**Electronic Supplementary Information** 

# A superior electrocatalyst toward the oxygen reduction reaction obtained by atomically dispersing copper on N, F co-doped graphene through atomic interface engineering

Jing-Ping Zhong <sup>a,c,‡</sup>, Cheng Hou <sup>a,‡</sup>, Miao-Lan Sun <sup>a,b,‡</sup>, Zhong-Yun Yang <sup>a</sup>, Du-Hong Chen <sup>a</sup>, You-Jun Fan <sup>a,\*</sup>, Wei Chen <sup>a,\*</sup>, Hong-Gang Liao <sup>b</sup> and Shi-Gang Sun <sup>b,\*</sup>

<sup>a</sup> Guangxi Key Laboratory of Low Carbon Energy Materials, School of Chemistry and Pharmaceutical Sciences, Guangxi Normal University, Guilin 541004, China

<sup>b</sup> State Key Laboratory of Physical Chemistry of Solid Surfaces, Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China

<sup>c</sup> Collaborative Innovation Centre of Regenerative Medicine and Medical Bio Resource Development and Application Co-constructed by the Province and Ministry, Guangxi Medical University, Nanning 530021, Guangxi, China

\* Corresponding authors.

E-mail addresses: youjunfan@mailbox.gxnu.edu.cn; weichen@mailbox.gxnu.edu.cn; sgsun@xmu.edu.cn.

<sup>‡</sup> These authors contributed equally to the work.

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### S1. Thermogravimetric analysis of graphene (G), F16CuPc, F16CuPc/G and Cu SA-NFG



Fig. S1. TGA curves of G, F<sub>16</sub>CuPc, F<sub>16</sub>CuPc/G and Cu SA-NFG.

In Fig. S1, about 10% weight loss of G within 168 °C is due to the release of adsorbed species in the material, and about 6 and 14% weight loss of  $F_{16}$ CuPc in the two respective ranges of 175 – 280 and 425 – 600 °C are attributed to the thermal decomposition of the phthalocyanine ring of  $F_{16}$ CuPc [1]. However, the decomposition temperature of  $F_{16}$ CuPc/G increases to 390 °C, indicating that the functionalization of  $F_{16}$ CuPc with G helps to improve its thermal stability [2]. The mass loss trend of  $F_{16}$ CuPc/G after 390 °C is similar to that of  $F_{16}$ CuPc, which is ascribed to the breakdown of the functionalization between phthalocyanine molecules and G. In addition, about 10% weight loss below 170 °C is attributed to the release of adsorbed substances in Cu SA-NFG [3], and no obvious weight loss occurred afterwards. At 800 °C, the weight percentage of G,  $F_{16}$ CuPc,  $F_{16}$ CuPc/G, and Cu SA-NFG samples are 87.3, 71.1, 72.2, and 83.5%, respectively, proving the highly thermal stability of Cu SA-NFG.

### S2. Cu K-edge EXAFS fitting results

Sample	Path	Ν	<i>R</i> (Å)	$\sigma^2 (\times 10^{-3} \text{ Å}^2)$	$\Delta E_0 ({ m eV})$	R factor
1	Cu-N	3.95	1.96	1.65	-0.221	0.0094

Table S1. Cu K-edge EXAFS fitting results.<sup>[a]</sup>

[a]: k range: 2-11.0 (Å<sup>-1</sup>); R range: 1-2 Å;  $S_0^2 = 0.8788$  was determined from the Cu foil and used for Cu

K-edge fitting.

## S3. Comparison of XPS peak position for the prepared materials

**Table S2** Peak position summary of high-resolution Cu 2p, F 1s XPS spectra for Cu SA-NFG, CuNG, and Pt/Cu SA-NFG materials.

	F 1s / eV	Cu 2p / eV				
Material	Semi ionio C E	Cu <sup>+</sup>		Cu <sup>2+</sup>		
	Semi-ionic C-F-	$Cu^{+}2p_{3/2}$	$Cu^{+}2p_{1/2}$	$Cu^{2+}2p_{3/2}$	$Cu^{2+}2p_{1/2}$	
Cu SA-NFG	689.90	932.50	952.30	934.90	954.80	
CuNG	—	932.30	952.11	934.70	954.60	
Pt/Cu SA-NFG	689.50	932.67	952.47	935.08	954.98	

## S4. High resolution XPS spectra of CuNG and NG



Fig. S2. (a, b) Cu 2P and N 1s XPS spectra of CuNG, (c) N 1s XPS spectrum of NG.

## S5. N2 adsorption-desorption isotherms and pore size distributions (insets) of Cu SA-NFG, CuNG and NG



Fig. S3. N<sub>2</sub> adsorption-desorption isotherms of Cu SA-NFG, CuNG and NG.

### S6. The LSV curves of CuNG before and after 10000 CV cycles



Fig. S4. The LSV curves of ORR on the CuNG before and after 10000 CV cycles.

## S7. TEM and HAADF-STEM analysis of Cu SA-NFG after 10000 CV tests



Fig. S5. TEM images (a, b), HAADF-STEM image (c) and the corresponding elemental mappings of C, N,

F and Cu (d-g) of Cu SA-NFG after 10000 CV cycles.

S8. Anti-poisoning tests of Cu SA-NFG and Pt/C



Fig. S6. Anti-poisoning tests of Cu SA-NFG (a) and Pt/C (b).

### **S9.** Computational model and data processing



Fig. S7. Schematic diagram of model a and b.

The calculated models are presented in Fig. S7, in order to distinguish different elements, gray atoms represent C atoms, blue atoms represent N atoms, light blue atoms represent F atoms, and orange atoms represent Cu atoms. At acidic environment, the ORR proceeds in four electron steps and can be written as follows:

$$* + O_2 + H_2O + e^- \rightarrow *OOH + OH^-$$
(S1)

$$*OOH + e^{-} \rightarrow *O + OH^{-}$$
(S2)

$$^{*}O + H_{2}O + e^{-} \rightarrow ^{*}OH + OH^{-}$$
(S3)

$$*OH + e^{-} \rightarrow * + OH^{-}$$
(S4)

where \* represents an active site on the catalyst surface, and OH\*, O\*, and OOH\* denote the corresponding adsorbed intermediates.

We can obtain the Gibbs free energy of each elementary step by using the computational hydrogen electrode (CHE) model proposed by Nørskov. According to this model, the free energy change ( $\Delta G$ ) is calculated as follows:

$$\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S + \Delta G_{pH} + eU$$
 (S5)

Among them,  $\Delta E$  is the adsorption energy of each reaction intermediate, which can be calculated by DFT.  $\Delta E_{ZPE}$  is the change of the zero-point energy and  $\Delta S$  is the entropy change before and after the reaction (T=298.15 K).  $\Delta G_{pH}$  is the free energy correction with respect to the H concentration in solution, e.g.,  $\Delta G_{pH} = k_B T \ln 10 \times pH$ , where  $k_B$  is Boltzmann's constant. In this work, the value of the pH was set to 13 to simulate a strong alkalinity environment e and U are the number of transferred electrons and the applied electrode potential, respectively. Then, at standard conditions, the free energy change for all ORR electrochemical steps ( $\Delta G_{1.4}$ ) can be expressed as:

$$\Delta G_1 = \Delta G_{*OOH} - 1.84 \tag{S6}$$

$$\Delta G_2 = \Delta G_{*O} - \Delta G_{*OOH} \tag{S7}$$

$$\Delta G_3 = \Delta G_{*OH} - \Delta G_{*O} \tag{S8}$$

$$\Delta G_4 = \Delta G_{*OH} \tag{S9}$$

It should be noted that we investigated the electrochemical processes employing the established computational hydrogen electrode (CHE) model. The theoretical basis for the validity of the CHE model is

that electrochemical reactions that happened in the solution normally possess small kinetic barriers, which are surmountable at room temperature. The reaction kinetics will thus be dictated by merely the free energy difference of each step. The step with the most positive free energy difference is the rate-determining step. Therefore, the theoretical overpotential  $\eta$  is defined in equation (S10):

$$\eta_{\text{Theory}} = 0.46 \text{ V} - \min\{\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4\}/e$$
(S10)

S10. TEM, HRTEM and HAADF-STEM images of Pt/Cu SA-NFG, Pt/CuNG and Pt/NG



Fig. S8. TEM, HRTEM images of Pt/CuNG (a-c), Pt/NG (d-f) and Pt/Cu SA-NFG (g-i); HAADF-STEM

image (j) and elemental mappings (k-o) of Pt/Cu SA-NFG.

As shown in Fig. S8a-c, only the strip-shape of Pt nanoparticles are seen on the CuNG surface, and no obvious network structure is formed. Similarly, the approximately spherical Pt nanoparticles are dispersed on the NG surface (Fig. S8d-f). Interestingly, a special nanonetwork-shape of Pt nanoparticles is uniformly and densely interwoven on the surface of Cu SA-NFG (Fig. S8g-i). The HAADF-STEM of Pt/Cu SA-NFG images further show that the elemental singles of Pt, Cu, N and F are uniformly distributed in the whole region of Pt/Cu SA-NFG nanohybrid (Fig. S8j-o). This indicates that G co-doped with Cu and F plays an important role in the formation of reticular Pt nanoparticles.

S11. High resolution XPS spectra of Pt/Cu SA-NFG and Pt/CuNG



Fig. S9. F 1s (a) and Cu 2p (b) spectra of Pt/Cu SA-NFG; (c) Cu 2p spectrum of Pt/CuNG.

The peak of F in Pt/Cu SA-NFG (689.50 eV, Fig. S9a) has a significant negative shift about 0.4 eV compared with that of Cu SA-NFG (689.90 eV, Fig. 3e inset). This can be due to the electronic transfer from Pt to F. Similarly, the peak of Cu<sup>2+</sup> in Pt/Cu SA-NFG (935.08 eV, Fig. S9b) has a significant positive shift about 0.19 eV compared with that of Pt/CuNG (934.89 eV, Fig. S9c). All the results of XPS suggest the strong interaction between the Pt nanoparticles and substrate of Cu SA-NFG.

### S12. Comparison of electrocatalytic properties of different catalysts for the ORR

Catalyst	E <sub>onset</sub> (V vs RHE)	E <sub>1/2</sub> (V vs RHE)	Limited current density (mA cm <sup>-2</sup> )	Reference
Fe-COF <sub>900</sub>	0.86	0.82	5.49	[4]
FeSA-FeNC@NSC	_	0.90	_	[5]
Fe-NHC	0.94	0.89	—	[6]
FeNi-DSAs/PNCH	1.04	0.89	5.3	[7]
Ni <sub>SA</sub> Fe <sub>SA</sub> -Ni@Fe <sub>NPs</sub> /CNTs-NGNS	0.92	0.87	—	[8]
Ni-N <sub>4</sub> /GHSs/Fe-N <sub>4</sub>	0.93	0.83	_	[9]
Ni SAs-NC	0.95	0.85	5.19	[10]
NiN <sub>4</sub> -C	0.97	0.86	5.65	[11]
Co-N/C+N <sub>G</sub>	1.04	0.91	—	[12]
Co-NCS-2	0.96	0.90	5.34	[13]
Co SA/N-CNS-900	1.004	0.872	—	[14]
N-Mo-holey G	0.99	0.85	—	[15]
Cu SA-NFG	0.978	0.89	5.93	This work

Table S3 Performance comparison of non-noble SACs for the ORR in 0.1 M KOH electrolyte

#### References

- [1] J. P. Zhong, M. L. Sun, S. Xiang, Y. J. Fan, M. Waqas, K. X. Huang, Y. H. Tang, W. Chen, J. Yang, Appl. Surf. Sci. 511 (2020) 145519.
- [2] X. D. Lu, Z. M. Chen, H. Wu, E. Cao, Y. Wang, S. C. Du, Y. Q. Wu, Z. Y. Ren, J. Mater. Chem. A 9 (2021) 4150.
- [3] W. B. Lou, B. H. Guan, Z. B. Wu, J. Therm. Anal. Calorim. 104 (2011) 661–669.
- [4] S. Yang, X. W. Li, T. Y. Tan, J. N. Mao, Q. Xu, M. H. Liu, Q. Y. Miao, B. B. Mei, P. Z. Qiao, S. Q. Gu,F. F. Sun, J. Y. Ma, G. F. Zeng, Z. Jiang, Appl. Catal. B 307 (2022) 121147.
- [5] W. J. Zhai, S. H. Huang, C. B. Lu, X. N. Tang, L. B. Li, B. Y. Huang, T. Hu, K. Yuan, X. D. Zhuang, Y.
   W. Chen, Small (2022) 2107225.

- [6] S. Y. Zhang, W. G. Yang, Y. L. Liang, X. Yang, M. N. Cao, R. Cao, Appl. Catal. B 285 (2021) 119780.
- [7] B. Wang, J. Tang, X. H. Zhang, M. Hong, H. K. Yang, X. Guo, S. Xue, C. C. Du, Z. X. Liu, J. H. Chen, Chem. Eng. J. 437 (2022) 135295.
- [8] T. H. Nguyen, P. K. L. Tran, D. T. Tran, T. N. Pham, N. H. Kim, J. H. Lee, Chem. Eng. J. 440 (2022) 135781.
- [9] J. Y. Chen, H. Li, C. Fan, Q. W. Meng, Y. W. Tang, X. Y. Qiu, G. T. Fu, T. Y. Ma, Adv. Mater. 32 (2020) 2003134.
- [10] H. Jiang, J. Xia, L. Jiao, X. M. Meng, P. F. Wang, C. S. Lee, W. J. Zhang, Appl. Catal. B 310 (2022) 121352.
- [11] Z. W. Cai, P. Du, W. H. Liang, H. Zhang, P. Wu, C. X. Cai, Z. J. Yan, J. Mater. Chem. A 8 (2020) 15012.
- [12] X. R. Zhang, X. M. Xu, S. X. Yao, C. Hao, C. Pan, X. Xiang, Z. Q. Tian, P. K. Shen, Z. P. Shao, S. P. Jiang, Small 18 (2022) 2105329.
- [13] C. W. Shi, Y. H. Liu, R. Y. Qi, J. T. Li, J. X. Zhu, R. H. Yu, S. D. Li, X. F. Hong, J. S. Wu, S. B. Xi,
   L. Zhou, L. Q. Mai, Nano Energy 87 (2021) 106153.
- [14] T. Shen, X. X. Huang, S. B. Xi, W. Li, S. N. Sun, Y. L. Hou, J. Energy Chem. 68 (2022) 184-194.
- [15] P. Du, K. L. Hu, J. Lyu, H. L. Li, X. Lin, G. Q. Xie, X. J. Liu, Y. S. kazuIto, H. J. Qiu, Appl. Catal. B 276 (2020) 119172.