Supporting Information

Heterointerface Engineering of Vanadium Oxide/Cobalt Nitride as Efficient

Electrocatalysts for Alkaline Overall Water Splitting

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1. Experimental section

1.1 Chemicals

All the reagents involved in experiments were analytical grade and used without further purification. The cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$), 2-methylimidazole, potassium hydroxide (KOH), and ammonium metavanadate (NH_4VO_3) were purchased from Aladdin Chemical Reagent Co., Ltd. Urea was purchased from Rhawn Chemical Reagent Co., Ltd. The hydrochloric acid, ethanol, and acetone were obtained from Tianjin Kemiou Chemical Reagent Co., Ltd. The nickel foam (NF) and carbon cloth (CC) were purchased from Suzhou Taili Material Technology Co. Ltd. The deionized water was used throughout the experiments.

1.2 Synthesis of electrocatalysts

Preparation of ZIF-67: 2 mmol of $Co(NO_3)_2 \cdot 6H_2O$ and 16 mmol of 2-methylimidazole was dissolved in the 40 mL of deionized water, respectively. The aqueous solution containing 2-methylimidazole was then rapidly poured into the $Co(NO_3)_2 \cdot 6H_2O$ solution, and the color of solution changed to purple. Subsequently, the cleaned NF (3 × 3) was immersed in the mixed solution and maintained at room temperature for 24 h. The ZIF-67 was then in situ grown on NF and rinsed several times with deionized water.

Preparation of V/ZIF-67: 1 mmol of NH_4VO_3 was dissolved in a mixed solution consisting of 60 mL of deionized water and 20 mL of ethanol. After the resulting solution was heated to 85 °C, the aforementioned ZIF-67 was immersed in this solution and kept at this temperature for 20 min. The obtained sample was denoted as V/ZIF-67. In addition, the V/NF was also prepared by immersing bare NF in the solution containing 1 mmol of NH_4VO_3 .

Synthesis of VO/CoN: The V/ZIF-67 and urea (1.5 g) were placed at the downstream and upstream of the tube furnace, and the reaction temperature raised to 400 °C at a heating rate of 5 °C/min for 1 h. The obtained black sample was rinsed several times with deionized water and dried at 60 °C for 6 h, the collected V_2O_5/Co_2N electrode was named as VO/CoN.

Synthesis of counterparts: The synthesis of Co_2N and V_2O_5 was similar to that of VO/CoN, except that the precursor of V/ZIF-67 was changed to ZIF-67 and V/NF, respectively. Moreover, the preparation of VO/CoN-1g and VO/CoN-2g was also similar to that of VO/CoN, except that the amount of urea during nitridation process changed to 1.0 g

and 2.0 g, respectively. The synthesis of VO(0.2)/CoN, and VO(2.0)/CoN was also similar to that of VO/CoN, except that the immersed NH_4VO_3 concertation changed to 0.2 M and 2 M, respectively. The VO/CoN-500 was prepared by a similar method, expect that the nitridation temperature raised to 500 °C.

1.3 Material characterizations

X-ray diffraction (XRD) patterns were recorded on an X-ray diffractometer (Rigaku D/max-IIIB, Cu K α , λ =1.5406 Å) at a scan rate of 10° min⁻¹ in the range from 10° to 80°. The chemical composition measurements were performed by X-ray photoelectron spectroscopy (XPS, Xray source energy: 1486.7 eV, binding energy calibration: 284.6 eV, background pressure: 4×10^{-9} Pa) using Al K α radiation. Scanning electron microscopy (SEM) were carried out by using a Hitachi S-4800 microscope. Transmission electron microscopy (TEM), highresolution TEM (HRTEM), and element mapping were obtained from JEM-3010 (JEOL, Japan) with a voltage of 200 kV.

1.4 Electrochemical measurements

Electrochemical tests were conducted on a CHI760E electrochemical workstation. The asprepared VO/CoN, Co₂N, and V₂O₅ can be used directly as working electrode. The graphite rod and the standard Hg/HgO electrode were used as counter electrode and reference electrode, respectively. Linear sweep voltammogram (LSV) was conducted at a 5 mV/s scan rate after 60 cycles of CV tests to stabilize the current. A 90 % *iR* compensation was employed in the electrochemical measurement of LSV. CV curve was carried out with scan rates of 20, 40, 60, 80, 100 mV s⁻¹ to assess the electrochemical double-layer capacitance (C_{dl}) within non-Faradaic potential range. The electrochemical impedance spectroscopy (EIS) can be obtained at the frequency range of 0.01-100,000 Hz. The electrochemical stability was assessed by chronopotentiometry measurements. The Faraday efficiency was deter4mined by comparing the experimental and theoretical amounts of H₂ and O₂. Gas analysis was performed using the drainage method in a closed H-type electrolyzer under the chronoamperometry test at 100 mA cm⁻² for 600 s. The electrochemical stability of VO/CoN and VO/CoN||VO/CoN was evaluated by the chronopotentiometry measurements.

1.5 Computational details

All calculations based on density functional theory (DFT) were carried out using the Vienna

ab initio simulation package (VASP)¹. Perdew-Burke-Ernzerhof functional with a generalized gradient approximation (GGA-PBE) form was adopted to deal with the exchange correlation energies of the systems². The plane-wave and pseudo-potential techniques were used, and the energy cutoff was 400 eV. To obtain a good numerical sampling of electron densities in Brillouin zone, a (2×2×1) Monkhorst-Pack mesh was applied to the Co₂N (022), V₂O₅ (211) and V₂O₅/Co₂N surface. The optimization procedure was repeated until the maximum residual force is less than 0.05 eV·Å⁻¹ in any directions. During the calculations, a vacuum layer of 15 Å is used to avoid the fake interactions between periodic images along z axis. Visualization of the atomic structures are made by using VESTA³.

2. Supporting data



Fig. S1 SEM images of (a, b) ZIF-67 and (c, d) V/ZIF-67.



Fig. S2 SEM images of (a, b) VO/CoN-1g and (c, d) VO/CoN-2g.



Fig. S3 SEM images of (a, b) VO(0.2)/CoN and (c, d) VO(2.0)/CoN.



Fig. S4 (a, b) SEM images of VO/CoN-500.



Fig. S5 SEM images of (a, b) Co₂N and (c, d) V₂O₅.



Fig. S6 XRD patterns of (a) Co_2N and (b) V_2O_5 .



Fig. S7 HER (left) and OER (right) Tafel slops of various electrocatalysts in 1.0 M KOH.



Fig. S8 Nyquist plots of various electrocatalysts during HER process.



Fig. S9 HER CV curves of (a) VO/CoN, (b) Co_2N , and (c) V_2O_5 with different scan rates.



Fig. S10 The C_{dl} of various electrocatalysts for HER (left) and OER (right) in 1.0 M KOH.



Fig. S11 XRD pattern of VO/CoN after HER stability test.



Fig. S12 SEM images of VO/CoN after HER stability test.



Fig. S13 Nyquist plots of various electrocatalysts during OER process.



Fig. S14 OER CV curves of (a) VO/CoN, (b) Co₂N, and (c) V₂O₅ with different scan rates.



Fig. S15 XRD pattern of VO/CoN after OER stability test.



Fig. S16 (a, b) SEM and (c, d) TEM images of VO/CoN after OER stability test.



Fig. S17 XPS spectra of (a) Co 2p, (b) V 2p, (c) N 1s, and (d) O 1s for VO/CoN after OER stability test.

Electrocatalysts	$\eta_{10, \text{OER}}$	$\eta_{10, \text{HER}}$	Cell voltage $(V_{10} \text{ mA cm}^{-2})$	References
	(111)	(111 V)	(*, 10 m/ cm)	
Co ₃ Mo ₃ N/Ni ₃ Mo ₃ N	-	36	-	4
CoFeP-N	219	64	1.516	5
V-Ni ₃ N@MoOx	-	56	-	6
Co ₂ NiN/CC	315	123	1.457@10	7
Ni ₂ P/Co	316	149	1.56@10	8
Co/N-CNF	380	241	1.8@10	9
Co@NC-20	301	172	1.68@10	10
NiCo-NiCoO2@Cu2O@CF	327	133	1.69@10	11
Co/CoN/Co ₂ P-NPC	272	99	1.60@10	12
Co/CoN-NC-1	290	115	1.657@10	13
NiCo-LDH-OH	317	180	1.89@10	14
VO/CoN	264.4	80.5	1.587@10	Our work

Table S1. Comparison of HER, OER, and overall water splitting performance with reported electrocatalysts at 10 mA cm⁻² in 1.0 M KOH.



Fig. S18 (a) HER and (b) OER LSV curves of VO/CoN, VO/CoN-1g, and VO/CoN-2g.



Fig. S19 (a) HER and (b) OER LSV curves of VO/CoN, VO(0.2)/CoN, and VO(2.0)/CoN.



Fig. S20 (a) HER and (b) OER LSV curves of VO/CoN and VO/CoN-500.



Fig. S21 The optimized models of (a) CoN/VO, (b) V_2O_5 , (c) Co_2N .

References:

- 1. G. Kresse and J. Furthmüller, Phys. Rev. B, 1996, 54, 11169-11186.
- 2. B. Hammer, L. B. Hansen and J. K. Nørskov, Phys. Rev. B, 1999, 59, 7413-7421.
- 3. K. Momma and F. Izumi, J. Appl. Crystall., 2011, 44, 1272-1276.
- J. Tang, S. Zhang, Y. Zeng, B. Yang, K. Zhang, Y. Li, Y. Yao and J. Hu, Chem. Eng. J., 2024, 487, 150439.
- R. Wang, X. Sun, J. Zhong, S. Wu, Q. Wang and K. Ostrikov, *Appl. Catal. B: Environ. Energy*, 2024, **352**, 124027.
- 6. J.-T. Ren, D. Yang, L. Chen and Z.-Y. Yuan, Small, 2024, 20, 2406335.
- S. Li, C. Xu, Q. Zhou, Z. Liu, Z. Yang, Y. Gu, Y. Ma and W. Xu, J. Alloys Compds., 2022, 902, 163627.
- S. Li, Y. Zhang, Y. Yuan, F. Chang, K. Zhu, G. Li, Z. Bai and L. Yang, *Int. J. Hydrogen Energy*, 2023, 48, 3355-3363.
- 9. J. Liu, J. Zhou and M. K. H. Leung, ACS Appl. Mater. Interfaces, 2022, 14, 4399-4408.
- 10. Q. Wu, J. Gu, J. Wang, N. Liu and S. Chaemchuen, *Int. J. Hydrogen Energy*, 2023, **48**, 2663-2676.
- 11. U. Y. Qazi, R. Javaid, M. Zahid, N. Tahir, A. Afzal and X.-M. Lin, *Int. J. Hydrogen Energy*, 2021, **46**, 18936-18948.
- L. Hu, Y. Hu, R. Liu, Y. Mao, M. S. Balogun and Y. Tong, *Int. J. Hydrogen Energy*, 2019, 44, 11402-11410.
- 13. J. Lei, Z. Li, C. Wang, H. Yao, X. Wang and J. Hu, Chem. Eng. Sci., 2024, 293, 120068.
- 14. H. Yang, Z. Zhou, H. Yu, H. Wen, R. Yang, S. Peng, M. Sun and L. Yu, J. Colloid Interface Sci., 2023, 636, 11-20.