Supporting Information

Construction of $Co/Co_2P/VN$ heterointerfaces enhances trifunctional hydrogen and oxygen catalytic reactions

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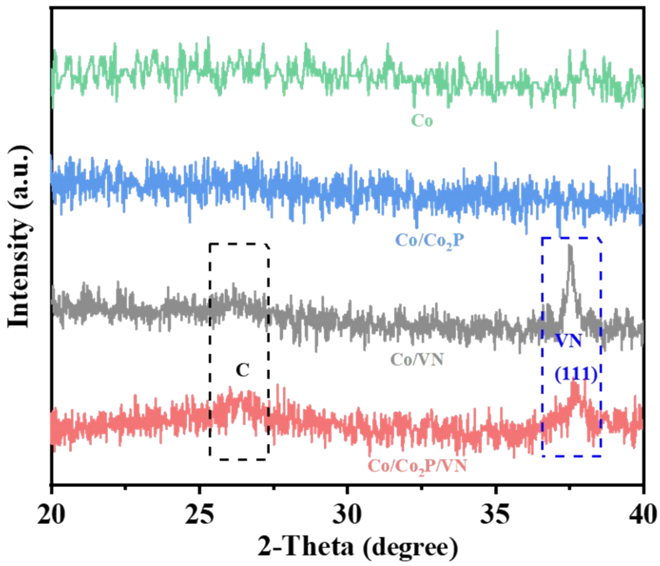

Fig. S1 XRD patterns with the zoomed-in image of Co, Co/Co_2P, Co/VN, and Co/Co_2P/VN.

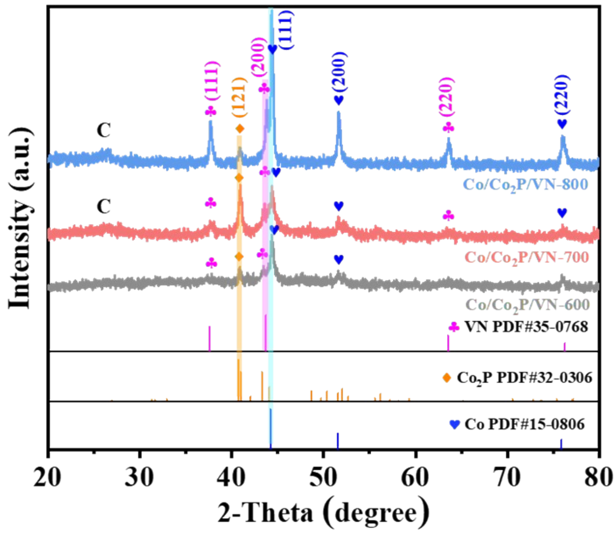

Fig. S2 XRD patterns of Co/Co_2P/VN with different pyrolysis temperatures (600, 700, and 800 ℃).

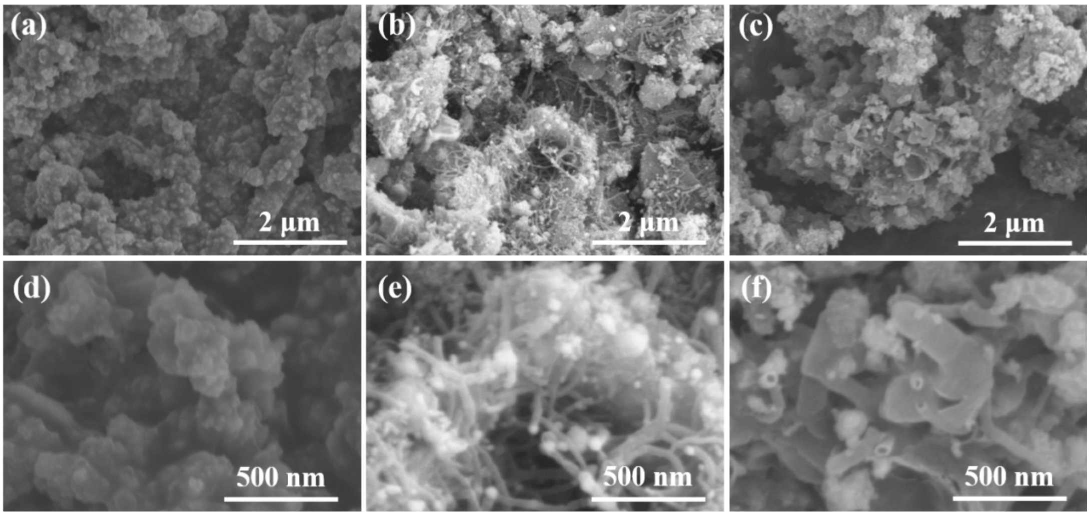

Fig. S3 SEM images of $Co/Co_2P/VN$ with different pyrolysis temperatures: (a, d) $Co/Co_2P/VN$-600; (b, e) $Co/Co_2P/VN$-700; (c, f) $Co/Co_2P/VN$-800.

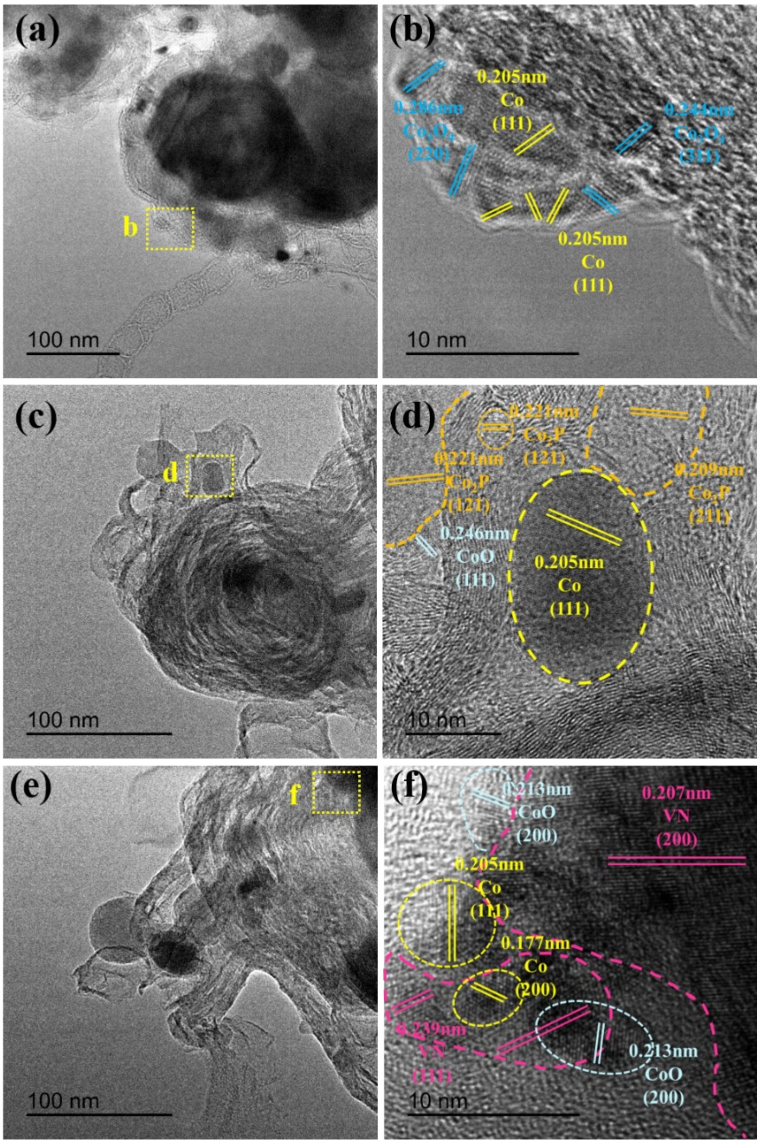

Fig. S4 TEM and HRTEM images of (a, b) Co, (c, d) Co/Co_2P, and (e, f) Co/VN.

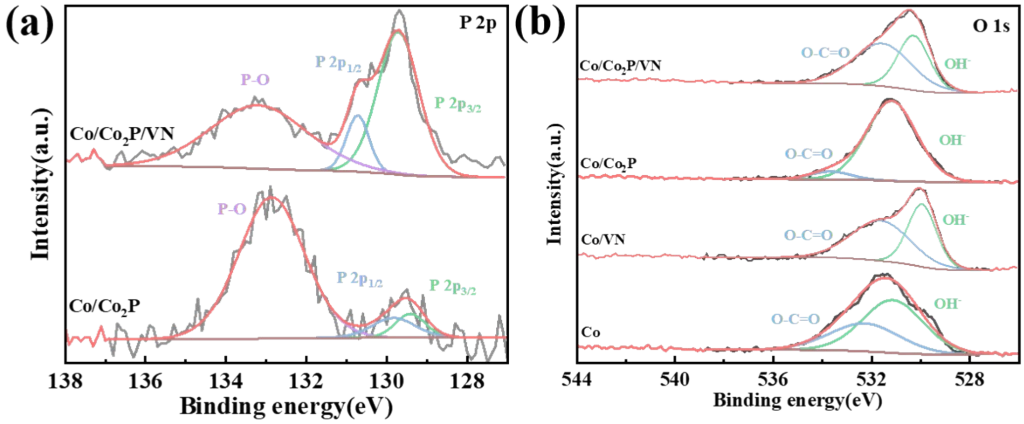

Fig. S5 The high-resolution XPS spectra: (a) P 2p of Co/Co_2P and Co/Co_2P/VN samples; and (b) O 1s of Co, Co/Co_2P, Co/VN and Co/Co_2P/VN samples.

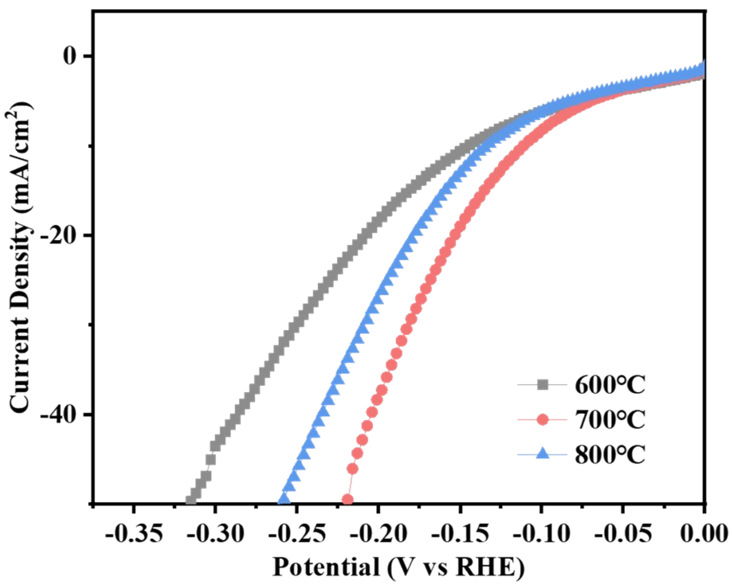

Fig. S6 HER polarization curves of $Co/Co_2P/VN$ with different pyrolysis temperatures in 1.0 M KOH solution.

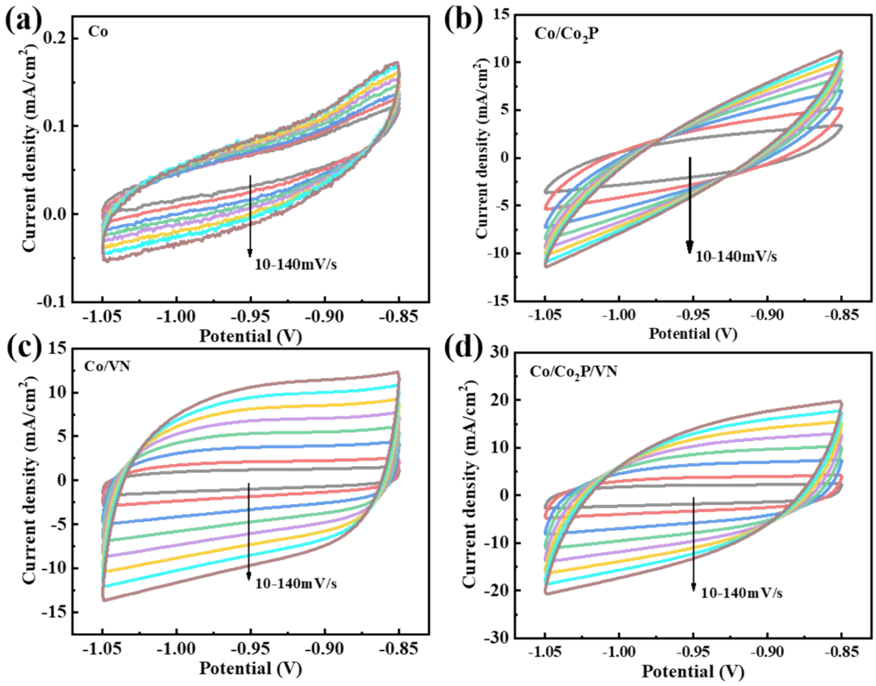

Fig. S7 Cyclic voltammetry curves of (a) Co, (b) Co/Co_2P, (c) Co/VN, and (d) Co/Co_2P/VN catalysts with different scanning rates (10, 20, 40, 60, 80, 100, 120, 140 mV/s) for HER in 1.0 M KOH solution.

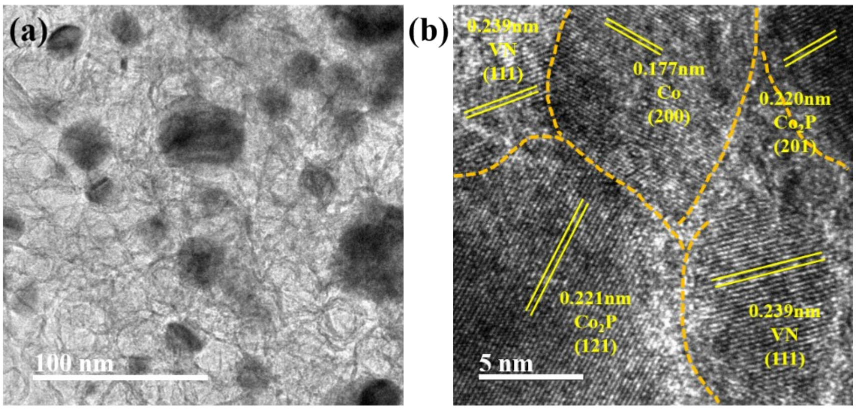

Fig. S8 (a) TEM and (b) HRTEM images of Co/Co_2P/VN after HER chronoamperometry test in 1.0 M KOH electrolyte.

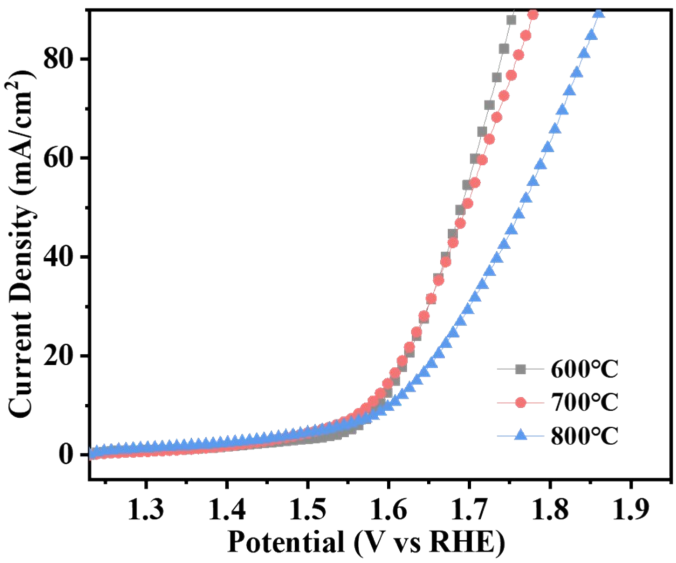

Fig. S9 LSV polarization curves of Co/Co_2P/VN with different pyrolysis temperatures in 1.0 M KOH solution.

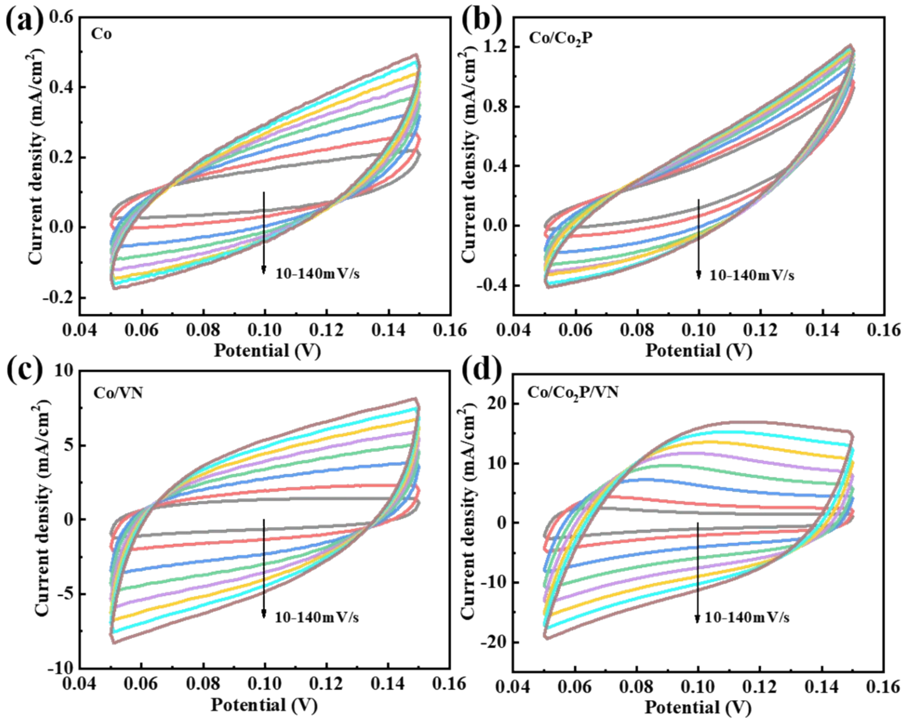

Fig. S10 Cyclic voltammetry curves of (a) Co, (b) Co/Co_2P, (c) Co/VN, and (d) Co/Co_2P/VN catalysts with different scanning rates (10, 20, 40, 60, 80, 100, 120, 140 mV/s) for OER in 1.0 M KOH solution.

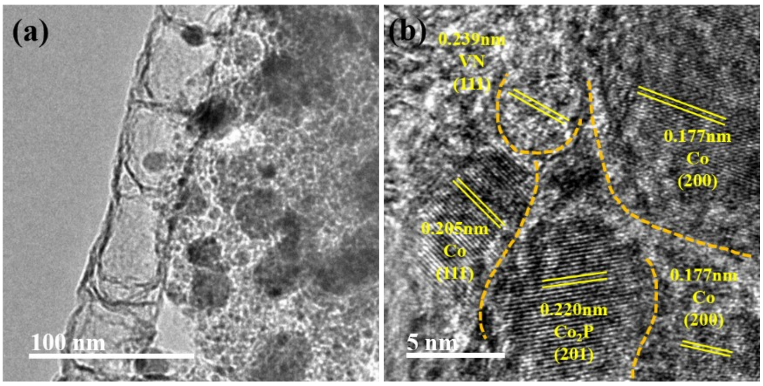

Fig. S11 (a) TEM and (b) HRTEM images of $Co/Co_2P/VN$ after OER chronoamperometry test in 1.0 M KOH electrolyte.

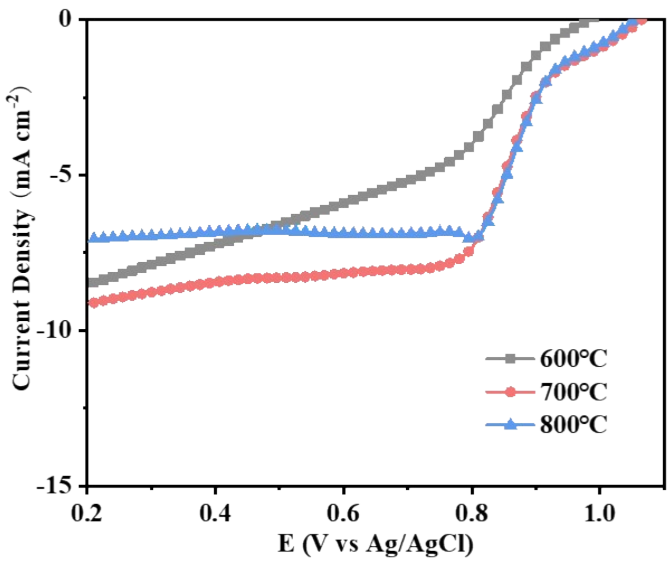

Fig. S12 RDE voltammetry curves of $Co/Co_2P/VN$ with different pyrolysis temperatures in 1.0 M KOH solution.

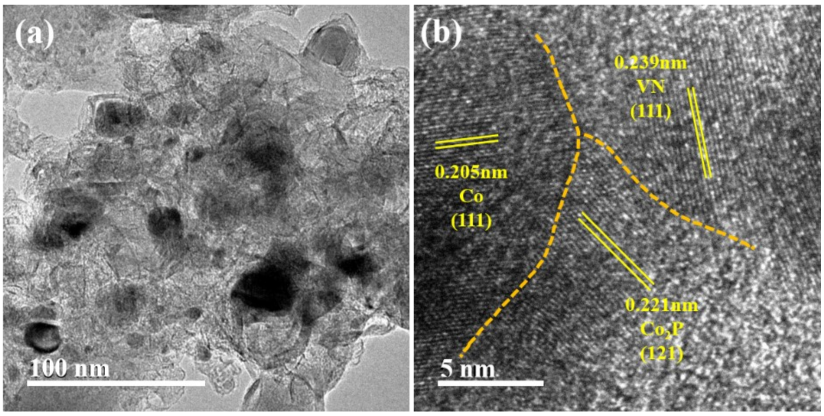

Fig. S13 (a) TEM and (b) HRTEM images of $Co/Co_2P/VN$ after ORR chronoamperometry test in 0.1 M KOH electrolyte.

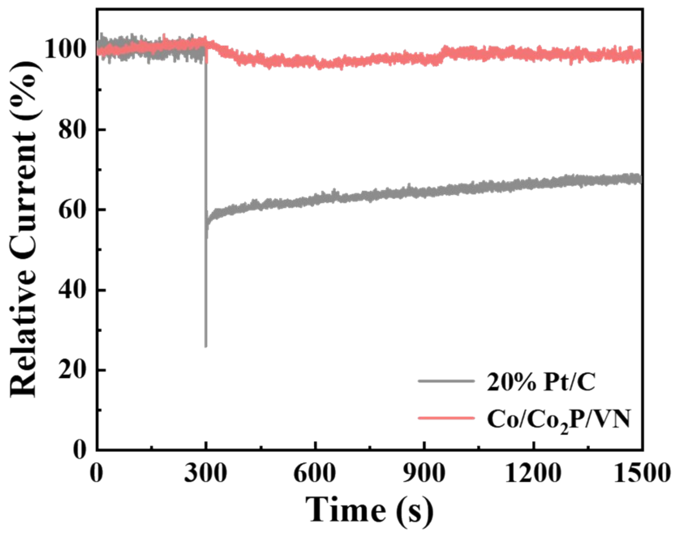

Fig. S14 The stability evaluation for Co/Co_2P/VN and Pt/C catalysts in O_2-saturated 0.1 M KOH with the injection of 3.0 M methanol.

Table S1. The details for calculated fractions of each nitrogen species in the N 1s XPS spectrum.

Fraction of each nitrogen species	**Metal-N [%]**	**Pyridinic-N [%]**	**Pyrrolic-N [%]**	**Graphitic-N [%]**	**Oxidized--N [%]**
$Co/Co_2P/VN$	11.33	20.79	23.98	39.22	4.69
Co/VN	27.75	28.91	19.13	17.69	6.52

Table S2. Fitted data from Nyquist plots of as-prepared samples toward HER.

Electrocatalysts	R_{ct} (Ω)
Co	80.96
Co/Co_2P	47.02
Co/VN	39.50
$Co/Co_2P/VN$	23.55

Table S3. Electrocatalytic HER performance of the $Co/Co_2P/VN$ material compared with that of reported Co-based, Co_2P-based, or VN-based electrocatalysts in 1.0 M KOH electrolyte.

Catalysts	Electrolyte	Current density (*j*, mA cm^{-2})	Overpotential at corresponding *j* (mV)	Stability test	Reference
$Co/Co_2P/VN$	1.0 M KOH	10	111	50 h	This work
$Co_2P/CoP@Co@NCNT$	1.0 M KOH	10	118	50 h	Chemical Engineering Journal. 2022, 430(2): 123877
Co/WN	1.0 M KOH	10	143	30 h	International Journal of Hydrogen Energy. 2022, 06(061): 0360-3199
Co‖Cu/NC	1.0 M KOH	10	210	24 h	ACS Sustainable Chemistry & Engineering. 2022, 10(18): 5986-5997
Co@NC	1.0 M KOH	10	220	40000 s	Journal of Solid State Chemistry. 2022, 309: 122989
$Co_2P/CoNPC$	1.0 M KOH	10	208	30000 s	Advanced Materials. 2022, 32(36): 2003649
$FeCo/Co_2P@NPCF$	1.0 M KOH	10	260	1000 cycles	Advanced Energy Materials. 2020, 10(10): 1903854
VN/Co–NC	1.0 M KOH	10	44	75 h	Energy & Environmental Science. 2021, 14(5): 3160-3173
VN/Co@NCNT	1.0 M KOH	10	180	60 h	Journal of Alloys and Compounds. 2021, 853: 157257
VN/WN@NC	1.0 M KOH	10	122	100 h	Chemical Engineering Journal. 2021, 429: 131945
Co/N-CNT/VN	1.0 M KOH	10	63	20 h	Nano Energy. 2020, 73: 104788

Table S4. Fitted data from Nyquist plots of as-prepared samples toward OER.

Electrocatalysts	**R_{ct} (Ω)**
Co	118.60
Co/Co_2P	92.36
Co/VN	86.17
Co/Co_2P/VN	55.71

Table S5. Electrocatalytic OER performance of the $Co/Co_2P/VN$ material compared with that of reported Co-based, Co_2P-based, or VN-based electrocatalysts in 1.0 M KOH electrolyte.

Catalysts	**Electrolyte**	**Current density (*j*, mA cm^{-2})**	**Overpotential at corresponding *j* (mV)**	**Stability test**	**Reference**
$Co/Co_2P/VN$	1.0 M KOH	10	379	50 h	This work
Co_2P/CoP@Co@NCNT	1.0 M KOH	10	256	60 h	Chemical Engineering Journal. 2022, 430(2): 123877
Co@N-PCNF	1.0 M KOH	10	440	200 h	Electrochimica Acta. 2022, 411: 140090
Co@NC	1.0 M KOH	10	350	40000 s	Journal of Solid State Chemistry. 2022, 309: 122989
Co_2P/CoNPC	1.0 M KOH	10	326	30000 s	Advanced Materials. 2022, 32(36): 2003649
$FeCo/Co_2P$@NPCF	1.0 M KOH	10	330	1000 cycles	Advanced Energy Materials. 2020, 10(10): 1903854
Ni_3FeN/VN–NG	1.0 M KOH	10	1.56V	-	Chemical Engineering Journal. 2022, 437(1): 135291
Co/N-CNT/VN	1.0 M KOH	10	240	20 h	Nano Energy. 2020, 73: 104788
D-Ni_3N QDs/VN	1.0 M KOH	10	226	10 h	Journal of Materials Chemistry A. 2020, 8(40): 21173-21180
CoFe-PBAs/VN	1.0 M KOH	10	398	30 h	International Journal of Hydrogen Energy. 2020, 45(56): 31410-31417

Table S6. Electrocatalytic ORR performance of the $Co/Co_2P/VN$ material compared with that of reported Co-based, Co_2P-based, or VN-based electrocatalysts in 1.0 M KOH electrolyte.

Catalysts	**E_{oneset} (V vs. RHE)**	**$E_{1/2}$ (V vs. RHE)**	**n[a)]**	**Reference**
$Co/Co_2P/VN$	1.070	0.865	3.9	This work
Co@N-PCNF	-	0.825	3.72	Electrochimica Acta. 2022, 411: 140090
TiCN-BCN-Co	0.94	0.83	4	International Journal of Hydrogen Energy. 2022, 47(48): 20894-20904
Co-N-PCN	0.90	0.82	about 4.0	Carbon, 2019, 141: 704-711
Co||Cu/NC	-	0.83	3.9	ACS Sustainable Chemistry & Engineering. 2022, 10(18): 5986-5997
Co_2P/CoNPC	0.963	0.843	3.87	Advanced Materials. 2022, 32(36): 2003649
FeCo/Co_2P@NPCF	0.85	0.79	3.85	Advanced Energy Materials. 2020, 10(10): 1903854
Ni_3FeN/VN–NG	-	0.87	3.87	Chemical Engineering Journal. 2022, 437(1): 135291
D-Ni_3N QDs/VN	0.963	0.837	3.95	Journal of Materials Chemistry A. 2020, 8(40): 21173-21180
Co-V-N/NC	0.98	0.85	3.87	Carbon. 2020, 159: 16-24