Supporting information

Modulation of bulk and surface electronic structures for oxygen evolution by Cr, P co-doped Co₃S₄

Yiting Chen,^{‡a} Xiaoyun Zhang,^{‡a} Xiaoshuang Ma^a and Yuqiao Wang^{*a}

^a Research Center for Photoelectrochemistry and Devices, School of Chemistry and Chemical

Engineering, Southeast University, Nanjing 211189, China

* Corresponding author. Tel: +86 25 52090619; Fax: +86 25 52090621

E-mail address: yqwang@seu.edu.cn (Y. Wang).

[‡] These authors contributed equally to this work.

Experimental Section

Chemicals

All chemical reagents were analytical grade and used directly without further purification. A piece of nickel foam (NF, 4 cm \times 3 cm) was pretreated by 3 M HCl under sonication and washed by deionized water and alcohol three times, respectively.

Materials Synthesis

Synthesis of Cr-Co precursor

Typically, 1.746 g Co(NO₃)₂·6H₂O, 0.296 g NH₄F, 1.441 g urea, and 0.036 g Cr(NO₃)₂·9H₂O were added into 60 mL of deionized water under stirring for 30 min to form a transparent solution. Then, the mixture was transferred into a 100 mL Teflon-lined stainless-steel autoclave with the clean NF at 120 °C for 8 h. The Cr-Co precursor was gained after being washed with absolute ethanol three times to remove impurities and dried at 60 °C overnight in a vacuum.

Synthesis of Cr-Co₃S₄ nanorods

The homogeneous solution was prepared with 0.27 g thioacetamide dissolved in 60 mL of absolute ethyl alcohol under stirring for 30 min to form a transparent solution. The solution was transferred into a 100 mL Teflon autoclave with an as-prepared Cr-Co precursor and maintained at $120 \,^{\circ}$ C for 4 h. Cr-Co₃S₄ was obtained after being washed with absolute ethanol three times to remove impurities and dried at 60 $^{\circ}$ C overnight in a vacuum.

Synthesis of P-Co₃S₄ nanorods

A piece of Co_3S_4/NF and 15 mg $NaH_2PO_2 \cdot H_2O$ were heated at 300 °C in N_2 atmosphere for 1 h to obtain P-Co₃S₄.

Synthesis of Cr, P-Co₃S₄ nanorods

A piece of Cr-Co₃S₄/NF and 15 mg NaH₂PO₂·H₂O were heated at 300 °C in N₂ atmosphere for 1 h to obtain Cr, P-Co₃S₄.

For comparison, Co_3S_4 , $Cr-Co_3S_4$, $P-Co_3S_4$ was synthesized by the same method. Co_3S_4 , $Cr-Co_3S_4$ were further annealed at 300 °C for 1 h with a heating rate of 5 °C min⁻¹ in N₂ atmosphere to improve the crystallinity of the material. The loading masses of Co_3S_4 , $Cr-Co_3S_4$, $P-Co_3S_4$ and Cr, $P-Co_3S_4$ were of 11.58, 6.95, 11.57 and 7.69 mg cm⁻², respectively.

Materials Characterizations

The morphologies and structures were characterized by scanning electron microscope (SEM, FEI Inspect F50), transmission electron microscope (TEM) and high-resolution TEM (HRTEM, FEI TECNAI G2 20) with the energy dispersive spectrometer mapping analysis. The crystal structure was analyzed by X-ray diffraction (XRD, Ultima IV). The X-ray photoelectron spectroscopy (XPS, AXIS Ultra) was used to detect surface bonding.

Electrochemical Measurements

All electrochemical measurements were carried out on the electrochemical workstation (CHI 760E) in 1.0 M KOH. The OER performance was recorded using a three-electron system with a graphite rod as a counter electrode and a standard calomel electrode (SCE) as a reference electrode.

Linear sweep voltammetry (LSV) curves were collected at a scan rate of 2 mV s⁻¹ with 90% iR compensation. Tafel slopes were obtained from the curves of the overpotential versus the logarithm of current density according to LSV curves. All potentials were converted to a reversible hydrogen electrode (RHE) using the equation: $E_{RHE} = E_{SCE} + 0.241 \text{ V} + 0.059 \times \text{ pH}$. The C_{dl} values were evaluated based on cyclic voltammetry (CV) curves under non-Faradaic region. Electrochemical active surface area (ECSA) was calculated as following equation: $ECSA = C_{dl} / C_s$, C_s means a general specific capacitance (0.04 mF cm⁻²). Electrochemical impedance spectroscopy (EIS) was monitored with an amplitude of 5 mV and the frequency range from 10 kHz to 0.01 Hz. The multicurrent processes and chronopotentiometry curve were investigated without iR compensation.

For comparison, the RuO_2 and Ni foam were evaluated. The working electrodes of RuO_2 was prepared by dispersing 2 mg powders into a water–ethanol solution containing 10 μ L Nafion and sonicating for 1 h to form a homogeneous catalyst ink. Then the catalyst ink was cast onto Ni foam and dried in air at room temperature.

Density Functional Theory Calculations

The difficulty of doping can be determined by the value of defect formation energy (ΔE_f). The defect formation energy can be calculated by the following equation:

 $\Delta Ef = Ef - E \text{ (supercell)} - \sum n_i^s \mu_i^s$

where E_f is the total energy of a supercell with the defect; E (supercell) is the energy of the perfect supercell; n_i^s is the number of atoms of type s that were added or removed to create the defect; μ_i^s is the chemical potential of atomic specie s.

The theoretical calculations based on density functional theory (DFT) were carried out using the Vienna ab initio simulation package (VASP).¹ The projected augmented wave (PAW) pseudopotential was used to depict the ion-electron interactions. The exchange-correlation energy was described by Perdew-Burke-Ernzerhof functional within the generalized gradient approximation (GGA-PBE).² The slab models were based on (220) plane to evaluate the surface properties.

OER process was considered as a four-electron reaction pathway in alkaline.

 $OH - + * \rightarrow * OH + e -$

* OH + OH - \rightarrow * O + H2O (l) + e -

* O + OH - \rightarrow * OOH + e -

* OOH + OH - \rightarrow * + O2 (g) + H2O (l) + e -

where * means an active site on the catalyst surface. *OH, *O, and *OOH are the adsorbed intermediates.

The change of Gibbs free energy (ΔG_i , i means 1, 2, 3, 4) for each OER step should be calculated as followings:

$$\Delta Gi = \Delta E + \Delta EZPE + T\Delta S$$

where ΔE means the total energy difference between the reactant and product models in each step.

 ΔE_{ZPE} and ΔS are the differences in the zero-point energy and entropic contribution.

The theoretical overpotential (η) can be calculated by the following equation:

 $\eta = \max \{ \Delta G1, \Delta G2, \Delta G3, \Delta G4 \} / e - 1.23 V$

The transport properties of the system can be regulated effectively when impurity atoms are mixed into semiconductor materials.



Fig. S1. Model of (a) Cr-Co₃S₄ and (b) P-Co₃S₄. Color codes: Co- blue, S- yellow, Cr- grey, P- purple.

	OH [.]	*ОН	*0	*OOH	O ₂
Co ₃ S ₄					
Cr-Co₃S₄					
P-Co ₃ S ₄					
Cr, P-Co₃S₄					

Fig. S2. Corresponding intermediate configurations of OER process are displayed in side views of Co_3S_4 , $Cr-Co_3S_4$, $P-Co_3S_4$ and Cr, $P-Co_3S_4$. Color codes: Co- blue, S- yellow, Cr- grey, P- purple, adsorbed O species- red, and H- white.



Fig. S3. Schematic illustration for the synthesis of Cr, P-Co₃S₄.



Fig. S4. SEM images of (a) Co_3S_4 , (b) $Cr-Co_3S_4$, (c) $P-Co_3S_4$, (d) Cr, $P-Co_3S_4$.



Fig. S5. (a) TEM and (b) HRTEM image of Co₃S₄; (c) Electron diffraction pattern of Co₃S₄; (d) Integrated elemental mapping image of Co₃S₄; EDS elemental mapping of (e) Co, (f) S.



Fig. S6. XRD patterns of Co₃S₄, Cr-Co₃S₄, P-Co₃S₄ and Cr, P-Co₃S₄.



Fig. S7. XPS survey patterns of Co_3S_4 , $Cr-Co_3S_4$, $P-Co_3S_4$ and Cr, $P-Co_3S_4$.



Fig. S8. Nitrogen adsorption-desorption isotherms for Co_3S_4 and Cr, P- Co_3S_4 nanorods (inset: pore size distribution curve for Cr, P- Co_3S_4).



Fig. S9. CV curves of (a) Co₃S₄, (b)Cr-Co₃S₄, (c) P-Co₃S₄ and (d) Cr, P-Co₃S₄.



Fig. S10. A summary of OER performance for Co₃S₄, Cr-Co₃S₄, P-Co₃S₄ and Cr, P-Co₃S₄.



Fig. S11. Chronoamperometric (i-t) curves at 50 mA cm⁻² (inset: comparison LSV plots before and after measurement of Cr, $P-Co_3S_4$).



Fig. S12. SEM images of Cr, P-Co₃S₄ after 48h.



Fig. S13. (a) XRD and (b)XPS patterns of Cr, P-Co₃S₄ after 48 h. XPS spectra of (c) Co 2p (d) S 2p (e) Cr 2p (d) P 2p for Cr, P-Co₃S₄ after 48 h.

Elements	Cr, P-Co ₃ S ₄
Cr	1.06
P	1.78

Table S1. Atomic ratio (%) of Cr and P in Cr, P-Co₃S₄ by ICP analysis

Electro estalvat	Overpotential (mV)			Tofal along (mV dag-1)
Electrocataryst	10 mA cm ⁻²	100 mA cm ⁻²	250 mA cm ⁻²	Tatel slope (mv dec ')
Co_3S_4	287	384	441	73.8
Cr-Co ₃ S ₄	272	358	414	50.2
P-Co ₃ S ₄	275	362	425	59.7
Cr, P-Co ₃ S ₄	257	328	377	44.0

Table S2. The corresponding overpotential at 10, 100 and 250 mA cm⁻².

 Table S3. Comparison of OER performance between the catalyst prepared in this work with other sulfide electrocatalysts in 1 M KOH.

El stra stalast	0	D.C.	
Electrocatalyst	η ₁₀ (mV)	Tafel slope (mV dec ⁻¹)	Kelerences
Cr, P–Co ₃ S ₄	257	44.0	This work
N-CoS ₂ /G	260	56.3	3
Fe ₃ O ₄ /Co ₃ S ₄	270	56.0	4
$CoS_2/MoS_2@CC$	274	57.5	5
Co ₉ S ₈ -HCT	277	54.0	6
N-CoS ₂ YSSs	278	56.0	7
Co ₃ S ₄ /MoS ₂ NR	280	52.0	8
H-Fe-CoMoS	282	58.0	9
P-CoS	283	87.6	10

CoS2-MoS2 MSHSs	288	44.2	11
CoP/CN@MoS ₂	289	69.0	12
NiCoS@CNT	295	78.0	13
$CoMo_2S_4$	306	66.0	14
Co ₉ S ₈ @Co/Mn-S, N-PC	320	50.2	15
MoS ₂ @Fe-N-C	360	98.2	16
CoS_2 -C@MoS_2	391	46.0	17

Table S4. OER performances of the Cr, P-Co₃S₄ compared with other advanced transitionmetal-based electrocatalysts in 1.0 M KOH alkaline solution.

Electro esteleret	OE	Deferences	
Electrocatalyst	η ₁₀ (mV)	Tafel slope (mV dec ⁻¹)	- Kelerences
Cr, P–Co ₃ S ₄	257	44.0	This work
NiPS ₃ /Ni ₂ P	260	78.0	18
NiO/Co ₃ O ₄	262	58.0	19
N1-CoP@NPCNFs	266	70.0	20
Co ₃ O ₄ -Ag@B	270	62.0	21
Co/CoO@COF	278	81.12	22
Mo-Co ₃ O ₄ /CNTs	280	63.0	23
NiO@CFs	280	62.0	24
Fe-CoO NT	282	78.26	25
Co/CoO@NC@CC	284	76.0	26
Mn-CoP	288	77.2	27
CoP/BP	300	56.0	28
P-CoP-NPs	320	73.76	29
Ru-CoP/NC	330	65.0	30
NP/NiO	332	65.6	31
Mn ₃ O ₄ /CoP	360	51.8	32

		P-Co ₃ S ₄ cataly	sts.	
	Co_3S_4	Cr-Co ₃ S ₄	P-Co ₃ S ₄	Cr, P-Co ₃ S ₄
R _s (ohm)	4.23	1.58	2.97	1.43
R ₁ (ohm)	6.04	3.05	4.81	1.65
R ₂ (ohm)	2.16	1.13	1.41	1.05
CPE1-T	2.30	2.01	1.23	1.06
CPEI-P	0.31	0.75	0.62	0.29
CPE2-T	2.07	2.33	1.69	1.34
CPE2-P	0.92	0.73	0.86	0.97

Table S5. The corresponding EIS parameters of the as-prepared Co_3S_4 , $Cr-Co_3S_4$, $P-Co_3S_4$ and Cr,

 Table S6. Average resistivity and conductivity of the as-prepared catalysts.

Catalysts	Average resistivity (m Ω cm ⁻¹)	Average conductivity (S cm ⁻¹)
$Cr, P-Co_3S_4$	0.57	1778.50
Cr-Co ₃ S ₄	0.62	1662.75
P-Co ₃ S ₄	1.07	951.35
Co_3S_4	2.01	541.18

References

- G. Kresse, J. Furthmüller, *Comp. Mater. Sci.*, 1996, 6, 15; G. Kresse, J. Furthmüller, *Phys. Rev.* B, 1996, 54, 11169.
- J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.*, 1996, 77, 3865; J. P. Perdew, M. Ernzerhof, K. Burke, *J. Chem. Phys.*, 1996, 105, 9982.
- 3 Y. Tong, Q. Sun, P. Z. Chen, L. Chen, Z. F. Fei and P. J. Dyson, *ChemSusChem*, 2020, 13, 5112-5118.
- 4 J. Du, T. Zhang, J. L. Xing and C. L. Xu, J. Mater. Chem. A, 2017, 5, 9210-9216.
- 5 G. Y. Zhou, X. M. Wu, M. M. Zhao, H. Pang, L. Xu, J. Yang and Y. W. Tang, *ChemSusChem*, 2021, **14**, 699-708.
- 6 J. Zhao, J. Zhou, Z. J. Zhang, Q. Li and R. Liu, Chem. Eng. J., 2021, 418.
- X. F. Lu, S. L. Zhang, E. B. Shangguan, P. Zhang, S. Y. Gao and X. W. Lou, *Adv. Sci.*, 2020, 7, 2001178.
- Z. L. Li, W. L. Xu, X. L. Yu, S. X. Yang, Y. Zhou, K. Zhou, Q. K. Wu, S. L. Ning, M. Luo, D.
 K. Zhao and N. Wang, *Inorg. Chem. Front.*, 2022, 9, 2139-2149.
- 9 Y. N. Guo, X. Zhou, J. Tang, S. Tanaka, Y. V. Kaneti, J. Na, B. Jiang, Y. Yamauchi, Y. S. Bando and Y. Sugahara, *Nano Energy*, 2020, 75.
- 10 Z. Li, C. L. Li, J. J. Huang, W. Sun, W. J. Cheng, C. C. He and L. Tian, *Int. J. Hydrogen Energ.*, 2022, 47, 15189-15197.
- S. S. Tang, X. G. Li, M. Courté, J. J. Peng and D. Fichou, *Inorg. Chem. Front.*, 2020, 7, 2241-2247.
- J.-G. Li, K. F. Xie, H. C. Sun, Z. S. Li, X. Ao, Z. H. Chen, K. K. Ostrikov, C. D. Wang and W. J. Zhang, *ACS Appl. Mater. Interfaces*, 2019, **11**, 36649-36657.
- 13 A. Ashok, A. Kumar, J. Ponraj and S. A. Mansour, *Carbon*, 2020, 170, 452-463.
- 14 V. Ganesan and J. Kim, Int. J. Hydrogen Energ., 2020, 45, 13290-13299.
- R.-M. Sun, L. Zhang, J.-J. Feng, K.-M. Fang and A.-J. Wang, *J. Colloid Interface Sci.*, 2022, 608, 2100-2110.
- 16 Y. Yan, S. Liang, X. Wang, M. Y. Zhang, S. M. Hao, X. Cui, Z. W. Li and Z. Q. Lin, Proc. Natl. Acad. Sci. U. S. A., 2021, 118.

- Y. Zhu, L. F. Song, N. Song, M. X. Li, C. Wang and X. F. Lu, ACS Sustain. Chem. Eng., 2019, 7, 2899-2905.
- 18 Q. H. Liang, L. X. Zhong, C. F. Du, Y. B. Luo, J. Zhao, Y. Zheng, J. W. Xu, J. M. Ma, C. T. Liu, S. Z. Li and Q. Y. Yan, ACS Nano, 2019, 13, 7975-7984.
- 19 J. Y. Zhang, J. M. Qian, J. Q. Ran, P. X. Xi, L. J. Yang and D. Q. Gao, ACS Catal., 2020, 10, 12376-12384.
- 20 Z. X. Cui, J. X. Lin, J. H. Wu, J. Q. Yu, J. H. Si and Q. T. Wang, J. Alloy. Compd., 2021, 854, 156830.
- 21 A. Saad, D. Q. Liu, Y. C. Wu, Z. Q. Song, Y. Li, T. Najam, K. Zong, P. Tsiakaras and X. K. Cai, *Applied Catalysis B: Environmental*, 2021, **298**, 120529.
- 22 X. Q. Ye, J. C. Fan, Y. L. Min, P. H. Shi and Q. J. Xu, Nanoscale, 2021, 13, 14854-14865.
- K. L. Lu, T. T. Gu, L. J. Zhang, Z. C. Wu, R. H. Wang and X. J. Li, *Chem. Eng. J.*, 2021, 408, 127352.
- 24 R. Atchudan, N. C. S. Selvam, T. N. J. I. Edison, S. Perumal, R. Vinodh and Y. R. Lee, *Fuel*, 2021, **294**, 120558.
- 25 F. Tang, S. J. Guo, Y. G. Sun, X. J. Lin, J. H. Qiu and A. M. Cao, *Small Structures*, 2022, 3, 2100211.
- 26 K. Q. Dai, N. Zhang, L. L. Zhang, L. X. Yin, Y. F. Zhao and B. Zhang, *Chem. Eng. J.*, 2021, 414, 128804.
- 27 Y. H. Liu, N. Ran, R. Y. Ge, J. J. Liu, W. X. Li, Y. Y. Chen, L. Y. Feng and R. C. Che, *Chem. Eng. J.*, 2021, **425**, 131642.
- 28 H. Xiao, X. L. Du, M. Zhao, Y. Li, T. J. Hu, H. S. Wu, J. F. Jia and N. J. Yang, *Nanoscale*, 2021, **13**, 7381-7388.
- 29 Y. X. Li, Z. Q. Zhang, M. G. Xie, C. G. Li, Z. Shi and S. H. Feng, *Appl. Surf. Sci.*, 2022, 583, 152402.
- 30 Y. R. Hao, H. Xue, J. Sun, N. K. Guo, T. S. Song, J. W. Sun and Q. Wang, ACS Appl. Mater. Interfaces, 2021, 13, 56035-56044.
- 31 P. Bhanja, Y. Kim, B. Paul, Y. V. Kaneti, A. A. Alothman, A. Bhaumik and Y. Yamauchi, *Chem. Eng. J.*, 2021, 405, 126803.
- 32 R. Dong, A. Q. Zhu, W. X. Zeng, L. L. Qiao, L. L. Lu, Y. Liu, P. F. Tan and J. Pan, Appl. Surf.

Sci., 2021, 544, 148860.