Supporting Information

Activating and optimizing activity of NiCoP nanosheets for electrocatalytic alkaline water splitting through V doping effect enhanced by P vacancies

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1. Experimental Section

Fabrication of Ni-Co precursors: The carbon cloth (CC) was treated with concentrated HNO_3 at 100 °C for 3 h, then washed with ethanol and deionized water several times. Firstly, 4 mmol $Ni(NO_3)_2 \cdot 6H_2O$, 4 mmol $Co(NO_3)_2 \cdot 6H_2O$ and 3.2 g hexamethylenetetramine were dissolved in 60 mL deionized water. Then, a piece of clean carbon cloth (2×5 cm^2) was put into a 100 mL Teflon-lined stainless steel autoclave with the prepared solution, and heated to 100 °C for 6 h. After that, the obtained carbon cloth with Ni-Co precursor nanosheet arrays was washed by deionized water and ethanol for several time, and dried at 60 °C overnight.

Fabrication of NiCoP nanosheets: The obtained Ni-Co precursor nanosheets were heated to 300 °C at a heating rate of 5 °C/min in a tube furnace under flowing Ar, with 0.15g $NaH_2PO_2 \cdot H_2O$ put at the upsteam as phosphorus source, and maintained for 1 h.

Fabrication of Ar-NiCoP|V nanosheets: The Ar-NiCoP|V-1, 2, 3, 4 samples were obtained in the following way. The obtained NiCoP nanosheets were immersed in the VCl_3 ethanol solution of different concentration (0.006 M, 0.012 M, 0.02 M and 0.024 M) for 10 min. After that, the samples were transferred to tubular PECVD system (PECVD, OTF-1200X-50-4CLV-PE) under the atmosphere pressure of 0.5 torr and heated at the rate of 10 °C min^{-1} with Ar flow of 10 sccm. When furnace was heated to 200 °C, the obtained samples were treated by Ar plasma at 200 W for 10 min. The obtained samples were denoted as Ar-NiCoP|V-1, 2, 3, 4, respectively. The optimal sample was Ar-NiCoP|V-3, shortly denoted as Ar-NiCoP|V.

Fabrication of Ar-NiCoP nanosheets: The Ar-NiCoP nanosheets were obtained in the same way of fabricating Ar-NiCoP|V without immersing in VCl_3 ethanol solution.

Fabrication of T-NiCoP|V nanosheets: After immersing in 0.02 M VCl_3 ethanol solution for 10 min, the NiCoP nanosheets were heated to 200 °C in the way of fabricating Ar-NiCoP|V nanosheets without the using of plasma and maintained for 120 min.

Fabrication of NiCo-LDH|V nanosheets: By using NiCo-LDH as substitute, the NiCo-LDH|V nanosheets were obtained in the same way of fabricating T-NiCoP|V.

2. Sample characterization

The obtained samples were characterized by scanning electronic microscopy (SEM, Helios Nanolab 600i), transmission electron microscope (TEM, Tecnai G2 F30), X-ray diffraction (XRD, D8 Advance) and X-ray photoelectron spectroscopy (XPS, Thermo Fisher).

3. Electrochemical measurements

All electrochemical performances were measured in the electrochemical workstation (CHI 760E). The HER and OER properties were measured in a three-electrode system, and the obtained samples, Hg/HgO and carbon rod were used as working electrode, reference electrode and counter electrode, respectively. All the potential was converted to RHE. The polarization curves were measured at 2 mV s^{-1}, and then compensated with iR-correction. Before tests, all samples were cycled at 10 mV s^{-1} until the stability of cyclic voltammetry (CV), then the data were collected. As a comparison, commercial Pt/C (20 wt% Pt) and RuO_2 were prepared on carbon cloth, and the detailed process was referred to previous reseaches.[1, 2] The calculation of Tafel slope was conducted in the following way. Firstly, for both HER and OER, the potential at 10 mA/cm^2 was read, shortly denoted as E_{10}. Next, an interval of about 0.04 V was selected around the E_{10} to obtain theoptimal linear relationship between Log j and E (j represents the current density and E represents the potential vs. RHE). Finally, the fitting slopes of samples were compared.

Reference

1. Y. Chen, Z. Ren, H. Fu, X. Zhang, G. Tian, H. Fu, *Small* 2018, **14**, 1800763.

2. X. Xiao, D. Huang, Y. Fu, M. Wen, X. Jiang, X. Lv, M. Li, L. Gao, S. Liu, M. Wang, C. Zhao, Y. Shen, *ACS Appl. Mater. Interfaces* 2018, **10**, 4689-4696.

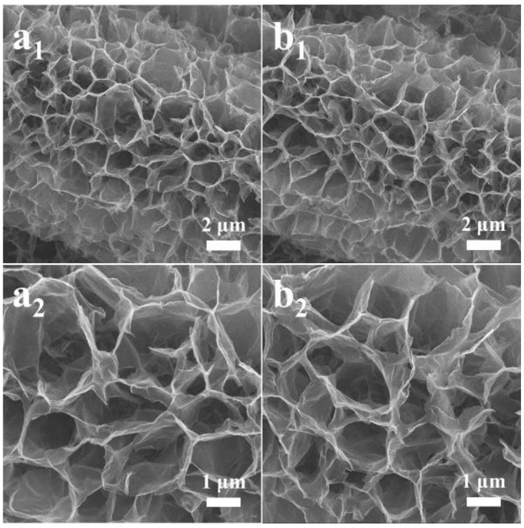

Fig. S1 SEM images of (a) NiCo-precursor, (b) NiCoP.

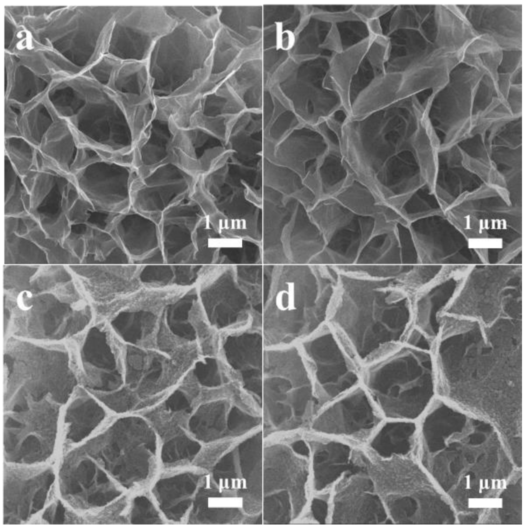

Fig. S2 SEM images of (a) NiCoP, (b) Ar-NiCoP, (c) Ar-NiCoP|V and (d) T-NiCoP|V.

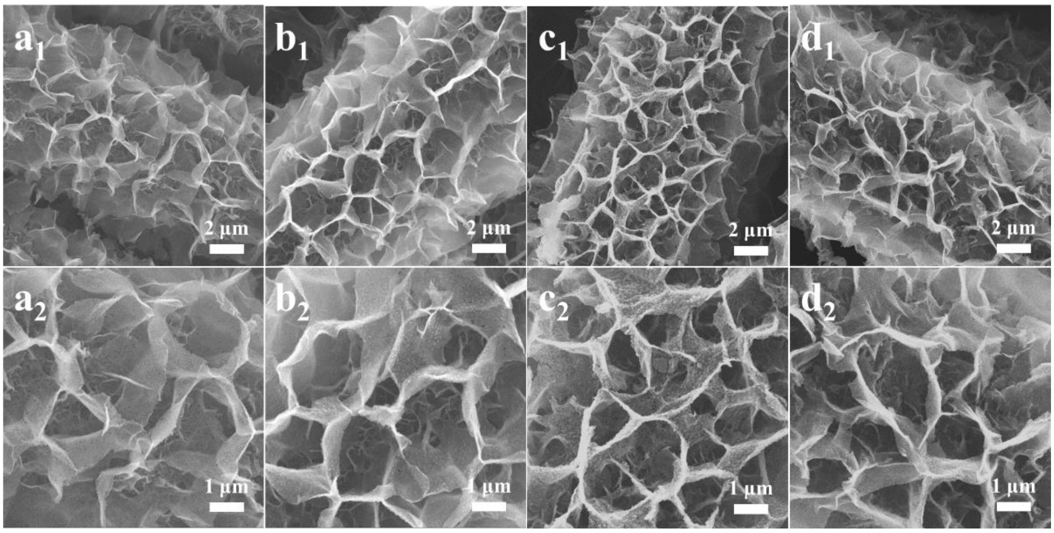

Fig. S3 SEM images of (a) Ar-NiCoP|V-1, (b) Ar-NiCoP|V-2, (c) Ar-NiCoP|V-3 and (d) Ar-NiCoP|V-4.

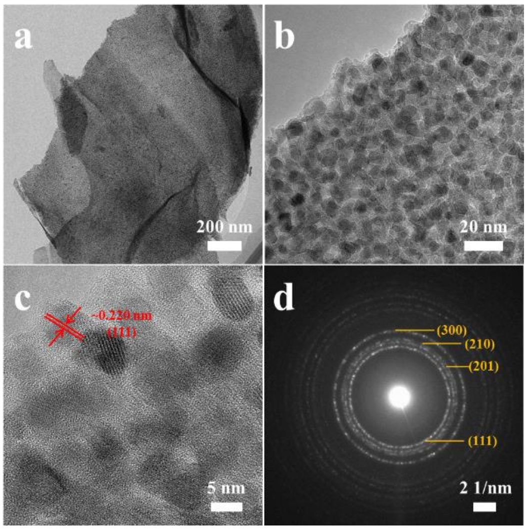

Fig. S4 (a,b) TEM, (c) HRTEM, and (d) SAED images of Ar-NiCoP.

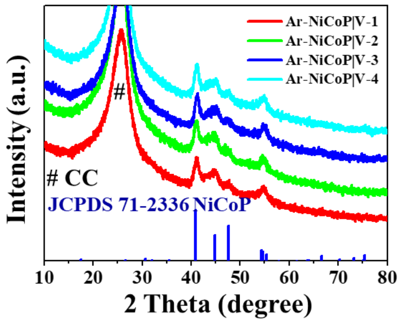

Fig. S5 XRD patterns of Ar-NiCoP|V-1, 2, 3, 4.

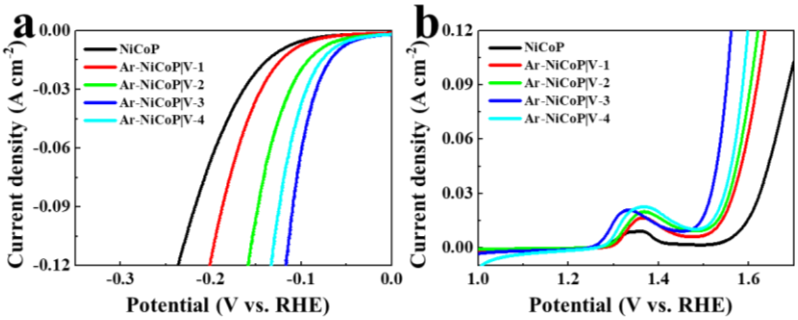

Fig. S6 (a) HER and (b) OER performances of NiCoP and Ar-NiCoP|V-1, 2, 3, 4.

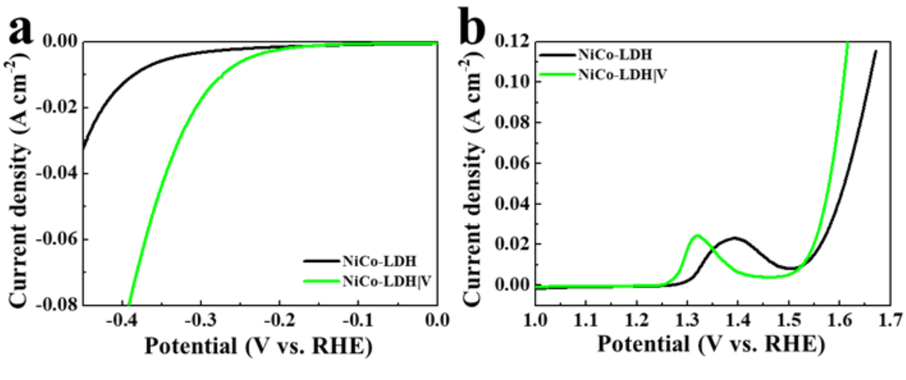

Fig. S7 The comparison of (a) HER and (b) OER polarization curves betweeen NiCo-LDH and NiCo-LDH|V.

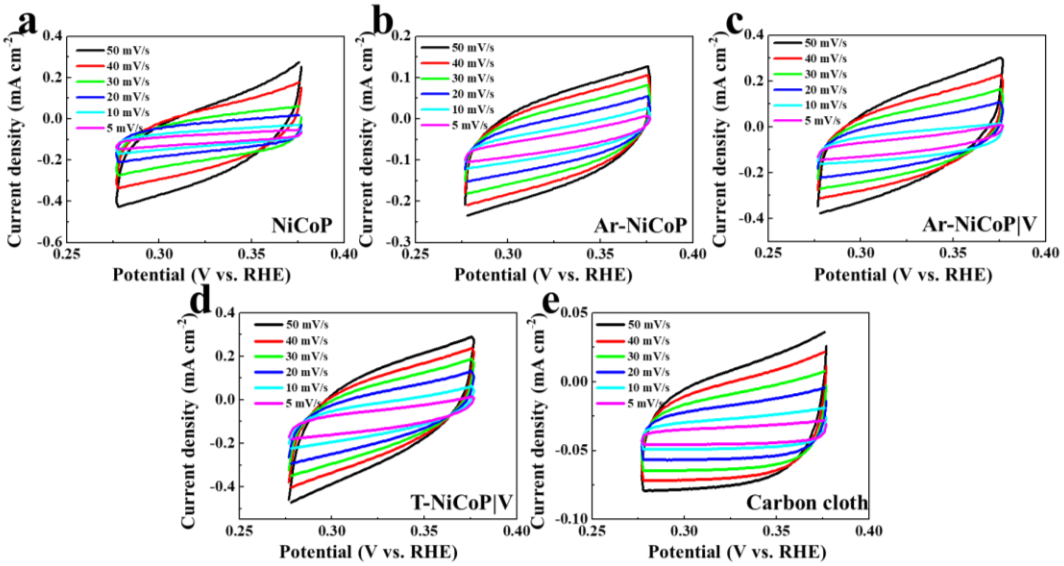

Fig. S8 CV curves of obtained samples for estimating the C_{dl} in HER tests.

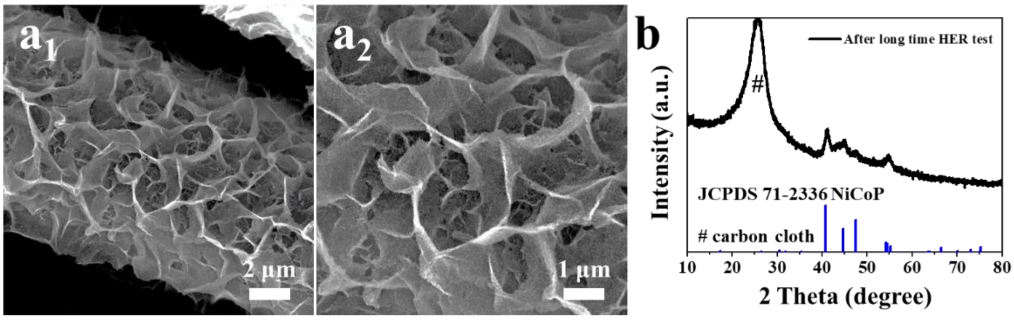

Fig. S9 (a) SEM images, (b) XRD pattern of Ar-NiCoP|V after long time HER test.

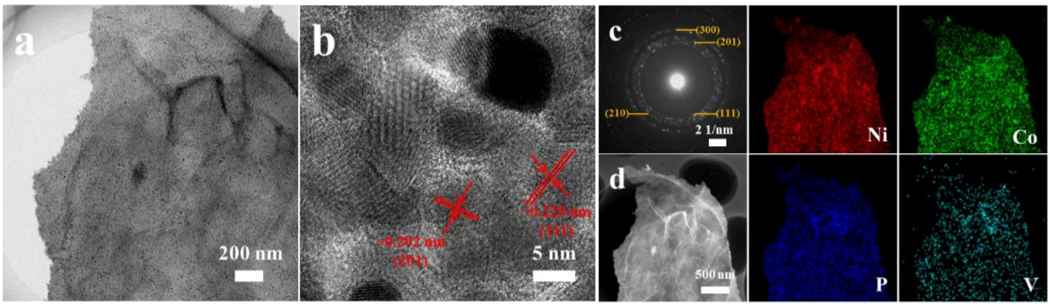

Fig. S10 (a) TEM, (b) High Resolution Transmission Electron Microscope (HRTEM), (c) selected area electron diffraction (SAED) images and (d) corresponding element mappings of Ar-NiCoP|V after long time HER test.

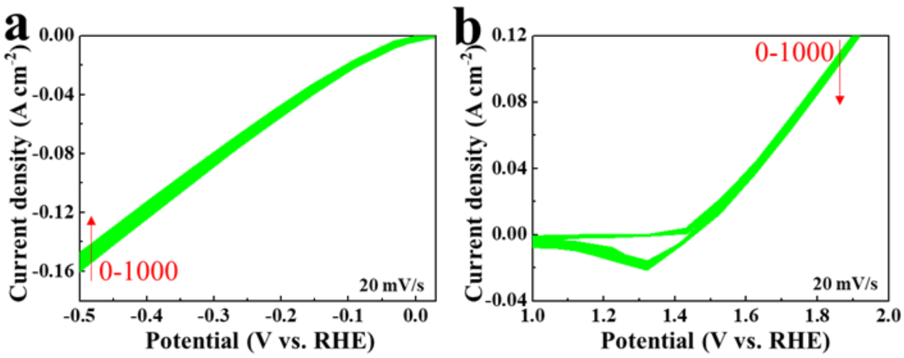

Fig. S11 The (a) HER and (b) OER cyclic voltammetry curves of 1000 cycles.

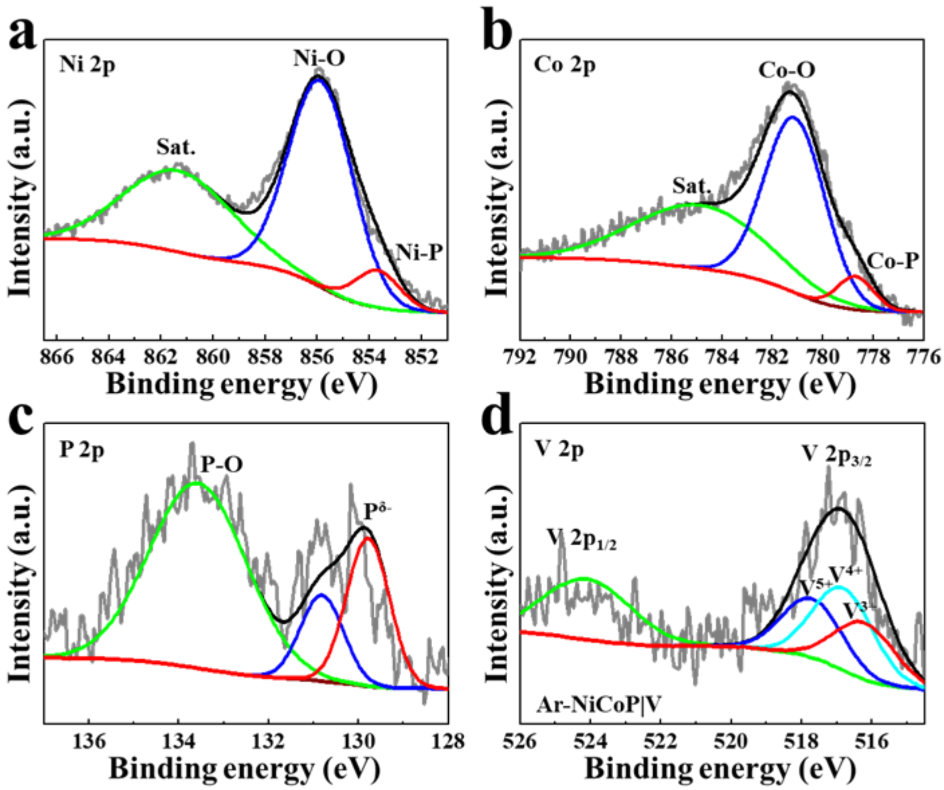

Fig. S12 XPS (a) Ni 2p, (b) Co 2p, (c) P 2p and (d) V 2p spectra of Ar-NiCoP|V after 1000 cycles in HER tests

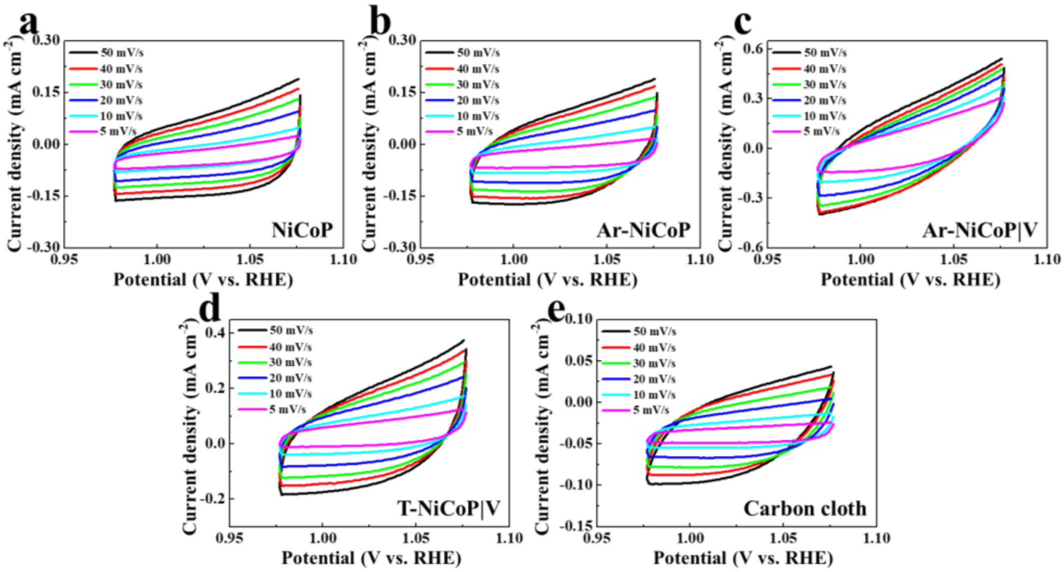

Fig. S13 CV curves of obtained samples for estimating the C_{dl} in OER tests.

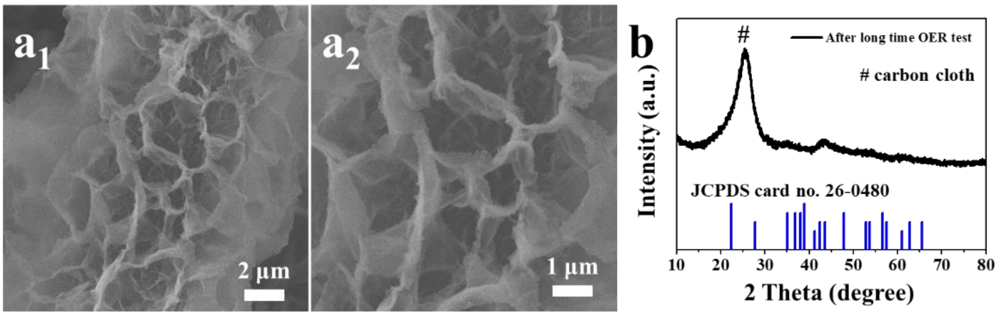

Fig. S14 (a) SEM images, (b) XRD pattern of Ar-NiCoP|V after long time OER test.

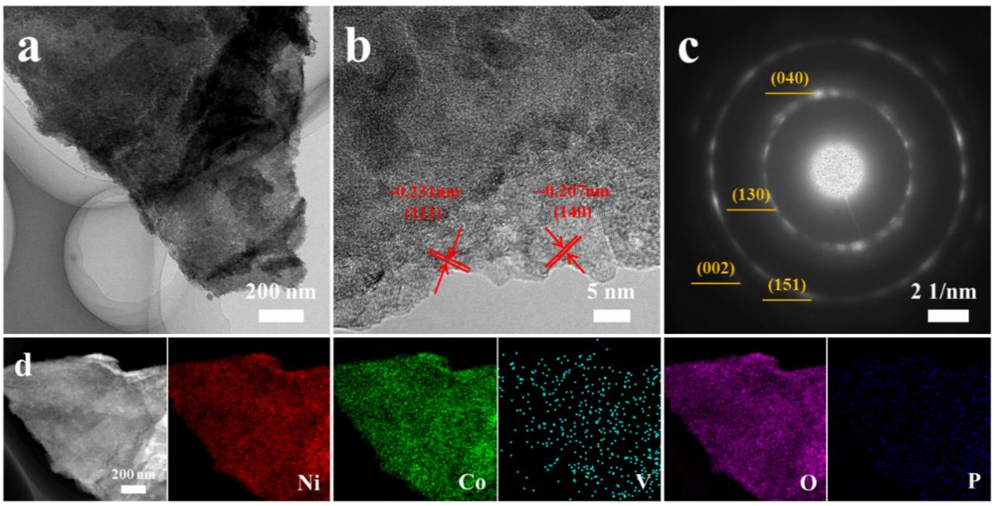

Fig. S15 (a) TEM, (b) HRTEM, (c) SAED images and (d) corresponding element mappings

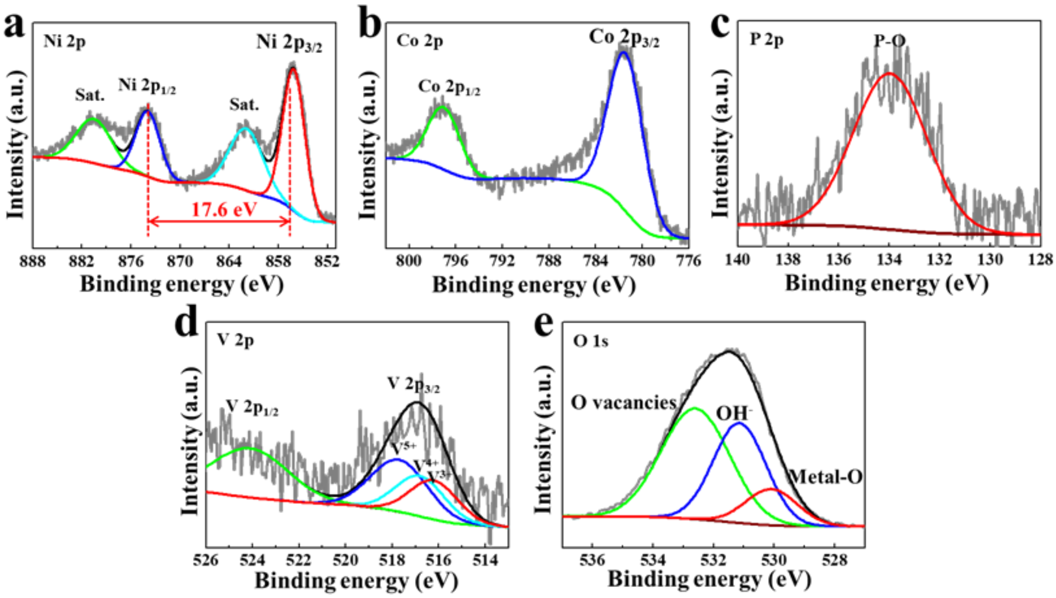

Fig. S16 XPS (a) Ni 2p, (b) Co 2p, (c) P 2p, (d) V 2p and (e) O 1s spectra of Ar-NiCoP|V after 1000 cycles in OER tests

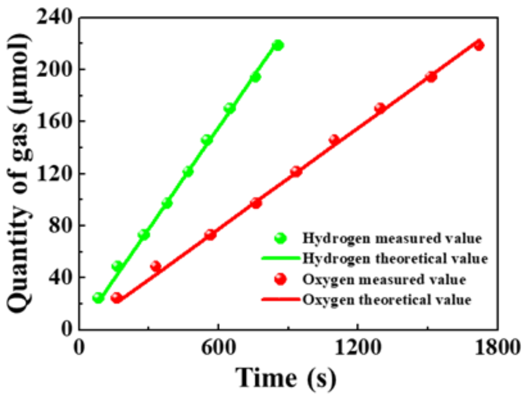

Fig. S17 Amounts of gas calculated and experimentally measured along reaction time for overall water splitting. The theoretical line represents the amount of H_2 or O_2 expected for a 100% Faraday efficiency

Table S1 Comparison of HER performances for Ar-NiCoP|V nanosheets with previsoulsy reported electrocatalysts in the alkaline media.

Electrocatalyst	Substrate	Overpotential (mV)	Tafel slope (mV dec^{-1})	Ref.
Ar-NiCoP|V	Carbon cloth	58 at 10 mA cm^{-2}	51.7	**This work**
NiMoN	Carbon cloth	109 at 10 mA cm^{-2}	95	*Adv. Energy Mater.* 2016, **11**, 1600221.
Ni_2P/Fe_2P	Ti foil	121 at 10 mA cm^{-2}	67	*Adv. Energy Mater.* 2018, **8**, 1800484
Co-Ni_3N	Carbon cloth	194 at 10 mA cm^{-2}	156	*Adv. Mater.* 2018, **13**, 1705516
WS_2/Ni_5P_4-Ni_2P	Ni foam	94 at 10 mA cm^{-2}	74	*Nano Energy* 2019, **55**, 193.
$Co_5Mo_{1.0}P$ nanoshets	Ni foam	173 at 10 mA cm^{-2}	190.1	*Nano Energy* 2018, **45**, 448.
S-CoP	Ni foam	109 at 10 mA cm^{-2}	79	*Nano Energy* 2018, **53**, 286
NiCoP nanocone	Ni foam	104 at 10 mA cm^{-2}	54	*J. Mater. Chem. A* 2017, **5**, 14828.
Ni-Co-P hollow nanobricks	Powder	107 at 10 mA cm^{-2}	46	*Energy Environ. Sci*. 2018, **11**, 872.
Hyperbranched NiCoP Arrays	Ni foam	71 at 10 mA cm^{-2}	57	*ACS Appl. Mater. Interfaces* 2018, **10**, 41237.
N-Ni_3S_2	Ni foam	110 at 10 mA cm^{-2}	-	*Adv. Mater.* 2017, **29**, 1701584.
$Co_{0.93}Ni_{0.07}P_3$ nanoneedle array	Carbon cloth	87 at 10 mA cm^{-2}	60.7	*ACS Energy Lett*. 2018, **3**, 1744.
TiO_2@Co_9S_8 core-branch arrays	Ni foam	139 at 10 mA cm^{-2}	65	*Adv. Sci*. 2018, **5**, 1700772
NiFe LDH@NiCoP	Ni foam	120 at 10 mA cm^{-2}	88.2	*Adv. Funct. Mater.* 2018, **28**, 1706847.

1. If not metioned specifically, all overpotentials were corrected with iR compensation. 2. If not metioned specifically, all electrocatalysts are directly synthesized on conductive substrates.

Table S2 Comparison of OER performances for Ar-NiCoP|V nanosheets with previsoulsy reported electrocatalysts in the alkaline media.

Electrocatalyst	Substrate	Overpotential (mV)	Tafel slope (mV dec^{-1})	Ref.
Ar-NiCoP|V	Carbon cloth	246 at 10 mA cm^{-2}	70.4	**This work**
S-CoP	Ni foam	270 at 10 mA cm^{-2}	82	*Nano Energy* 2018, **53**, 286
CoS_2 nanotube	Carbon cloth	276 at 10 mA cm^{-2}	81	*Nanoscale Horiz.* 2017, **2**, 342.
Hyperbranched NiCoP Arrays	Ni foam	268 at 10 mA cm^{-2}	75	*ACS Appl. Mater. Interfaces* 2018, **10**, 41237.
Ni@NC	glassy carbon electrodes	280 at 10 mA cm^{-2}	45	*Adv. Mater.* 2017, **29**, 1605957
N-$NiMoO_4$/NiS_2	Carbon cloth	267 at 10 mA cm^{-2}	44.3	*Adv. Funct. Mater.* 2019, **29**, 1805298.
Mo-CoOOH	Carbon cloth	305 at 10 mA cm^{-2}	56	*Nano Energy* 2018, **48**, 73.
$Co_5Mo_{1.0}O$ nanosheets	Ni foam	270 at 10 mA cm^{-2}	54.4	*Nano Energy* 2018, **45**, 448.
Co-Ni_3N	Carbon cloth	307 at 10 mA cm^{-2}	57	*Adv. Mater.* 2018, **13**, 1705516
plasma-assisted synthesized NiCoP	Ni foam	280 at 10 mA cm^{-2}	87	*Nano Lett*. 2016, **16**, 7718.
$NiCo_2O_4$ hollow microcuboids	Ni foam	290 at 10 mA cm^{-2}	53	*Angew.Chem.Int. Ed.* 2016, **55**, 6290
Ni_3S_2@MoS_2/FeOOH	Ni foam	260 at 10 mA cm^{-2}	49	*Appl. Catal. B* 2019, **244**, 1004.
C@Ni_8P_3	Ni foam	267 at 10 mA cm^{-2}	51	*ACS Appl. Mater. Interfaces* 2016, **8**, 27850.

1.If not metioned specifically, all overpotentials were corrected with iR compensation. 2. If not metioned specifically, all electrocatalysts are directly synthesized on conductive substrates.

Table S3 Comparison of water-splitting performances for Ar-NiCoP|V nanosheets with previsoulsy reported electrocatalysts in the alkaline media.

Electrocatalyst	Substrate	Potential	Ref.
Ar-NiCoP|V	Carbon cloth	1.55 V at 10 mA cm^{-2}	**This work**
$NiCo_2P_2$/graphene quantum dot	Ti mesh	1.61 V at 10 mA cm^{-2}	*Nano Energy* 2018, **48**, 284.
P-Co_3O_4	Ni foam	1.63 V at 10 mA cm^{-2}	*ACS Catal.* 2018, **8**, 2236.
$NiMoP_2$ nanowires	Carbon cloth	1.67 V at 10 mA cm^{-2}	*J. Mater. Chem. A* 2017, **5**, 7191.
Ni_3S_2/VS_2|| N-Ni_3S_2/VS_2	Ni foam	1.65 V at 10 mA cm^{-2}	*Electrochim. Acta* 2018, **269**, 55
N-$NiMoO_4/NiS_2$	Carbon cloth	1.60 V at 10 mA cm^{-2}	*Adv. Funct. Mater.* 2019, **29**, 1805298.
FeCoP ultrathin arrays	Ni foam	1.60 V at 10 mA cm^{-2}	*Nano Energy* 2017, **41**, 583.
$CuCo_2O_4$-NWs	Ni foam	1.61 V at 10 mA cm^{-2}	*Adv. Funct. Mater.* 2016, **26**, 8555
$NiCo_2O_4$ hollow microcuboids	Ni foam	1.65 V at 10 mA cm^{-2}	*Angew.Chem.Int. Ed*. 2016, **55**, 6290