Supporting Information

## **A composite containing of vanadium metaphosphate and cobalt metaphosphate as an efficient electrocatalyst for both hydrogen evolution and oxygen evolution in alkaline water splitting**

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**Figure** S1 SEM images of the samples with the repetition number of (A) one, (B) three and (D) four.



**Figure S2** Atomic ratio of the samples with various repetition number based on SEM-EDS.



**Figure S3.** BET results of (A) pore properties and (B) area for  $CoV(PO<sub>3</sub>)<sub>2</sub>$ .



Figure S4. (A) TEM, (B) HRTEM and (D) HADDFT-STEM images of Co(PO<sub>3</sub>)<sub>2</sub>, and (D) the corresponding EDS, the elemental distribution of (E) O, (F) Co and (G) P, (H) the cross-sectional EDX line scanning according to the arrow in (C). The scale bars in (A), (B) and (C) are 100 nm, 10 nm and 50 nm, respectively.



**Figure S5.** (A) TEM, (B) HRTEM and (D) HADDFT-STEM images of  $V_X(PO_3)_2$ , and (D) the corresponding EDS, the elemental distribution of (E) O, (F) V and (G) P, (H) the cross-sectional EDX line scanning according to the arrow in (C). The scale bars in (A), (B) and (C) are 50 nm, 10 nm and 50 nm, respectively.



**Figure S6.** XPS of Co(PO<sub>3</sub>)<sub>2</sub> and the calibrated carbon.



**Figure S7.** XPS of  $V_X(PO_3)_2$  and the calibrated carbon.



**Figure S8.** XPS of  $CoV_X(PO_3)_2$  and the calibrated carbon.



**Figure S9**. HER comparison of the samples with different repetition number.



**Figure S10**. OER Comparison of the samples with different repetition number.



**Figure S11**. CV curves of  $Co(PO_3)_2$ ,  $CoV(PO_3)_2$  and  $V_X(PO_3)_2$  at various scanning speed and (D) the calculated  $C_{d}$ .



Figure S12 SEM of the sample  $CoV(PO<sub>3</sub>)<sub>2</sub>$  after (A) HER and (B) OER durability test.



Figure S13 HRTEM of  $CoV(PO<sub>3</sub>)<sub>2</sub>$  after (A) HER and (B) OER durability test.



**Figure S14** XRD of the sample after (A) HER and (B) OER durability test.



**Figure S15** XPS of (A) Co, (B) P, (C) V and (D) O after durability test.

**Table S1** Comparison of HER catalytic activity with reported HER catalysts for nonprecious materials in 1 M KOH.

Catalyst	$\eta$ (a) 10 mA cm <sup>-2</sup> mV	Electrolyte	Ref.
CoV(PO <sub>3</sub> ) <sub>2</sub>	96	1.0 M KOH	This work
Ni-Coalloy	107	1.0 M KOH	$\mathbf{1}$
$Co0.2$ -VOOH	130	1.0 M KOH	$\overline{c}$
V-doped $WS_2$	134	1.0 M KOH	3
NiCoP/rGO	209	1.0 M KOH	$\overline{4}$
$Ni$ -Co-P	150	1.0 M KOH	5
Janus Co/CoP	193	1.0 M KOH	6
CoOx@CN	232	1.0 M KOH	$\overline{7}$
mac-CoO@Co/NGC	145	1.0 M KOH	8
CuCo <sub>2</sub> O <sub>4</sub>	115	1.0 M KOH	9

**Table S2** Comparison of OER catalytic activity with reported OER catalysts for nonprecious materials in 1 M KOH.



## **References**

- 1. G. B. Darband, M. Aliofkhazraei, A. S. Rouhaghdam and M. A. Kiani, Three-dimensional Ni-Co alloy hierarchical nanostructure as efficient non-noble-metal electrocatalyst for hydrogen evolution reaction, *Appl. Surf. Sci.*, 2019, **465**, 846-862.
- 2. B. X. Tao, X. L. Li, C. Ye, Q. Zhang, Y. H. Deng, L. Han, L. J. Li, H. Q. Luo and N. B. Li, Onestep hydrothermal synthesis of cobalt–vanadium based nanocomposites as bifunctional catalysts for overall water splitting, *Nanoscale*, 2019, **11**, 18238-18245.
- 3. A. Jiang, B. Zhang, Z. Li, G. Jin and J. Hao, Vanadium-Doped WS2 Nanosheets Grown on Carbon Cloth as a Highly Efficient Electrocatalyst for the Hydrogen Evolution Reaction, *Chemistry – An Asian Journal*, 2018, **13**, 1438-1446.
- 4. J. Li, M. Yan, X. Zhou, Z.-Q. Huang, Z. Xia, C.-R. Chang, Y. Ma and Y. Qu, Mechanistic Insights on Ternary Ni2−xCoxP for Hydrogen Evolution and Their Hybrids with Graphene as Highly Efficient and Robust Catalysts for Overall Water Splitting, *Adv. Funct. Mater.*, 2016, **26**, 6785-6796.
- 5. Y. Feng, X.-Y. Yu and U. Paik, Nickel cobalt phosphides quasi-hollow nanocubes as an efficient electrocatalyst for hydrogen evolution in alkaline solution, *Chem. Commun.*, 2016, **52**, 1633-1636.
- 6. Z.-H. Xue, H. Su, Q.-Y. Yu, B. Zhang, H.-H. Wang, X.-H. Li and J.-S. Chen, Janus Co/CoP Nanoparticles as Efficient Mott–Schottky Electrocatalysts for Overall Water Splitting in Wide pH Range, *Adv. Energy Mater.*, 2017, **7**, 1602355.
- 7. H. Jin, J. Wang, D. Su, Z. Wei, Z. Pang and Y. Wang, In situ Cobalt–Cobalt Oxide/N-Doped Carbon Hybrids AsSuperior Bifunctional Electrocatalysts for Hydrogen and Oxygen Evolution, *J. Am. Chem. Soc.*, 2015, **137**, 2688-2694.
- 8. L.-F. Gu, J.-J. Chen, T. Zhou, X.-F. Lu and G.-R. Li, Engineering cobalt oxide by interfaces and pore architectures for enhanced electrocatalytic performance for overall water splitting, *Nanoscale*, 2020, **12**, 11201-11208.
- 9. A. T. Aqueel Ahmed, S. M. Pawar, A. I. Inamdar, H. Kim and H. Im, A Morphologically Engineered Robust Bifunctional CuCo2O4 Nanosheet Catalyst for Highly Efficient Overall Water Splitting, *Advanced Materials Interfaces*, 2020, **7**, 1901515.
- 10. P. Li, X. Duan, Y. Kuang, Y. Li, G. Zhang, W. Liu and X. Sun, Tuning Electronic Structure of

NiFe Layered Double Hydroxides with Vanadium Doping toward High Efficient Electrocatalytic Water Oxidation, *Adv. Energy Mater.*, 2018, **8**, 1703341.

- 11. F. Song and X. Hu, Exfoliation of layered double hydroxides for enhanced oxygen evolution catalysis, *Nat. Commun.*, 2014, **5**, 4477.
- 12. M. Al-Mamun, Y. Wang, P. Liu, Y. L. Zhong, H. Yin, X. Su, H. Zhang, H. Yang, D. Wang, Z. Tang and H. Zhao, One-step solid phase synthesis of a highly efficient and robust cobalt pentlandite electrocatalyst for the oxygen evolution reaction, *J. Mater. Chem. A*, 2016, **4**, 18314- 18321.
- 13. Y. P. Zhu, T. Y. Ma, M. Jaroniec and S. Z. Qiao, Self-Templating Synthesis of Hollow Co3O4 Microtube Arrays for Highly Efficient Water Electrolysis, *Angew. Chem. Int. Ed.*, 2017, **56**, 1324-1328.
- 14. S. Zhang, B. Ni, H. Li, H. Lin, H. Zhu, H. Wang and X. Wang, Cobalt carbonate hydroxide superstructures for oxygen evolution reactions, *Chem Commun (Camb)*, 2017, **53**, 8010-8013.
- 15. S. Du, Z. Ren, Y. Qu, J. Wu, W. Xi, J. Zhu and H. Fu, Co3O4 nanosheets as a high-performance catalyst for oxygen evolution proceeding via a double two-electron process, *Chem. Commun.*, 2016, **52**, 6705-6708.
- 16. S. Meghdadi, M. Amirnasr, M. Zhiani, F. Jallili, M. Jari and M. Kiani, Facile Synthesis of Cobalt Oxide Nanoparticles by Thermal Decomposition of Cobalt(II) Carboxamide Complexes: Application as Oxygen Evolution Reaction Electrocatalyst in Alkaline Water Electrolysis, *Electrocatalysis*, 2017, **8**, 122-131.
- 17. B. Zhang, X. Zheng, O. Voznyy, R. Comin, M. Bajdich, M. García-Melchor, L. Han, J. Xu, M. Liu, L. Zheng, F. P. García de Arquer, C. T. Dinh, F. Fan, M. Yuan, E. Yassitepe, N. Chen, T. Regier, P. Liu, Y. Li, P. De Luna, A. Janmohamed, H. L. Xin, H. Yang, A. Vojvodic and E. H. Sargent, Homogeneously dispersed multimetal oxygen-evolving catalysts, *Science*, 2016, **352**, 333-337.
- 18. D. Wang, Q. Li, C. Han, Q. Lu, Z. Xing and X. Yang, Atomic and electronic modulation of selfsupported nickel-vanadium layered double hydroxide to accelerate water splitting kinetics, *Nat. Commun.*, 2019, **10**, 3899.
- 19. K. Fan, H. Chen, Y. Ji, H. Huang, P. M. Claesson, Q. Daniel, B. Philippe, H. Rensmo, F. Li, Y. Luo and L. Sun, Nickel–vanadium monolayer double hydroxide for efficient electrochemical

water oxidation, *Nat. Commun.*, 2016, **7**, 11981.

- 20. Y. Xiao, C. Tian, M. Tian, A. Wu, H. Yan, C. Chen, L. Wang, Y. Jiao and H. Fu, Cobaltvanadium bimetal-based nanoplates for efficient overall water splitting, *Sci. Chin. Mater.*, 2018, **61**, 80-90.
- 21. P. Zhou, X. Lv, D. Xing, F. Ma, Y. Liu, Z. Wang, P. Wang, Z. Zheng, Y. Dai and B. Huang, High-efficient electrocatalytic overall water splitting over vanadium doped hexagonal Ni0.2Mo0.8N, *Appl. Catal. B Environ.*, 2020, **263**, 118330.
- 22. C. Guan, W. Xiao, H. Wu, X. Liu, W. Zang, H. Zhang, J. Ding, Y. P. Feng, S. J. Pennycook and J. Wang, Hollow Mo-doped CoP nanoarrays for efficient overall water splitting, *Nano Energy*, 2018, **48**, 73-80.
- 23. L. Huang, G. Gao, H. Zhang, J. Chen, Y. Fang and S. Dong, Self-dissociation-assembly of ultrathin metal-organic framework nanosheet arrays for efficient oxygen evolution, *Nano Energy*, 2020, **68**.