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## **Supporting Information**

## Mesoporous cobalt-iron-organic frameworks: plasma-enhanced oxygen evolution electrocatalyst

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Scheme S1 Multichannel structure of (a)  $Fe_1Co_3$ -800, (b) mesoporous triangle-cheese shaped catalyst.



Fig. S1 SEM images of original Co-MOF@CC.



Fig. S2 (a) and (b) SEM images of Co-MOF@CC modified by  $O_2$ -Ar plasma at 100 W.



Fig. S3 (a) and (b) SEM images of Co-MOF@CC modified by O<sub>2</sub>-Ar plasma at 150 W.



Fig. S4 SEM images of Co-MOF@CC modified by O<sub>2</sub>-Ar plasma at 180 W.



Fig. S5 (a) and (b) SEM images of Co-MOF@CC modified by O<sub>2</sub>-Ar plasma at 200 W.



Fig. S6 XPS spectra of (a) Co 2p, (b) O 1s, (c) C 1s and (d) N 1s regions for the 2D Co-MOF samples.



**Fig. S7** XPS spectra of (a) Co 2p, (b) O 1s, (c) C 1s and (d) N 1s regions for the 2D Co-MOF samples treated by O<sub>2</sub>-Ar RF plasma with 180 W power.

For C 1s spectrum, it can be curved into three peak components located at 284.7, 285.8 and 287.7 eV, which are assigned to C-C, C-N and C=O, respectively. Compared to the 2D Co-MOF samples, the negative shift of binding energy is about 4.5 eV for C 1s at 287.7 eV, suggesting the transition of  $\pi \rightarrow \pi^*$  to C=O groups. It confirms that the elemental chemical component of the 2D Co-MOF samples have changed by O<sub>2</sub>-Ar RT plasma effect. The N 1s at 398.7, 400.1 and 407.1 eV are relevant to pyridine-like N, pyrrole-type N and oxidized N varieties in original 2D Co-MOF, respectively (Fig. S 6d). Nevertheless, the increased graphitic-N at 400.6 and 401.5 eV can enhance conductivity of the material and promote electronic transfer rapidly (Fig. S 7d).



Fig. S8 SEM images of (a) and (b)  $Fe_1Co_3/V_0$ -700, (c) and (d)  $Fe_1Co_3/V_0$ -900 with O<sub>2</sub>-Ar RF plasma treatment.



Fig. S9 Thermogravimetric analysis (TGA) curve of the Fe<sub>1</sub>Co<sub>3</sub>/V<sub>0</sub>-800 under N<sub>2</sub> with a ramp of  $10 \ ^{\circ}C \cdot min^{-1}$ .



Fig. S10 SEM images of (a) and (b)  $Fe_1Co_3$ -700, (c) and (d)  $Fe_1Co_3$ -800, (e) and (f)  $Fe_1Co_3$ -900 without using  $O_2$ -Ar RF plasma treatment.



Fig. S11 XPS spectra of (a) survey and (b) C 1s of the  $Fe_1Co_3/V_0$ -800 samples treated by O<sub>2</sub>-Ar RF plasma with 180 W power.



**Fig. S12** (a) LSV polarization curves of original Co-MOF,  $Fe_1Co_3$ -700,  $Fe_1Co_3$ -800 and  $Fe_1Co_3$ -900 without using O<sub>2</sub>-Ar RF plasma treatment at the scan of 5 mV s<sup>-1</sup>, and (b) the corresponding overpotential.



**Fig. S13** SEM images of (a)  $Fe_2Co_2/V_0$ -800 and (b)  $Fe_3Co_1/V_0$ -800, (c) LSV polarization curves of Co-MOF, Co-MOF/V\_0-800,  $Fe_2Co_2/V_0$ -800 and  $Fe_3Co_1/V_0$ -800 modified by O<sub>2</sub>-Ar RF plasma, and (d) the corresponding overpotential.



**Fig. S14** CV curves in a potential range of -0.02-0.02 V versus RHE of (a)  $Fe_1Co_3/V_0$ -700, (c)  $Fe_1Co_3/V_0$ -800, (e)  $Fe_1Co_3/V_0$ -900, and (b), (d) and (f) the corresponding current density difference at 0 V plotted against scan rate in a non-Faradaic range.



Fig. S15 (a) TEM and (b) HRTEM images of Fe $_1Co_3/V_0$ -800 after OER testing.



Fig. S16 The EDX spectral analysis of the electrolytes after the OER of the  $Fe_1Co_3/V_0$ -800 catalyst.

Table S1 Summary of the atomic compositions of the  $Fe_1Co_3/V_0$ -800 before and after OER calculated with the XPS data.

Sample	Atomic concentration (%)					Atomic ratio
	С	Ν	0	Fe	Co	Co/Fe
<b>Before OER</b>	72.31	2.77	19.81	1.25	3.86	3.08
After OER	63.84	2.68	28.49	1.19	3.80	3.19

Materials	Supports	Electrolytes	EJ=10mAcm <sup>-2</sup> (V)	References
Fe <sub>1</sub> Co <sub>3</sub> /V <sub>0</sub> -800	Carbon cloth	1 M KOH	1.49	This work
Co-Pt/C	Carbon cloth	1 M KOH	1.55	1
Hollow Mo-CoOOH nanoarrays	Carbon cloth	1 M KOH	1.535	2
Co <sup>2+</sup> -buserite	Carbon cloth	1 M KOH	1.607	3
CoO@FeOOH- NWAs	Carbon cloth	1 M KOH	1.71	4
CoP	Carbon cloth	1 M KOH	1.511	5
Fe-CoP	Carbon cloth	1 M KOH	1.612	6
PANI-FeCo/M WCNT	Carbon cloth	1 M KOH	1.51	7
meso/micro- FeCo-N <sub>x</sub> -CN-30	Carbon cloth	1 M KOH	1.60	8

**Table S2** The comparison of OER activities for various catalysts.

## References

- 1 Hong Zhang, Yanyu Liu, Haijun Wu, Wei Zhou, Zongkui Kou, Stephen John Pennycook, Jianping Xie, Cao Guan and John Wang, J. Mater. Chem. A, 2018, **6**, 20214-20223.
- 2 C. Guan, W. Xiao, H. J. Wu, X. M. Liu, W. J. Zang, H. Zhang, J. Ding, Y. P. Feng, S. J. Pennycook, J. Wang, Nano Energy, 2018, **48**,73-80.
- 3 M. Nakayama, K. Fujimoto, T. Kobayakawa and T. Okada, Electrochem. Commun., 2017, 84, 24-27.
- 4 Y. Wang, Y. M. Ni, B. Liu, S. X. Shang, S. Yang, M. H. Cao, C. W. Hu, Electrochim. Acta, 2017, **257**, 356-363.
- 5 P. Wang, F. Song, R. Amal, Y. H. Ng, X. L. Hu, ChemSusChem, 2016, 9, 472-477.
- 6 M. Ma, G. L. Zhu, F. Y. Xie, F. L. Qu, Z. A. Liu, G. Du, A. M. Asiri, Y. D. Yao, X. P. Sun, ChemSusChem, 2017, **10**, 3188-3192.
- 7 C. C. Zhao, Y. H. Jin, X. Du, W. B. Du, J. Power Sources, 2018, 399, 337-342.
- 8 S. Li, C. Cheng, X. J. Zhao, J. Schmidt, A. Thomas, Angew. Chem., Int. Edit., 2018, 57, 1856-1862.