# **Supplementary Material**

# Surface Reconstruction through Cathodic Activation of First-row Transition Metal Phosphides for Enhanced Hydrogen Evolution

Bin Dong \*a, Meng-Xuan Li a, Xiao Shang a, Ya-Nan Zhou a, Wen-Hui Hu b,c, Yong-Ming Chai a

<sup>a</sup>State Key Laboratory of Heavy Oil Processing, College of Chemistry and Chemical Engineering,

China University of Petroleum (East China), Qingdao 266580, PR China

<sup>b</sup>Department of Chemistry, Marquette University, Milwaukee, Wisconsin 53201, United States

<sup>c</sup>X-ray Science Division, Argonne National Laboratory, Argonne, Illinois 60349, United States

<sup>\*</sup> Corresponding author. Email: dongbin@upc.edu.cn (B. Dong)

Tel: +86-532-86981156, Fax: +86-532-86981156

#### **Electrochemical measurements**

The electrochemical measurements were performed in the same three-electrode system. Linear sweep voltammetry (LSV) was undertaken at a scan rate of 5 mV s<sup>-1</sup>. Electrochemical impedance spectroscopy (EIS) was conducted at -1.18 V (vs. SCE) from  $10^5$  to  $10^{-2}$  Hz with an AC voltage of 5 mV. The double-layer capacitance (C<sub>dl</sub>) was estimated by cyclic voltammogram (CV) at the non-Faradic region (-0.9 to -1.1 V vs. SCE) at a series of scan rates (40, 60, 80, 100 and 120 mV s<sup>-1</sup>). The stabilities were estimated by chronoamperometry (*i*-*t*) or CV (-1.0 to -1.6 V vs. SCE). The calibration of SCE was displayed in the supporting information. All electrochemical data were corrected against the ohmic potential drop with the iR correction of 100 %. The potentials conversion from SCE to reversible hydrogen electrode (RHE) is based on the equation as follows:

$$E (vs. RHE) = E (vs. SCE) + 0.244 V + (0.059 V) pH$$

According to previous literature [27,28], the metal impurity in KOH often poison catalysts, leading to decreased HER performance. Besides, taking the low content into account, this work applied 1.0 M unpurified KOH as alkaline electrolyte.

#### **Material characterization**

X-ray diffraction (XRD) patterns were collected on the X'Pert PRO MPD diffractometer (Cu Kα). Scanning electron microscopy (SEM) images were obtained on the Hitachi S-4800 instrument. X-ray fluorescence elemental analysis (EDX) was undertaken over a representative area of the samples. X-ray photoelectron spectra (XPS) were conducted on a ThermoFisher Scientific II spectrometer with Al as a

photo source. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were carried out on FEI Tecnai G2. The inductively coupled plasma optical emission spectrometry (ICP-OES) for asprepared catalysts was analyzed on Shidmadzu ICPE-9000.

#### Steady state X-ray Absorption spectroscopy (XAS)

XAS spectra were measured at the beamline 12-BM at the Advanced Photon Source, Argonne National Laboratory. The XAS data were collected under room temperature with fluorescence mode using a 13-element germanium solid-state detector. There are three ion chambers. One of them is placed before the sample and used as the incident X-ray flux reference signal. The other two ion chambers (second and third chambers) are placed after the samples. The cobalt/vanadium foil is placed between the second and third ion chambers and used for energy calibration and collecting the cobalt/vanadium metal spectrum. The powder samples were dispersed on Kapton tape during the measurement. Qualitatively, the available information from the EXAFS oscillations was the amplitude, the frequency, and the phase, as shown in Fig. S23.

To a first approximation, amplitude is proportional to coordination number, while frequency is inversely related to bond length. The phase of the EXAFS and the shape of the amplitude envelope provide information about scatterer type. The EXAFS oscillations of Co K-edge indicates that the collected EXAFS spectra was with well noise-signal ratio. Least square EXAFS fitting was performed to quantificational extract the local atomic structure parameters of samples. The fitting result was displayed in Fig. 6-8, and the obtained parameters were listed in Table 1 and Table S6.

| Samples                                   | Со     | V      | Р      | mass loading,<br>mg cm <sup>-2</sup> |
|---|--------|--------|--------|--------------------------------------|
| Co <sub>0.95</sub> V <sub>0.05</sub> P/TF | 54.5 % | 3.1 %  | 42.4 % | 1.01                                 |
| Co <sub>0.9</sub> V <sub>0.1</sub> P/TF   | 52.5 % | 8.0 %  | 39.5 % | 0.67                                 |
| Co <sub>0.5</sub> V <sub>0.5</sub> P/TF   | 58.1 % | 13.8 % | 28.2 % | 0.53                                 |

 Table S1 Elemental mass ratio of catalysts by ICP-OES.



Fig. S1 SEM images. (a) CoP/TF, (b) A-CoP/TF, (c)  $Co_{0.9}V_{0.1}P/TF$  and (d) A- $Co_{0.9}V_{0.1}P/TF$ .



Fig. S2 HRTEM image with related FFT images (insets) from yellow dashed box: (a) CoP/TF, (b) A-CoP/TF, (c)  $Co_{0.9}V_{0.1}P/TF$  and (d) A-Co<sub>0.9</sub> $V_{0.1}P/TF$ .

| Samula                                    | alamanta | Sample elemental content |  |
|---|----------|--------------------------|--|
| Sample                                    | elements | (mg L <sup>-1</sup> )    |  |
| A-Co <sub>0.9</sub> V <sub>0.1</sub> P/TF | Со       | 2.877                    |  |
|   | V        | 0.237                    |  |
|   | Р        | 1.808                    |  |

 Table S2. Elemental contents in electrolyte after activation by ICP-OES measurement.



Fig. S3 EDX spectra of (a)  $Co_{0.9}V_{0.1}P/TF$  and (b) A- $Co_{0.9}V_{0.1}P/TF$ .



Fig. S4 Elemental mapping of (a)  $Co_{0.9}V_{0.1}P/TF$  and (b) A- $Co_{0.9}V_{0.1}P/TF$ .



Fig. S5 XPS spectra of CoP/TF and Co $_{0.9}V_{0.1}P/TF$ : (a) P 2p and (b) V 2p.

| Samples                                   |                          | Co 2p <sub>3/2</sub> | Co 2p <sub>1/2</sub> |            |  |
|---|--------------------------|----------------------|----------------------|------------|--|
|   | $\mathrm{Co}^{\delta^+}$ | Negative             | $C \circ \delta^+$   | Negative   |  |
|   |                          | shift (eV)           | Co                   | shift (eV) |  |
| CoP/TF                                    | 778.88                   |                      | 793.78               |            |  |
| A-CoP/TF                                  | 778.48                   | -0.40                | 793.36               | -0.42      |  |
| Co <sub>0.9</sub> V <sub>0.1</sub> P/TF   | 779.02                   |                      | 793.66               |            |  |
| A-C0 <sub>0.9</sub> V <sub>0.1</sub> P/TF | 778.36                   | -0.66                | 793.06               | -0.60      |  |

Table S3 The negative shift of binding energy of  $Co^{\delta^+}$  before and after cathodic activation.

#### The saturated calomel electrode (SCE) calibration [1]

The calibration of SCE electrode is performed in a three-electrode setup, containing Pt foils as both working and counter electrodes with the SCE as reference electrode. The 1.0 M KOH electrolyte is saturated with  $H_2$  gas. Linear scanning voltammetry (LSV) is performed at a scan rate of 1 mV s<sup>-1</sup>. As shown in Fig. S9, the zero current point is at -1.04 V, thus E (RHE) = E (SCE) + 1.04 V.



Fig. S6 Polarization curve for calibrating the SCE reference electrode.



Fig. S7. Schematic illustration of the catalytic roles of  $OH_{ad}$ - $(H_2O)_x$ - $AM^+$  in the

alkaline HER kinetics.



Fig. S8 (a) XRD patterns of  $Co_{0.95}V_{0.05}P/TF$ ,  $Co_{0.9}V_{0.1}P/TF$  and  $Co_{0.5}V_{0.5}P/TF$ . SEM images of (b)  $Co_{0.95}V_{0.05}P/TF$  and (c)  $Co_{0.5}V_{0.5}P/TF$ . Co 2p XPS spectra of (d)  $Co_{0.95}V_{0.05}P/TF$  and (e)  $Co_{0.5}V_{0.5}P/TF$  before and after cathodic activation.



Fig. S9 (a) HER polarization curves of  $Co_{0.95}V_{0.05}P/TF$ ,  $Co_{0.9}V_{0.1}P/TF$ and  $Co_{0.5}V_{0.5}P/TF$  before and after cathodic activation. (b) Comparison of overpotentials at the current density of -100 mA cm<sup>-2</sup> varied by V doping. (c) HER polarization curves normalized by ECSA.

Table S4 Comparison of HER activities between  $A-Co_{0.9}V_{0.1}P/TF$  and CoP-based materials in 1.0 M KOH. (J, Current density,  $\eta$ , overpotential at corresponding J, b, Tafel slope)

| Sample  | J (mA cm <sup>-2</sup> ) | η (mV) | B (mV dec <sup>-1</sup> ) | Ref.      |
|---|--------------------------|--------|---------------------------|-----------|
| (Ni <sub>0.33</sub> Fe <sub>0.67</sub> ) <sub>2</sub> P | 50                       | 214    | 73.2                      | [2]       |
| MoP/NF  | 10                       | 114    | 54.6                      | [3]       |
| CP@Ni-P   | 10                       | 117    | 60                        | [4]       |
| Fe-CoP/Ti   | 10                       | 78     | 75                        | [5]       |
| NiCoP@Cu <sub>3</sub> P/CF                              | 10                       | 54     | 73                        | [6]       |
| Ni1M01P NSs@MCNTs                                       | 10                       | 135    | 137.5                     | [7]       |
| Мо-СоР  | 10                       | 40     | 65                        | [8]       |
| NiCoP/rGO   | 10                       | 209    | 124.1                     | [9]       |
| O3-V10-Ni <sub>2</sub> P                                | 10                       | 257    | 43.5                      | [10]      |
| Co-P film   | 10                       | 94     | 42                        | [11]      |
| Ni <sub>0.51</sub> Co <sub>0.49</sub> P                 | 10                       | 83     | 43                        | [12]      |
| CoP/NCNHP   | 10                       | 115    | 66                        | [13]      |
| CoP NWs/CoP NPs@NC/CC                                   | 10                       | 113    | 87                        | [14]      |
| Ce1–CoP   | 10                       | 144    | 70                        | [15]      |
| CoP-NCDs-0.5/NF   | 10                       | 103    | 92                        | [16]      |
| CoP/Co <sub>2</sub> P                                   | 10                       | 133    | 60                        | [17]      |
| W-CoP NAs/CC  | 10                       | 94     | 58                        | [18]      |
| CoP-FeP   | 10                       | 198    | 51                        | [19]      |
| N-C@CoP/Ni <sub>2</sub> P                               | 10                       | 176    | 86                        | [20]      |
| CoP <sub>3</sub> /Ni <sub>2</sub> P                     | 10                       | 115    | 49                        | [21]      |
| Cu-CoP NRAs/CC  | 10                       | 81     | 102                       | [22]      |
| Fe <sub>0.25</sub> -CoP                                 | 10                       | 111    | 62                        | [23]      |
| Mn-CoP  | 10                       | 195    | 85                        | [24]      |
| A-C0 <sub>0.9</sub> V <sub>0.1</sub> P/TF               | 10                       | 75     | 72                        | This work |



Fig. S10 Comparison of HER activities between  $A-Co_{0.9}V_{0.1}P/TF$  and CoP-based materials from Table S3 in 1.0 M KOH.



Fig. S11 Physical characterization of V-O-P/TF. (a) XRD patterns, (b) SEM image, (c) V 2p and (d) P 2p XPS spectra.



Fig. S12 HER polarization curve of V-O-P/TF before and after activation.



**Fig. S13** Nyquist plots of as-prepared catalysts. The insertion is the electric circuit. The R1, R2 and CPE1 represent the charge transfer resistance, contact resistance and Constant phase angle element.

## Calculation method of electrochemically active surface area (ECSA)

According to previous report [25], the calculation of ECSA and roughness factor (RF) are based on the following equation:

$$ECSA = C_{dl}/C_s \tag{1}$$

In eq (1),  $C_{dl}$  is the measured double layer capacitance of samples in 1.0 M KOH (mF) and  $C_s$  is the specific capacitance of the catalyst ( $C_s = 0.04$  mF cm<sup>-2</sup> in 1.0 M KOH).



Fig. S14 CV plots for measuring the  $C_{dl}$  values. (a) CoP and A-CoP/TF. (b) Co<sub>0.9</sub>V<sub>0.1</sub>P/TF and A-Co<sub>0.9</sub>V<sub>0.1</sub>P/TF. (c) Determined double-layer capacitance (C<sub>dl</sub>).



Fig. S15 CV plots for measuring  $C_{dl}$  values: (a)  $Co_{0.95}V_{0.05}P/TF$  and (b)  $Co_{0.5}V_{0.5}P/TF$  with (c) determined  $C_{dl}$  values.

#### **Calculation of turnover frequency (TOF)**

The turnover frequency (TOF) of catalysts for HER was calculated based on a previously reported. [26] Figure S16a shows CV curves for CoP/TF, A-CoP/TF,  $Co_{0.9}V_{0.1}P/TF$  and A- $Co_{0.9}V_{0.1}P/TF$  in the region of -0.2 to 0.6V (relative to RHE) in 1M phosphate buffer solution (PBS, pH=7) with a scan rate of 50mV S<sup>-1</sup>. The absolute voltammetric charge (Q) can be obtained from the CVs, which calculates the number of active sites (n) by the equation: n = Q/2F.

Assuming one electron redox process, the integrated charge over the whole potential range was divided by two. Then, the value was divided by the Faraday constant to get the number of active sites for different samples. The turnover frequency (s<sup>-1</sup>) can be estimated according to this equation: TOF = I/2nF.

where I is the current (A) during the linear sweep measurement and F is the Faraday constant (96485.3 C mol<sup>-1</sup>).

The Determined TOF values calculated by the above equation are shown in FigureS16b.



Fig. S16 (a) CV plots for measuring TOF values in 1.0 M PBS solution (pH=7) with scan rate of 50 mV s<sup>-1</sup>. (b) Determined TOF values.

|   | C <sub>dl</sub> | Cs                     | ECSA               |
|---|-----------------|------------------------|--------------------|
| Sample                                      | (mF)            | (mF cm <sup>-2</sup> ) | (cm <sup>2</sup> ) |
| A-C0 <sub>0.95</sub> V <sub>0.05</sub> P/TF | 44.4            | 0.04                   | 1110.0             |
| A-C0 <sub>0.9</sub> V <sub>0.1</sub> P/TF   | 44.5            | 0.04                   | 1112.5             |
| A-C0 <sub>0.5</sub> V <sub>0.5</sub> P/TF   | 47.1            | 0.04                   | 1177.5             |

 Table S4 The calculated ECSA of all samples.



**Fig. S17** Comparison of XPS spectra of A-Co<sub>0.9</sub>V<sub>0.1</sub>P/TF before and after stability test. (a) Co 2p, (b) V 2p and (c) P 2p.



Fig. S18 LSV plot of (a) A-Co<sub>0.9</sub>V<sub>0.1</sub>P/TF and (b) Pt/C catalyst before and after 1000 CV scan.



Fig. S19 Derivative spectra of XANES region of the prepared electrocatalysts at the

Co K edge.



Fig. S20 (a) FEFF input  $V_2O_5$  model. The grey atom is V atom and the red atom is O atom. (b) Fourier-transformed R-space spectra with fitting line for V K-edge of the prepared electrocatalysts.

| Samples                                   | shell | CN | $\sigma^2$ (Å <sup>2</sup> ) | R(Å)  | ΔE     |
|---|-------|----|------------------------------|-------|--------|
| Co <sub>0.9</sub> V <sub>0.1</sub> P/TF   | V-01  | 1  | 0.006                        | 1.626 | -5.0   |
|   | V-02  | 1  | 0.0095                       | 1.826 | -5.0   |
|   | V-O3  | 3  | 0.001                        | 1.961 | -5.0   |
|   | V-V   | 2  | 0.0085                       | 2.942 | -5.0   |
|   |       |    |                              |       |        |
| A-C0 <sub>0.9</sub> V <sub>0.1</sub> P/TF | V-01  | 1  | 0.009                        | 1.64  | -4.567 |
|   | V-02  | 1  | 0.00929                      | 1.85  | -4.567 |
|   | V-O3  | 3  | 0.00324                      | 1.986 | -4.567 |
|   | V-V   | 2  | 0.01                         | 2.99  | -4.567 |

Table S6 EXAFS fitting parameter for V edge.



Fig. S21 XRD patterns: (a) NiP/TF, Ni<sub>0.9</sub>V<sub>0.1</sub>P/TF and A-Ni<sub>0.9</sub>V<sub>0.1</sub>P/TF, (b) FeP/TF, Fe<sub>0.9</sub>V<sub>0.1</sub>P/TF and A-Fe<sub>0.9</sub>V<sub>0.1</sub>P/TF.



Fig. S22 (a) HER polarization curves of (a) NiP/TF and Ni<sub>0.9</sub>V<sub>0.1</sub>P/TF, (b) FeP/TF and Fe<sub>0.9</sub>V<sub>0.1</sub>P/TF before and after cathodic activation, (c) comparison of A-Co<sub>0.9</sub>V<sub>0.1</sub>P/TF,

A-Ni<sub>0.9</sub>V<sub>0.1</sub>P/TF

and

A-Fe<sub>0.9</sub>V<sub>0.1</sub>P/TF.



Fig. S23 Co K-edge EXAFS oscillations for (a) CoP-TF and A-CoP-TF and (b)  $Co_{0.9}V_{0.1}P/TF$  and A-Co<sub>0.9</sub> $V_{0.1}P/TF$ .

### REFERENCES

- 1. Y. Li, W. Zhou, H. Wang, L. Xie, Y. Liang, F. Wei, J.-C. Idrobo, S. J. Pennycook and H. Dai, *Nat. Nanotechnol.*, 2012, **7**, 394-400.
- Y. Li, H. Zhang, M. Jiang, Q. Zhang, P. He and X. Sun, *Adv. Funct. Mater.*, 2017, 27, 1702513.
- 3. Y. Jiang, Y. Lu, J. Lin, X. Wang and Z. Shen, Small Methods, 2018, 2, 1700369.
- X. Wang, W. Li, D. Xiong, D. Y. Petrovykh and L. Liu, *Adv. Funct. Mater.*, 2016,
   26, 4067-4077.
- 5. C. Tang, R. Zhang, W. Lu, L. He, X. Jiang, A. M. Asiri and X. Sun, *Adv. Mater.*, 2017, **29**, 1602441.
- 6. X. Ma, Y. Chang, Z. Zhang and J. Tang, J. Mater. Chem. A, 2018, 6, 2100-2106.
- 7. H. Xu, J. Wei, K. Zhang, Y. Shiraishi and Y. Du, ACS Appl. Mater. Inter., 2018, 10, 29647-29655.
- C. Guan, W. Xiao, H. Wu, X. Liu, W. Zang, H. Zhang, J. Ding, Y. P. Feng, S. J.
   Pennycook and J. Wang, *Nano Energy*, 2018, 48, 73-80.
- J. Li, M. Yan, X. Zhou, Z. Q. Huang, Z. Xia, C. R. Chang, Y. Ma and Y. Qu, *Adv. Funct. Mater.*, 2016, 26, 6785-6796.
- K. N. Dinh, X. Sun, Z. Dai, Y. Zheng, P. Zheng, J. Yang, J. Xu, Z. Wang and Q.
   Yan, *Nano Energy*, 2018, 54, 82-90.
- 11. N. Jiang, B. You, M. Sheng and Y. Sun, Angew. Chem. Int. Ed., 2015, **127**, 6349-6352.
- 12. J. Yu, Q. Li, Y. Li, C. Y. Xu, L. Zhen, V. P. Dravid and J. Wu, Adv. Funct. Mater.,

2016, **26**, 7644-7651.

- 13. Y. Pan, K. Sun, S. Liu, X. Cao, K. Wu, W.-C. Cheong, Z. Chen, Y. Wang, Y. Li and Y. Liu, *J. Am. Chem. Soc.*, 2018, **140**, 2610-2618.
- J. Fu, Y. Wu, P. Xin, Z. Jin, Q. Zhang, J. Zhang, Z. Hu, Z. Chen and S. Huang, *Int. J. Energy Res.*, 2022, 46, 11359-11370.
- 15. J. Li, S. Zou, X. Liu, Y. Lu and D. Dong, ACS Sustain. Chem. Eng., 2020, 8, 10009-10016.
- H. Liu, Z. Liu, Y. Wang, J. Zhang, Z. Yang, H. Hu, Q. Zhao, H. Ning, L. Zhi and M. Wu, *Carbon*, 2021, **182**, 327-334.
- 17. G. Liu, M. Wang, Y. Xu, X. Wang, X. Li, J. Liu, X. Cui and L. Jiang, *J. Power Sources*, 2021, **486**, 229351.
- X. Wang, Y. Chen, B. Yu, Z. Wang, H. Wang, B. Sun, W. Li, D. Yang and W. Zhang, *Small*, 2019, 15, 1902613.
- 19. Y. Du, Z. Wang, H. Li, Y. Han, Y. Liu, Y. Yang, Y. Liu and L. Wang, *Int. J. Hydrog. Energ.*, 2019, **44**, 19978-19985.
- 20. T. Feng, F. Wang, Y. Xu, M. Chang, X. Jin, J. Piao and J. Lei, *Int. J. Hydrog. Energ.*, 2021, **46**, 8431-8443.
- K. Wang, X. She, S. Chen, H. Liu, D. Li, Y. Wang, H. Zhang, D. Yang and X.
   Yao, J. Mater. Chem. A, 2018, 6, 5560-5565.
- 22. L. Wen, Y. Sun, C. Zhang, J. Yu, X. Li, X. Lyu, W. Cai and Y. Li, ACS Appl. Energy Mater., 2018, 1, 3835-3842.
- 23. Q. Yang, H. Dai, W. Liao, X. Tong, Y. Fu, M. Qian and T. Chen, Dalton Trans.,

- 2021, **50**, 18069-18076.
- 24. Y. Li, B. Jia, B. Chen, Q. Liu, M. Cai, Z. Xue, Y. Fan, H.-P. Wang, C.-Y. Su andG. Li, *Dalton Trans.*, 2018, 47, 14679-14685.
- 25. C. C. McCrory, S. Jung, J. C. Peters and T. F. Jaramillo, *J. Am. Chem. Soc.*, 2013, 135, 16977-16987.
- 26. D. Merki, S. Fierro, H. Vrubel and X. Hu, Chem. Sci., 2011, 2, 1262-1267.
- 27. D. Weber, C. Dosche and M. Oezaslan, J. Electrochem. Soc., 2020, 167, 024506.
- 28. L. Brossard and J.-Y. Huot, J. Appl. Electrochem., 1989, 19, 882-888.