## Supporting Information

## Electronic coupling-tunable of cobalt sulfide/carbon composites for optimizing oxygen evolution reaction activity

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**S1** 

According to the previous studies, OER involves multiple proton-transfer processes with the following steps<sup>S1</sup>:

$$* + OH - \rightarrow *OH + e -$$
(S1)

$$*OH + OH - \rightarrow *O + H_2O + e -$$
(S2)

$$*O + OH \rightarrow *OOH + e -$$
 (S3)

$$*OOH + OH - \rightarrow *O_2 + e -$$
(S4)

$$*O_2 \to *+O_2 \tag{S5}$$

in which the asterisk represents the surface-bound species. During these steps, the various intermediates, e.g., \*OH, \*O, \*OOH, and \*O<sub>2</sub>, are generated. The energetically favorable low-index  $Co_9(S, O)_8$  (100) plane was selected as the active regions. Furtheermore, the free energy landscape of the intermediates during OER were calculated in different charge doping states.

The free energy differences for each step ( $\Delta G_i$ ) during OER are theoretically calculated as following equations described<sup>S2</sup>:

$$\Delta G_{1} = G(*OH) - G(*) - \mu_{OH} = E(*OH) - E(*) - E(H_{2}O) + 1/2E(H_{2}) - eU + \Delta G_{H+}(pH) + \Delta (ZPE - T\Delta S)$$
(S6)  

$$\Delta G_{2} = G(*O) - G(*OH) + \mu_{OH} = E(*O) - E(*OH) - E(H_{2}O) + 1/2E(H_{2}) - eU + \Delta G_{H+}(pH) + \Delta (ZPE - T\Delta S)$$
(S7)  

$$\Delta G_{3} = G(*OOH) - G(*O) - \mu_{OH} = E(*OOH) - E(*O) - E(H_{2}O) + 1/2E(H_{2}) - eU + \Delta G_{H+}(pH) + \Delta (ZPE - T\Delta S)$$
(S8)  

$$\Delta G_{4,5} = 4 \cdot (1.23 \text{ eV} - eU + \Delta G_{H+}(pH)) - (\Delta G_{1} + \Delta G_{2} + \Delta G_{3})$$
(S9)

where U represents the potential obtained against the normal hydrogen electrode (NHE) under standard conditions. According to the  $\Delta G_{H+}(pH) = -k \cdot BT \log(pH)$ , the change of Gibbs free energy for a proton relative to the pH is obtained.  $\Delta G_i$  are calculated from zero-point energy (ZPE), entropy correction, and the DFT energy to  $\Delta G_i = \Delta ZPE_i + \Delta E_i - \Delta T\Delta S_i$ . To avoid the calculation including  $O_{2(gas)}$ , which is difficult to calculated within the GGA-DFT scheme, the sum of  $\Delta G_{1-5}$  was fixed at the experimental  $\Delta G$  value (4.92 eV) in  $2H_2O > 2H_2 + O_2$ . On the basis of above analysis, the theoretical  $\eta$  could be calculated from the  $\Delta G_i$  as the following equation presented:

$$\eta = max(\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_{4,5})/e - 1.23 \text{ V}$$
(S10)

Sample	Phase	Space group	Lattice parameters (Å)		Amount
			a	с	(wt.%)
Co <sub>9</sub> S <sub>8</sub> -500	Co <sub>9</sub> S <sub>8</sub>	Fm-3m	9.9220(6)	_	100
Co <sub>9</sub> S <sub>8</sub> -800	$Co_9S_8$	Fm-3m	9.9228(6)	-	100
Co <sub>9</sub> S <sub>8</sub> @NC-500	$Co_9S_8$	Fm-3m	9.9223(9)	_	98
	С	<i>P</i> 6 <sub>3</sub> / <i>mmc</i>	2.48(1)	6.75(1)	2
Co <sub>9</sub> S <sub>8</sub> @NC-600	$\mathrm{Co}_9\mathrm{S}_8$	Fm-3m	9.9275(8)	_	95
	С	P6 <sub>3</sub> /mmc	2.48(1)	6.75(1)	5
Co <sub>9</sub> S <sub>8</sub> @NC-700	$Co_9S_8$	Fm-3m	9.9316(7)	_	93
	С	P6 <sub>3</sub> /mmc	2.48(1)	6.74(1)	7
Co <sub>9</sub> S <sub>8</sub> @NC-800	$Co_9S_8$	Fm-3m	9.9418(5)	_	92
	С	P6 <sub>3</sub> /mmc	2.48(1)	6.73(1)	8
Co-PBA sulfidated at 900 °C	Co <sub>9</sub> S <sub>8</sub>	Fm-3m	9.9222(4)	_	100

**Table S1.** Rietveld refinement results for the XRD patterns of the  $Co_9S_8$ -*T*,  $Co_9S_8$  NP@NC-*T*, and the products of Co-PBA sulfidated at 900 °C.

Material	Electrolyte (KOH)	Scan rate (mV s <sup>-1</sup> )	η <sub>10</sub> (mv)	Ref.
Co <sub>9</sub> S <sub>8</sub> @S,N-doped carbon	0.1 M	10	330	S3
Co <sub>1-x</sub> S@rGO	1.0 M	5	310	S4
Co <sub>3</sub> S <sub>4</sub> @NCNTs	0.1 M	5	430	S5
Fe <sub>3</sub> O <sub>4</sub> @Co <sub>9</sub> S <sub>8</sub> @rGO	0.1 M	5	340	S6
Co <sub>9</sub> S <sub>8</sub> @graphene	0.1 M	10	280	S7
Co <sub>9</sub> S <sub>8</sub> @NSPC	0.1 M	5	310	<b>S</b> 8
CoS <sub>2</sub> @N,S-GO	0.1 M	10	390	S9
$Co_9S_8$ hollow microplates	1.0 M	2	278	S10
Amorphous CoSe film	1.0 M	5	292	S11
Coral-like CoSe	1.0 M	1	295	S12
CoSe2@C	1.0 M	10	330	S13
CoSe <sub>2</sub> @C	1.0 M	5	322	S14
Co <sub>9</sub> S <sub>8</sub> @N,P-doped PC	1.0 M	5	261	S15
Zn-Doped CoSe <sub>2</sub>	1.0 M	2	356	S16
Co <sub>3</sub> O <sub>4</sub> @rGO	1.0 M	2	313	S17
Co <sub>3</sub> O <sub>4</sub> @PCNA	0.1 M	5	290	S18
Crystalline Co <sub>3</sub> O <sub>4</sub>	1.0 M	50	401	S19
Porous Co <sub>3</sub> O <sub>4</sub>	0.1 M	5	600	S20
Hollow Co <sub>3</sub> O <sub>4</sub> Cages	1.0 M	50	400	S21
CoO@rGO	0.1 M	10	348	S22
Co <sub>3</sub> O <sub>4</sub> Nanoflakes	1.0 M	5	451	S23
N-doped Co <sub>3</sub> O <sub>4</sub>	0.1 M	5	310	S24
Co <sub>9</sub> S <sub>8</sub> @NC-800	0.1 M	10	302	This work

**Table S2.** Comparison of OER performance of  $Co_9S_8$ @NC electrode with previously reported cobalt oxide- and cobalt chalcogenides-based materials.



Fig. S1. The (a, b) FESEM images and (c) schematic illustration of Prussian blue analogue.



**Fig. S2.** XRD pattern of the  $Co_3(Co(CN)_6)_2$  precursors.



**Fig. S3.** FESEM images of the products obtained by sulfidating Co-PBA at 600 °C.



Fig. S4. FESEM images of the products obtained by sulfidating Co-PBA at 900 °C.



Fig. S5. XRD patterns of the  $Co_9S_8$ @NC-500,  $Co_9S_8$ @NC-600,  $Co_9S_8$ @NC-700, and  $Co_9S_8$ @NC-800 composites.



Fig. S6. Raman spectra of the  $Co_9S_8$ @NC-500,  $Co_9S_8$ @NC-600,  $Co_9S_8$ @NC-700, and  $Co_9S_8$ @NC-800 composites.



Fig. S7. TEM images for the (a-c)  $Co_9S_8$ @NC-500, (d-f)  $Co_9S_8$ @NC-600, and (g-i)  $Co_9S_8$ @NC-800 composites.



Fig. S8. Comparison of the XRD patterns for  $Co_9S_8$ @NC-500,  $Co_9S_8$ @NC-600,  $Co_9S_8$ @NC-700, and  $Co_9S_8$ @NC-800 composites in the 2 $\theta$  range of 29-32 °.



Fig. S9. Rietveld refinement of the XRD patterns for (a)  $Co_9S_8$ @NC-500, (b)  $Co_9S_8$ @NC-600, (c)  $Co_9S_8$ @NC-700, and (d)  $Co_9S_8$ @NC-800 composites.

To obtain the lattice parameters of Co<sub>9</sub>S<sub>8</sub> in Co<sub>9</sub>S<sub>8</sub>@NC-*T* samples, the XRD patterns of the Co<sub>9</sub>S<sub>8</sub>@NC-*T* samples were refined by the RIETAN-2000 software based on the Rietveld method. During the refinement, both the Brindley correction and the pseudo-Voigt function containing a Lorentzian part and a Gaussian part have been applied. To assess the quality of refinement, the reliability factors  $R_{wp}$  (*R*-weighted pattern),  $R_p$  (*R*-pattern) and the goodness of fit *S* were provided. In general, an acceptable result requires that the values of  $R_{wp}/R_p$  and *S* should be simultaneously less than 13% and 3, respectively. In addition, on the basis of our samples, the structure models of cubic-Co<sub>9</sub>S<sub>8</sub> (Space group: *Fm*-3*m*) and graphitic carbon (Space group:  $P6_3/mmc$ ) were employed during the refinement. Figure S8a, S8b, S8c and S8d displayed the Rietveld refinement of XRD patterns of Co<sub>9</sub>S<sub>8</sub>@NC-500, Co<sub>9</sub>S<sub>8</sub>@NC-600, Co<sub>9</sub>S<sub>8</sub>@NC-700 and Co<sub>9</sub>S<sub>8</sub>@NC-800, respectively, from which it could be seen that the

fitted data were well consistent with the observed ones for all XRD patterns of  $Co_9S_8@NC-T$  samples. Noted that the "Fitted data", "Observed data" as well as "Differentiation" have been also captioned in the Figures. The refined lattice parameters of  $Co_9S_8@NC-T$  samples were listed in Table S1, from which the lattice parameters of  $Co_9S_8@NC-T$  samples were listed from 9.9223 ( $Co_9S_8@NC-500$ ), 9.9275 ( $Co_9S_8@NC-600$ ), 9.9316 ( $Co_9S_8@NC-700$ ) to 9.9418 Å ( $Co_9S_8@NC-800$ ).



Fig. S10. Rietveld refinement of the XRD patterns for (a) bare  $Co_9S_8$ -500 and (b)  $Co_9S_8$ -800 products.

To obtain the lattice parameters of  $Co_9S_8$  in  $Co_9S_8$ -500 and  $Co_9S_8$ -800 samples, the XRD patterns of the  $Co_9S_8$ -500 and  $Co_9S_8$ -800 samples were refined by the RIETAN-2000 software based on the Rietveld method. During the refinement, the structural model of cubic- $Co_9S_8$  (Space group: *Fm*-3*m*) was employed. Figure S9a and S9b displayed the Rietveld refinement of XRD patterns of  $Co_9S_8$ -500 and  $Co_9S_8$ -800, respectively, from which it could be seen that the fitted data were well consistent with the observed ones. Noted that the "Fitted data", "Observed data" as well as "Differentiation" have been also captioned in the Figures. The refined lattice parameters of  $Co_9S_8$  in  $Co_9S_8$ -500 and  $Co_9S_8$ -800 samples were listed in Table S1, from which the lattice parameters of  $Co_9S_8$  were 9.9220 Å ( $Co_9S_8$ -500) and 9.9228 Å ( $Co_9S_8$ -800), respectively, indicating that the effect of sulfidating temperature on increasing the lattice parameters are negligible.



Fig. S11. High-resolution Co 2p spectra of  $Co_9S_8$ @NC-500,  $Co_9S_8$ @NC-600,  $Co_9S_8$ @NC-700, and  $Co_9S_8$ @NC-800 composites.



**Fig. S12.** Rietveld refinement of the XRD pattern (a) and Raman spectrum (b) for the products obtained by sulfidating Co-PBA at 900 °C.



Fig. S13. CVs of (a)  $Co_9S_8@NC-500$ , (b)  $Co_9S_8@NC-600$ , and (c)  $Co_9S_8@NC-700$  at different scan rates; (d) current density at overpotential of -0.1 V as functions of the scan rates.



**Fig. S14.** Comparison of the LSVs for C-500, C-800, Co<sub>9</sub>S<sub>8</sub>@NC-500, and Co<sub>9</sub>S<sub>8</sub>@NC-800 composites



Fig. S15. Comparison of the 1st LSV curve and the 500th LSV curve for the  $Co_9S_8@NC-800$  composite.



Fig. S16. Comparison of high-resolution (a) Co 2p, (b) O 1s XPS spectra for the  $Co_9S_8$ @NC-800 electrodes before and after cycle test.

Compared to the Co 2p spectra before cycle test (Fig. S16a), the main peak of Co 2p spectra after cycle is slightly shifted to the high binding energy, which should be ascribed to the higher valence Co species, suggesting the partial oxidation of  $Co_9S_8$  during the OER process. This also can be verified in the deconvolution peaks of the O

1s spectrum for the cycled sample (Fig. S16b), from which peaks centered at 530, 531.7, and 533.2 eV are assigned to metal-oxygen bonds, low-coordinated oxygen ions at the surface and defect sites, and adsorbed water, respectively. These suggest the formation of the cobalt oxides/hydroxides on the surface of the  $Co_9S_8$ @NC-800 electrode.



Fig. S17. (a, b) TEM images and (c, d) High-resolution TEM images of the  $Co_9S_8@NC-800$  electrodes after cycle test.



Fig. S18. The LSV curve of  $Co(OH)_2$  measured at the scan rate of 10 mV s<sup>-1</sup> in 0.1 M KOH electrolyte.



Fig. S19. (a) Model structure of  $Co_9(S, O)_8$  for the DFT calculation; (b) DFT calculated free energy landscape for OER at 1.23 V vs. RHE (the standard potential for OER) on  $Co_9S_8$  (100) surface and  $Co_9(S, O)_8$  (100) surface under the same charging state.

## References

- (S1) J. X. Feng, H. Xu, Y. T. Dong, S. H. Ye, Y. X. Tong and G. R. Li, Angew. Chem. Int. Ed., 2016, **55**, 3694.
- (S2) J. S. Kim, I. Park, E. Jeong, K. Jin, W. M. Seong, G. Yoon, H. Kim, B. Kim, K. T. Nam and K. Kang, *Adv. Mater.*, 2017, **29**, 1606893.
- (S3) S. W. Liu, M. Y. Tong, G. Q. Liu, X. Zhang, Z. M. Wang, G. Z. Wang, W. P. Cai,H. M. Zhang and H. J. Zhao, *Inorg. Chem. Front.*, 2017, 4. 491.
- (S4) J. Q. Zhu, Z. Y. Ren, S. C. Du, Y. Xie, J. Wu, H. Y. Meng, Y. Z. Xue and H. G. Fu, Nano Res., 2017, 10, 1819.
- (S5) H. J. Wang, Z. P. Li, G. H. Li, F. Peng and H. Yu, Catalysis Today, 2015, 245, 74.
- (S6) J. Yang, G. X. Zhu, Y. J. Liu, J. X. Xia, Z. Y. Ji, X. P. Shen and S. K. Wu, *Adv. Funct. Mater.*, 2016, *26*, 4712.
- (S7) S. Dou, L. Tao, J. Huo, S. Y. Wang and L. M. Dai, *Energy Environ. Sci.*, 2016, 9, 1320.
- (S8) H. X. Zhong, K. Li, Q. Zhang, J. Wang, F. L. Meng, Z. J. Wu, J. M. Yan and X. B. Zhang, NPG Asia Mater., 2016, 8, e308.
- (S9) P. Ganesan, M. Prabu, J. Sanetuntikul and S. Shanmugam, ACS Catal., 2015, 5, 3625.
- (S10) H. Liu, F. X. Ma, C. Y. Xu, L. Yang, Y. Du, P. P. Wang, S. Yang and L. Zhen, ACS Appl. Mater. Interfaces, 2017, 9, 11634.
- (S11) T. T. Liu, Q. Liu, M. Abdullah, Y. L. Luo and X. P. Sun, *Chem. Commun.*, 2015, 51, 16683.

(S12) M. Liao, G. F. Zeng, T. T. Luo, Z. Y. Jin, Y. J. Wang, X. M. Kou and D. Xiao, *Electrochim. Acta*, 2016, **194**, 59.

(S13) X. B. Liu, Y. C. Liu and L. Z. Fan, J. Mater. Chem. A, 2017, 5, 15310.

- (S14) C. C. Sun, Q. C. Dong, S. Yang, Z. Y. Dai, J. J. Lin, P. Chen, W. Huang and X. C. Dong, *Nano Res.*, 2016, **9**, 2234.
- (S15) R. R. Liu, H. M. Zhang, X. Zhang, T. X. Wu, H. J. Zhao and G. Z. Wang, *RSC Adv.*, 2017, 7, 19181.
- (S16) Q. C. Dong, Q. Wang, Z. Y. Dai, H. J. Qiu and X. C. Dong, ACS Appl. Mater. Interfaces, 2016, 8, 26902.
- (S17) Y. F. Zhao, S. Q. Chen, B. Sun, D. W. Su, X. D. Huang, H. Liu, Y. M. Yan, K. N. Sun and G. X. Wang, *Sci. Rep.* 2015, **5**, 7629.
- (S18) T. Y. Ma, S. Dai, J. Mietek and S. Z. Qiao, J. Am. Chem. Soc., 2014, 136, 13925.
- (S19) A. K. Jakub, Z. He, S. M. Andrew and A. S. Jay, Chem. Mater., 2012, 24, 3567.
- (S20) L. L. Li, T. Tian, J. Jiang and L. H. Ai, J. Power Sources, 2015, 294, 103.
- (S21) X. M. Zhou, X. T. Shen, Z. M. Xia, Z. Y. Zhang, J. Li, Y. Y. Ma and Y. Q. Qu, ACS Appl. Mater. Interfaces, 2015, 7, 20322.
- (S22) Y. F. Zhao, B. Sun, X. D. Huang, H. Liu, D. W. Su, K. N. Sun and G. X. Wang, J.Mater. Chem. A, 2015, 3, 5402.
- (S23) S. Q. Chen, Y. F. Zhao, B. Sun, Z. M. Ao, X. Q. Xie, Y. Y. Wei and G. X. Wang, ACS Appl. Mater. Interfaces, 2015, 7, 3306.
- (S24) L. Xu, Z. M. Wang, J. L. Wang, Z. H. Xiao, X. B. Huang, Z. G. Liu and S. Y.Wang, *Nanotechnology*, 2017, 28, 165402.