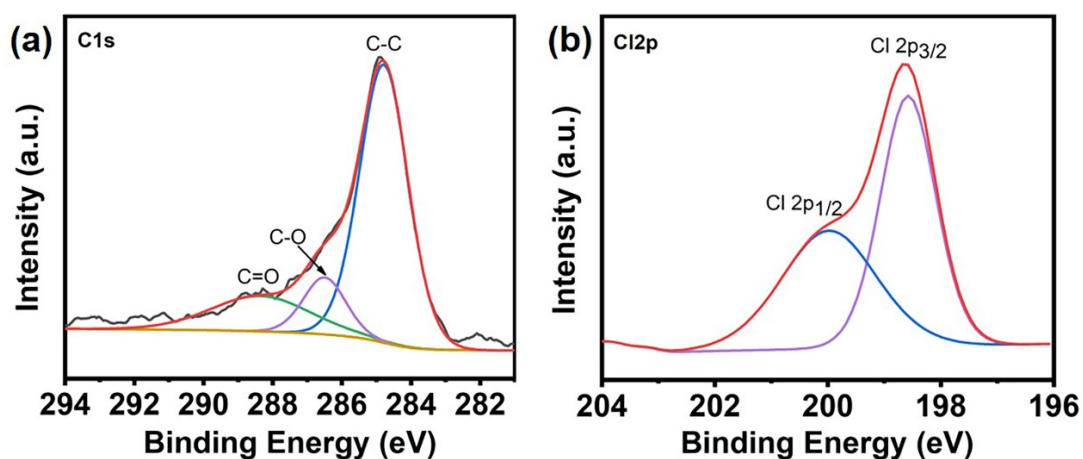


Figure S5. The high resolution spectra of C1s (a) and Cl2p (b) of BOC/GS-45.

As shown in **Figure S5a**, the asymmetric C1s main peak can be split into three peaks at 284.8, 286.5 and 288.4 eV, which corresponding to C-C, C-O and C=O.⁴ In **Figure S5b**, the binding energy peaks located at 198.4 and 199.9 eV correspond for Cl 2p_{3/2} and Cl 2p_{1/2}, confirming the existence of Cl⁻ in BiOCl.⁵

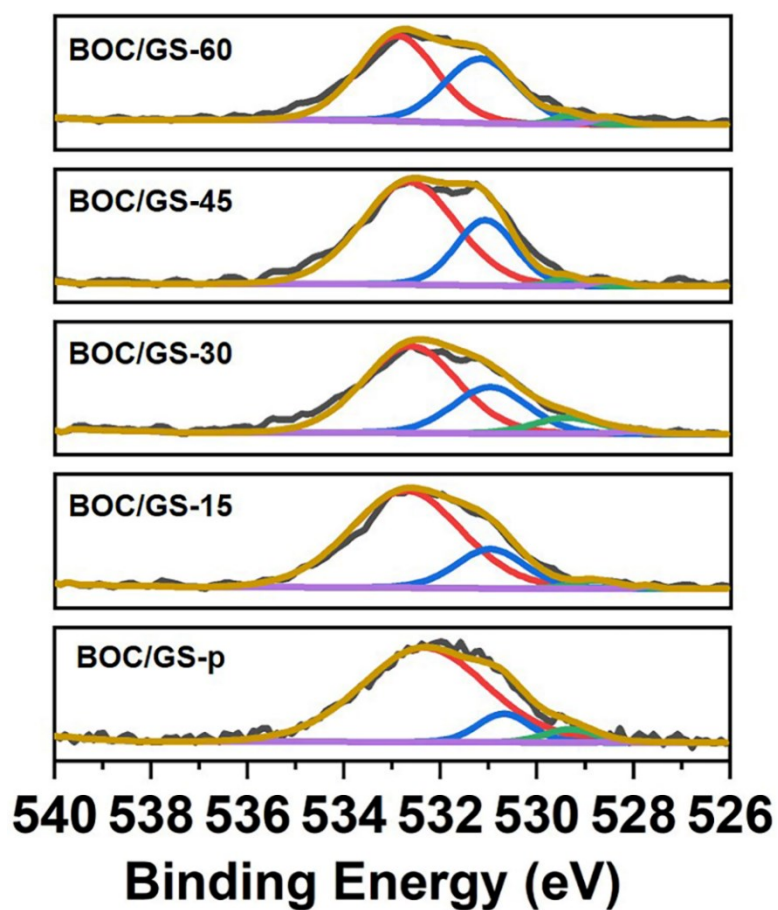


Figure S6. The high resolution of O1s of all samples.

	BOC/GS- p	BOC/GS- 15	BOC/GS- 30	BOC/GS- 45	BOC/GS- 60
Peak (eV)	531.06	531.4	531.1	531.0	531.2
Area	575.12	4231.40	6158.36	6888.50	10268.11
Oxygen defect%	1.01	5.83	8.77	12.15	17.64

Table S2. The comparison of oxygen defects of all samples.

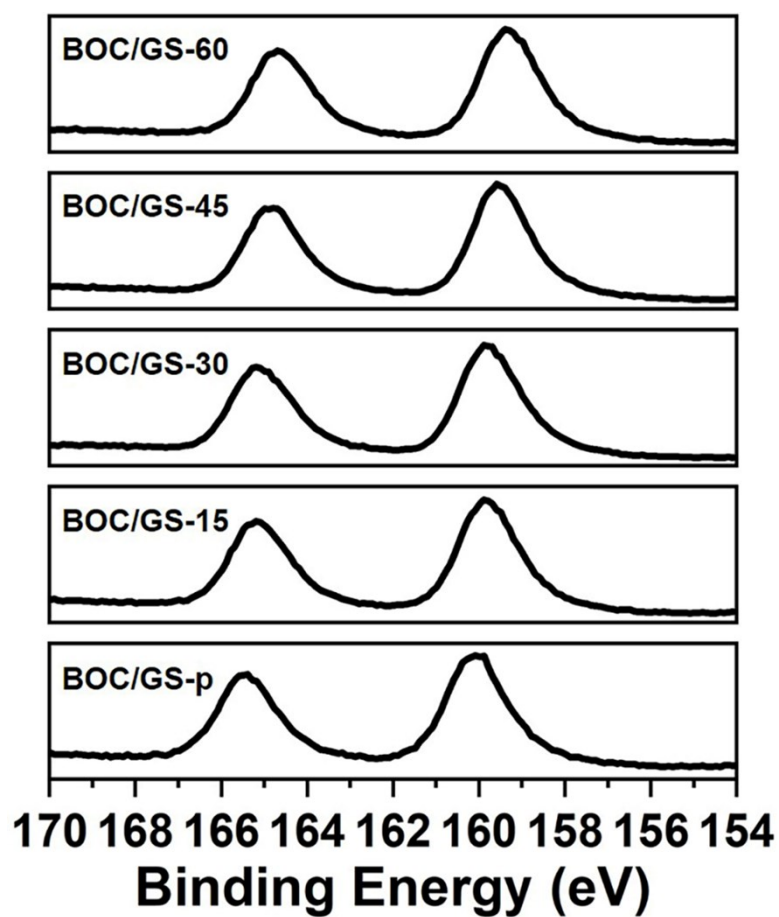


Figure S7. The high resolution of Bi 4f of all samples.

	BOC/GS- p	BOC/GS- 15	BOC/GS- 30	BOC/GS- 45	BOC/GS- 60
Peak at Bi 4f_{5/2} (eV)	165.4	165.3	165.3	165.1	164.8
Peak at Bi 4f_{7/2} (eV)	159.9	159.8	159.6	159.6	159.5

Table S3. The comparison of Bi4f of all samples.

	BOC/GS-p	BOC/GS-15	BOC/GS-30	BOC/GS-45	BOC/GS-60
E_g	2.85	2.79	2.62	2.48	2.22
E_{CB}	0.42	0.45	0.53	0.60	0.73
E_{VB}	3.27	3.24	3.15	3.08	2.95
R^2	0.73556	0.8287	0.86066	0.79239	0.98798

Table S4. E_g , E_{CB} and E_{VB} of all samples (eV vs NHE).

	BOC/GS-p	BOC/GS-15	BOC/GS-30	BOC/GS-45	BOC/GS-60
E_g	2.85	2.79	2.62	2.48	2.22
E_{CB}	1.25	1.28	1.36	1.43	1.56
E_{VB}	4.10	4.07	3.98	3.91	3.78

Table S5. E_g , E_{CB} and E_{VB} of all samples (eV vs RHE).

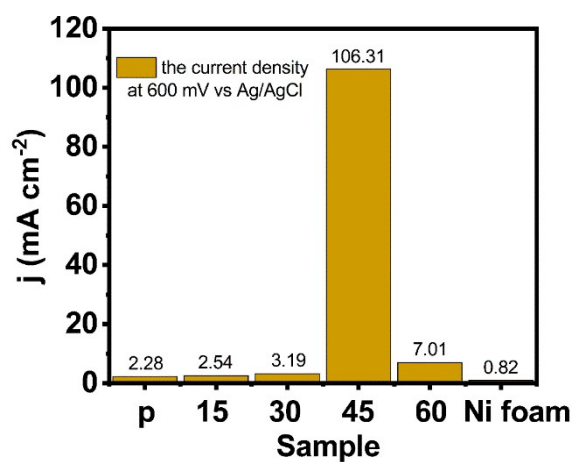


Figure S8. The comparison of current density of all samples at 600 mV vs Ag/AgCl.

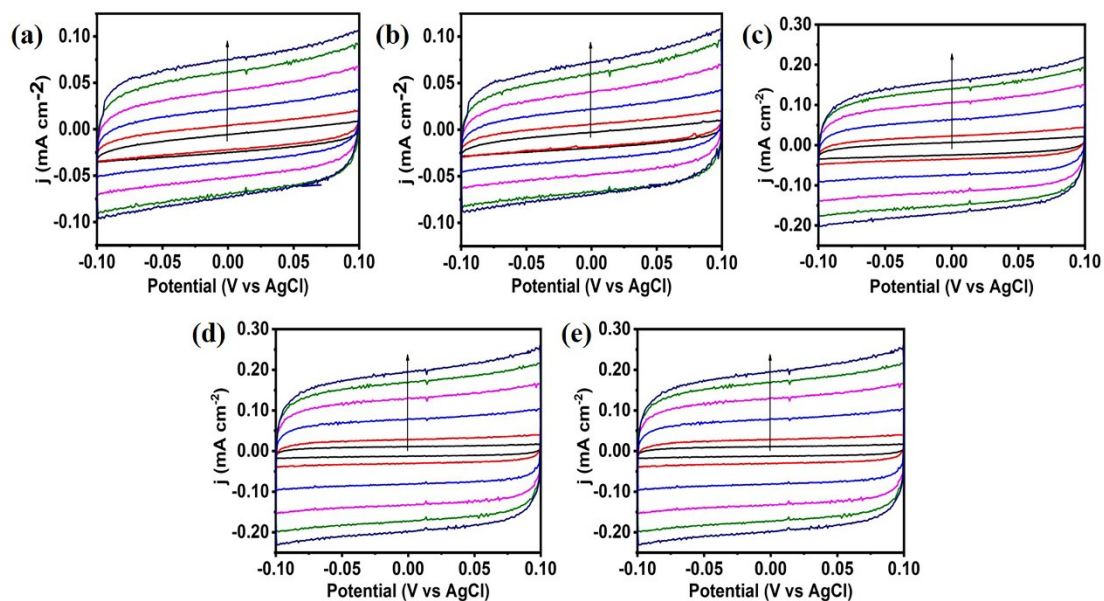


Figure S9. CV curves of BOC/GS-p (a), BOC/GS-15 (b), BOC/GS-30 (c), BOC/GS-45 (d) and BOC/GS-60 (e) in the potential range of -0.10—0.10 V vs Ag/AgCl. The scanning rate from the inside out along the arrow direction is 10, 20, 40, 60, 80, 100 mV/s.

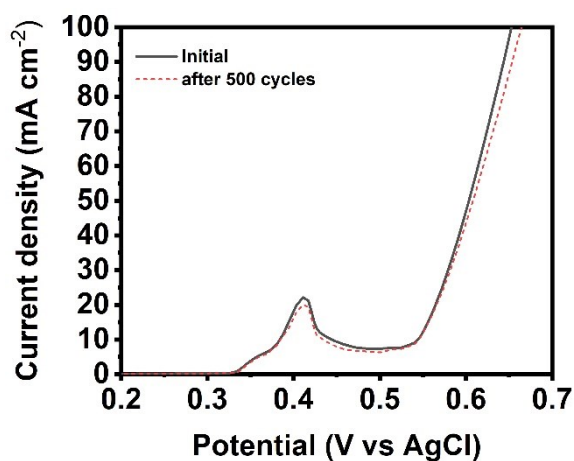


Figure S10. LSV curves for BOC/GS-45 electrode before and after 500 cycles.

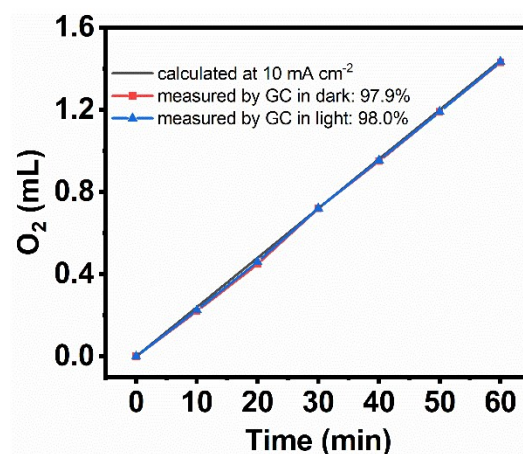


Figure S11. The Faraday efficiency of BOC/GS-45 for OER in light and dark conditions in 1M KOH solution.

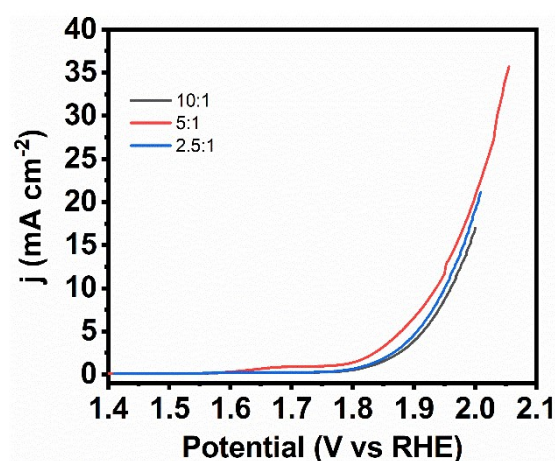


Figure S12. The LSV curves of the mass ratio between BiOCl and GS. The BOC/GS composites show the lowest overpotential when the ratio is 5:1.

Reference

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