

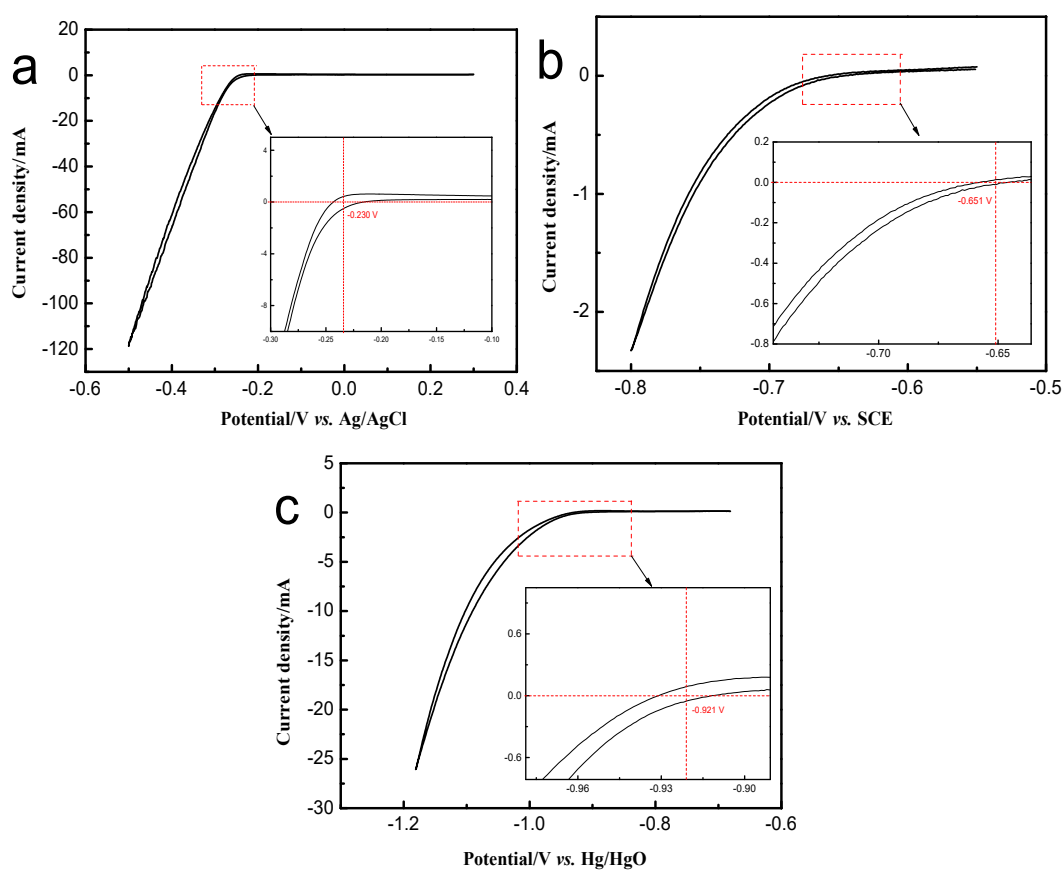
## Electronic Supplementary Material

### Tuning the electronic structure of NiCoP arrays through V doping for pH-universal hydrogen evolution reaction electrocatalyst

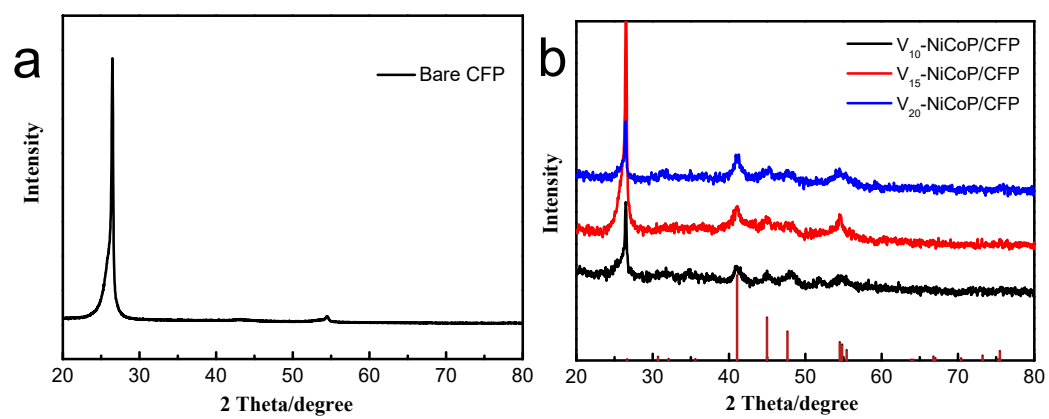
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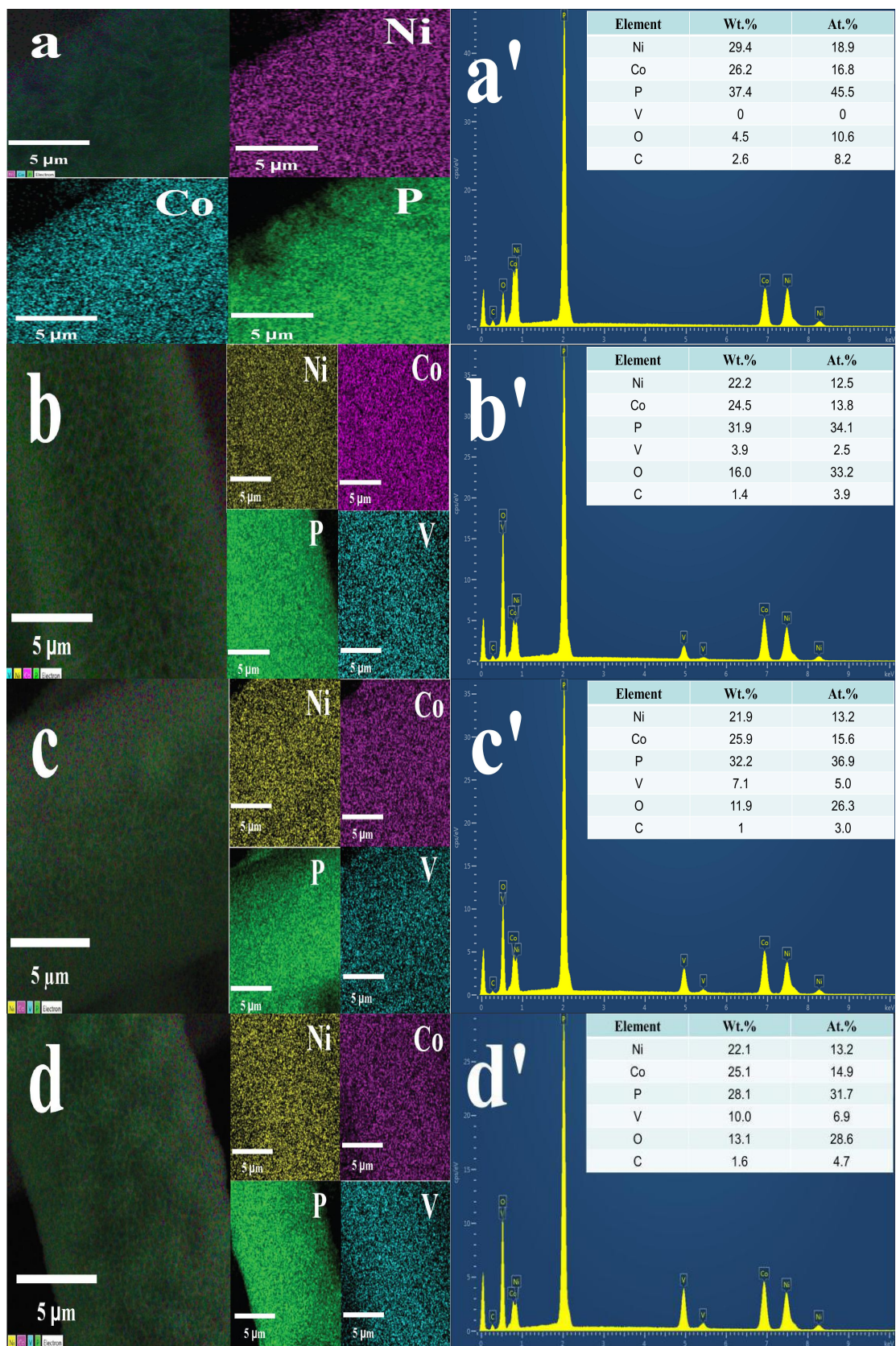
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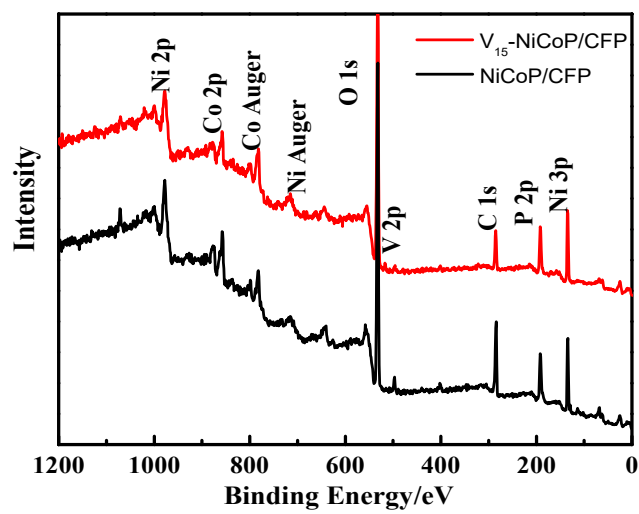
**Fig. S1** RHE calibration at a scan rate of  $1 \text{ mV s}^{-1}$ : (a) Ag/AgCl, KCl (sat) reference electrode in 0.5 M H<sub>2</sub>SO<sub>4</sub>. (b) Hg/HgCl<sub>2</sub>, KCl (sat) reference electrode in 1 M PBS (pH=7). (c) Hg/HgO, KOH (1 M) reference electrode in 1 M KOH.



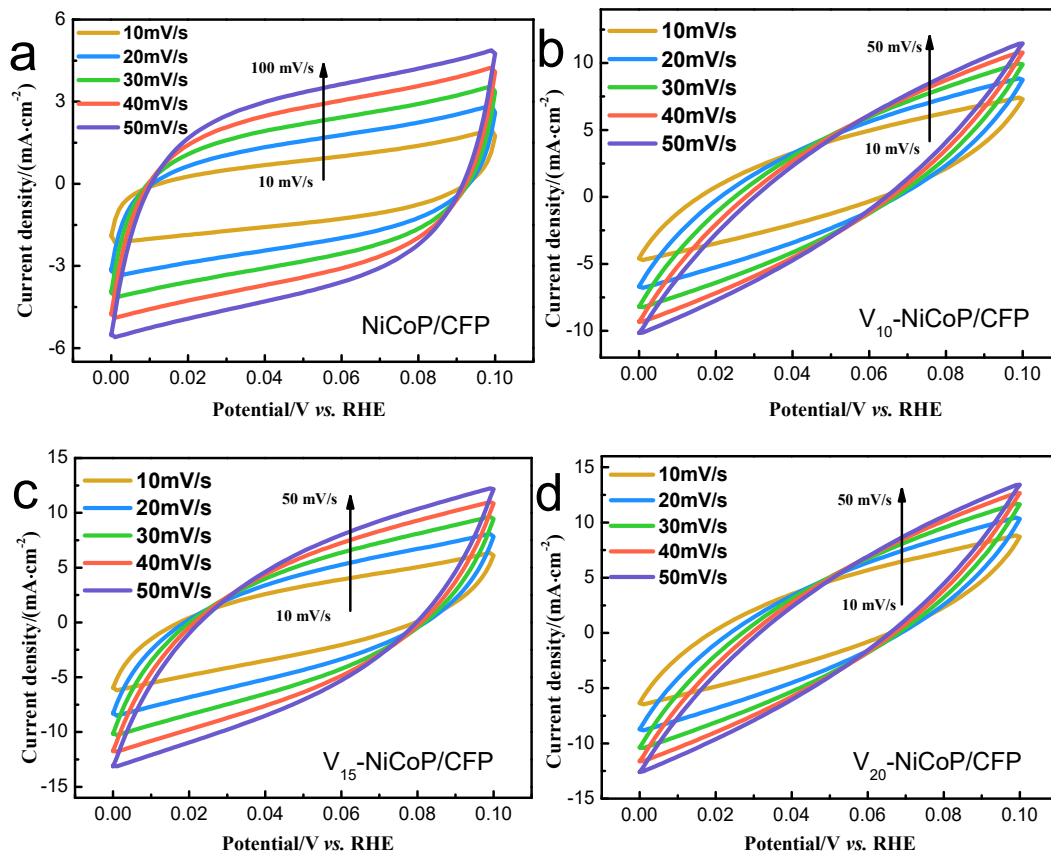
**Fig. S2** XRD patterns of (a) bare carbon fiber paper and (b) V<sub>10</sub>-NiCoP/CFP, V<sub>15</sub>-NiCoP/CFP, and V<sub>20</sub>-NiCoP/CFP.



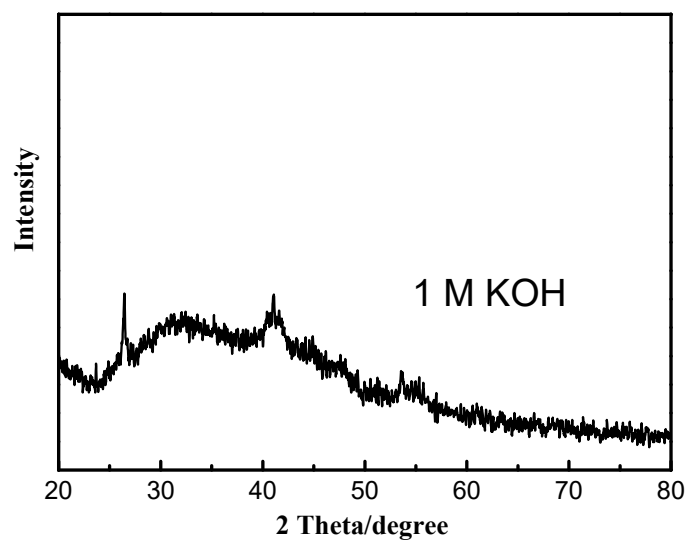
**Fig. S3** EDX elemental mapping and corresponding EDX spectrum of (a, a') NiCoP/CFP, (b, b') V<sub>10</sub>-NiCoP/CFP, (c, c') V<sub>15</sub>-NiCoP/CFP, and (d, d') V<sub>20</sub>-NiCoP/CFP.



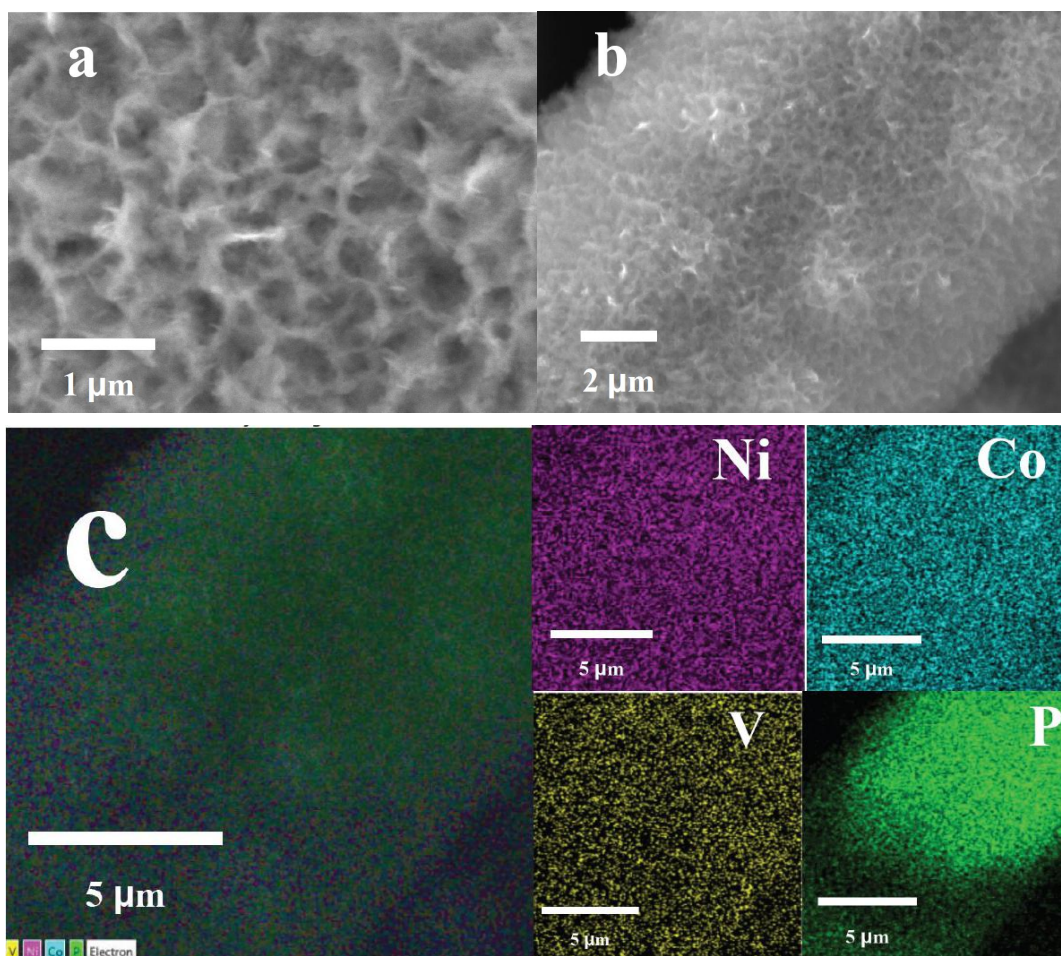
**Fig. S4** The XPS survey spectra of NiCoP/CFP and V<sub>15</sub>-NiCoP/CFP.



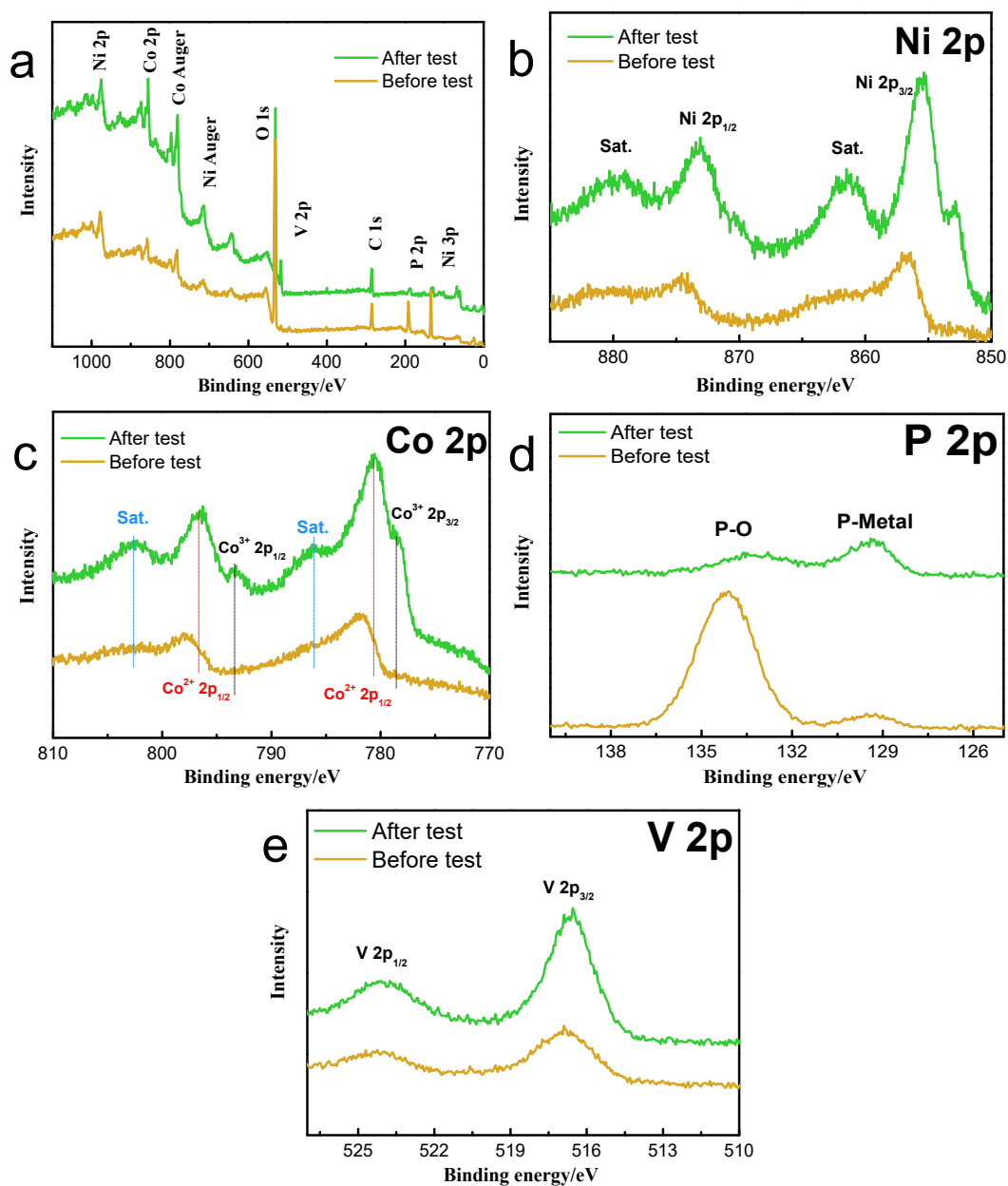
**Fig. S5** Cyclic voltammograms of (a) NiCoP/CFP, (b) V<sub>10</sub>-NiCoP/CFP, (c) V<sub>15</sub>-NiCoP/CFP, and (d) V<sub>20</sub>-NiCoP/CFP electrodes between the potential regions of 0 and 0.1 V vs. RHE at different scan rates (10, 20, 30, 40, and 50 mV/s) toward HER in 1 M KOH solution.



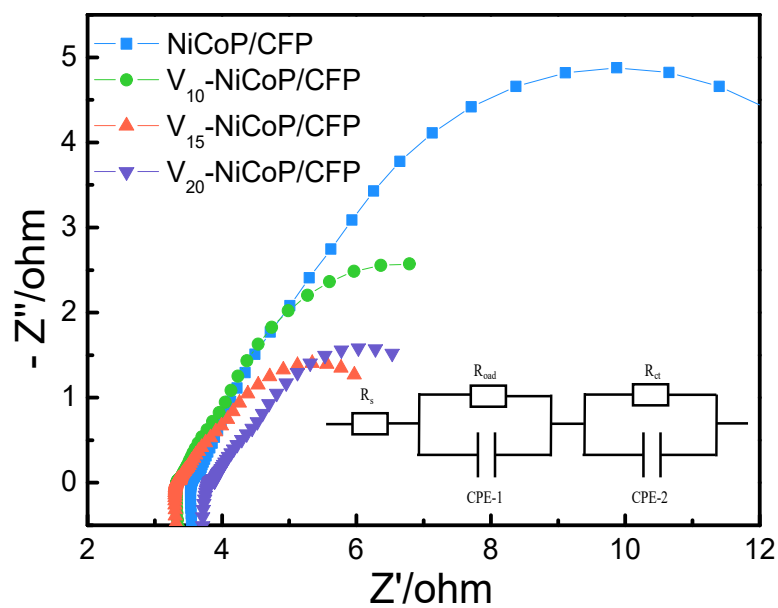
**Fig. S6** XRD pattern of the V<sub>15</sub>-NiCoP/CFP electrocatalyst after 48 h durability tests (1 M KOH).



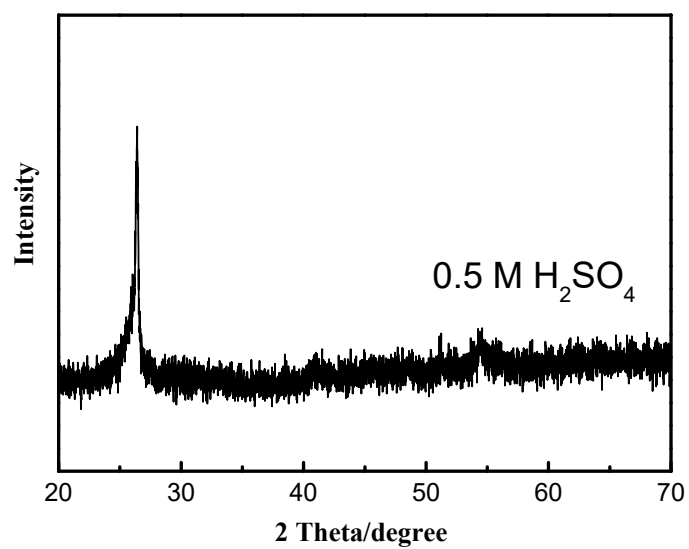
**Fig. S7** (a, b) SEM images of  $V_{15}$ -NiCoP/CFP after 48h stability test (1 M KOH) and (c) EDX elemental mapping.



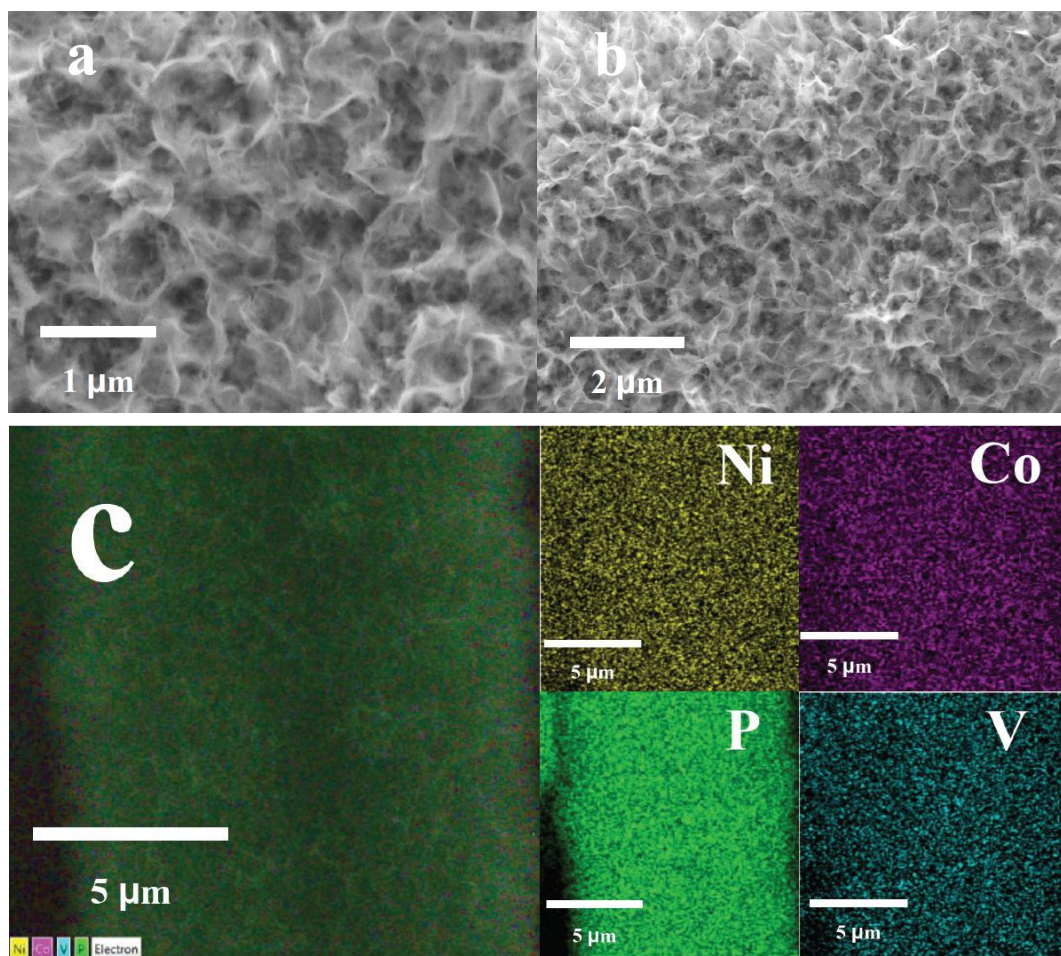
**Fig. S8** XPS data of V<sub>15</sub>-NiCoP/CFP sample after 48h stability test (1 M KOH): (a) survey, (b) Ni 2p, (c) Co 2p, (d) P 2p, and (e) V 2p.



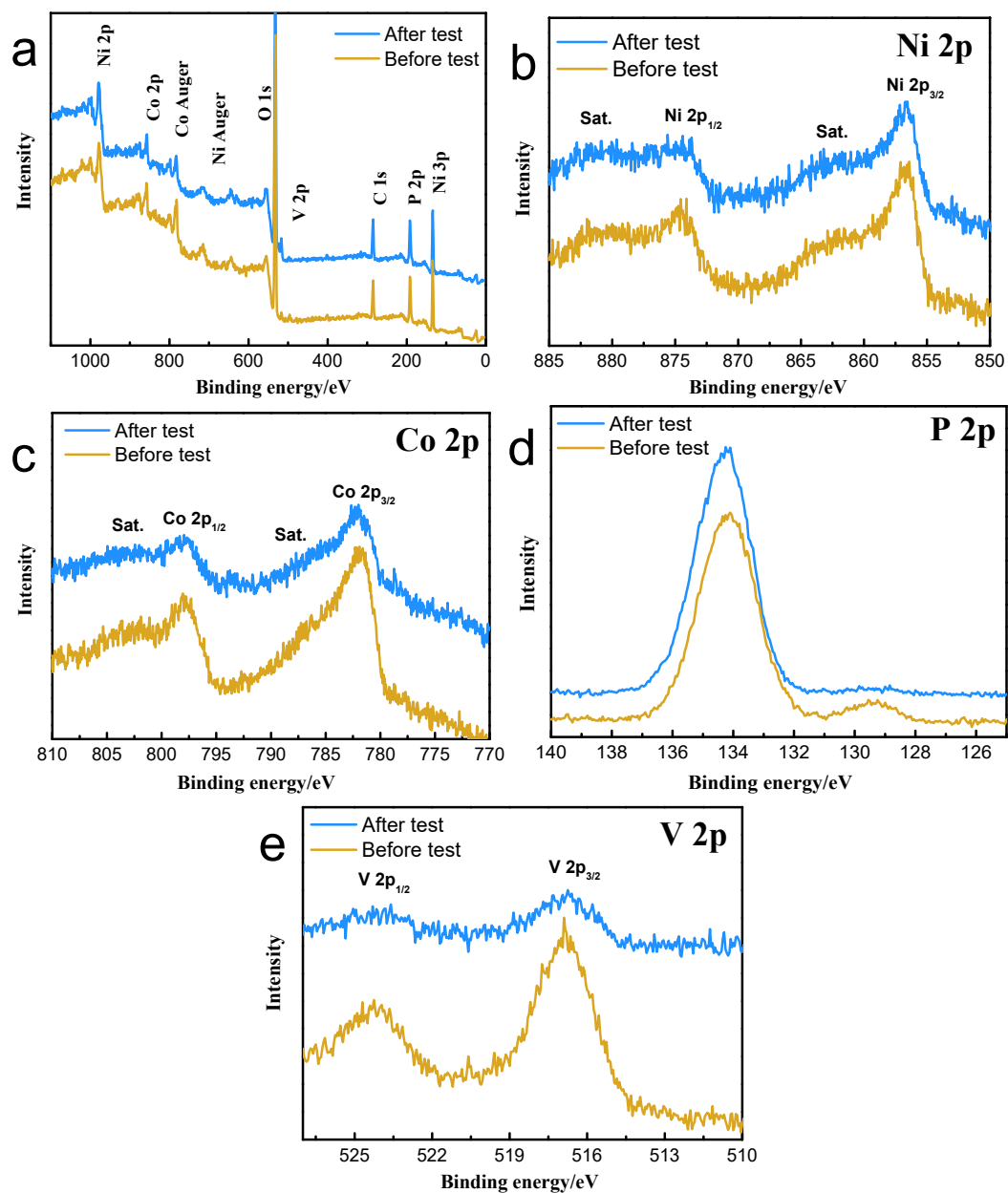
**Fig. S9** Nyquist plots of the NiCoP/CFP, V<sub>10</sub>-NiCoP/CFP, V<sub>15</sub>-NiCoP/CFP, and V<sub>20</sub>-NiCoP/CFP in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution at an overpotential of -100 mV vs. RHE.



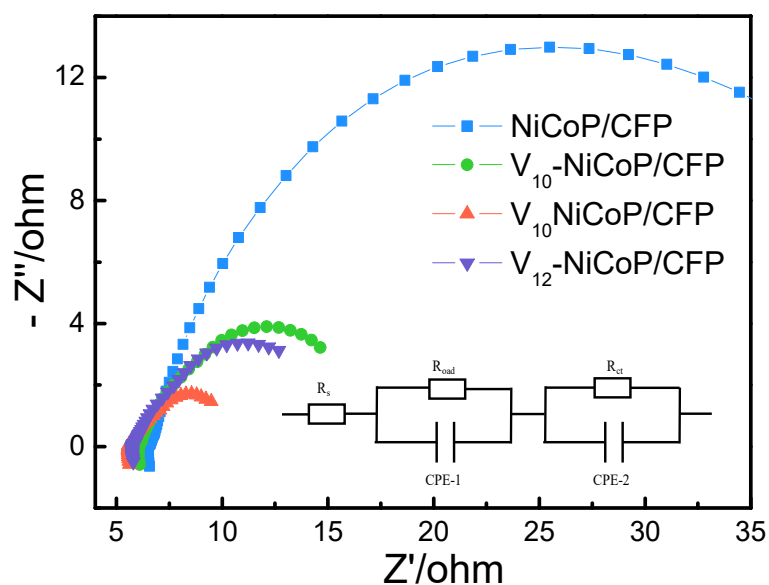
**Fig. S10** XRD pattern of the V<sub>15</sub>-NiCoP/CFP electrocatalyst after 48 h durability tests (0.5 M H<sub>2</sub>SO<sub>4</sub>).



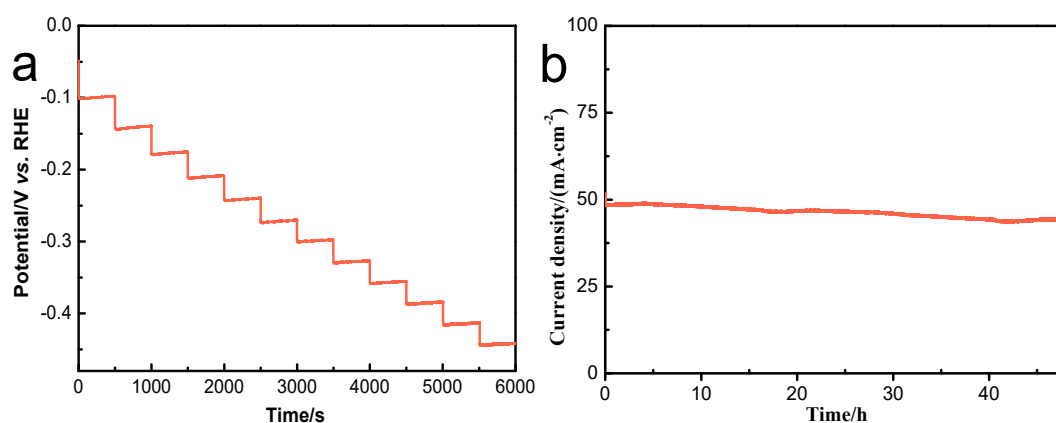
**Fig. S11** (a, b) SEM images of V<sub>15</sub>-NiCoP/CFP after 48h stability test (0.5 M H<sub>2</sub>SO<sub>4</sub>) and (c) EDX elemental mapping.



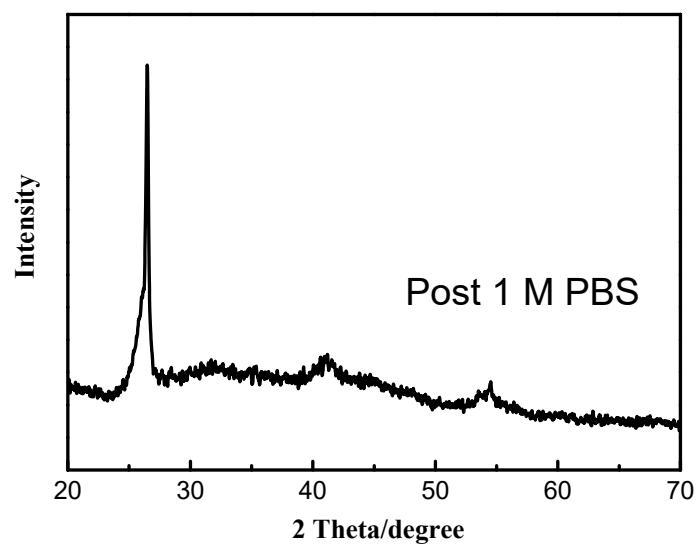
**Fig. S12** XPS data of V<sub>15</sub>-NiCoP/CFP sample after 48h stability test (0.5 M H<sub>2</sub>SO<sub>4</sub>): (a) survey, (b) Ni 2p, (c) Co 2p, (d) P 2p, and (e) V 2p.



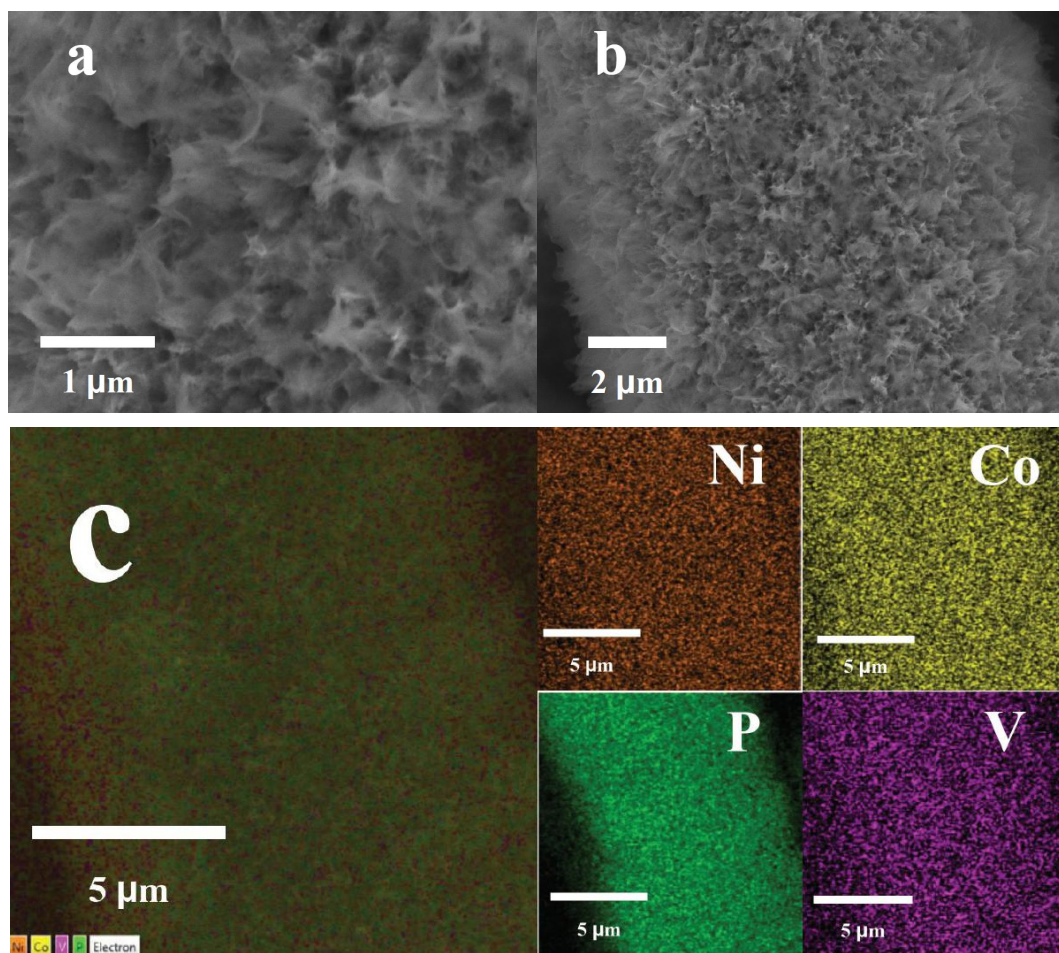
**Fig. S13** Nyquist plots of the NiCoP/CFP,  $V_{10}$ -NiCoP/CFP,  $V_{15}$ -NiCoP/CFP, and  $V_{20}$ -NiCoP/CFP in 1 M PBS solution at an overpotential of -100 mV vs. RHE.



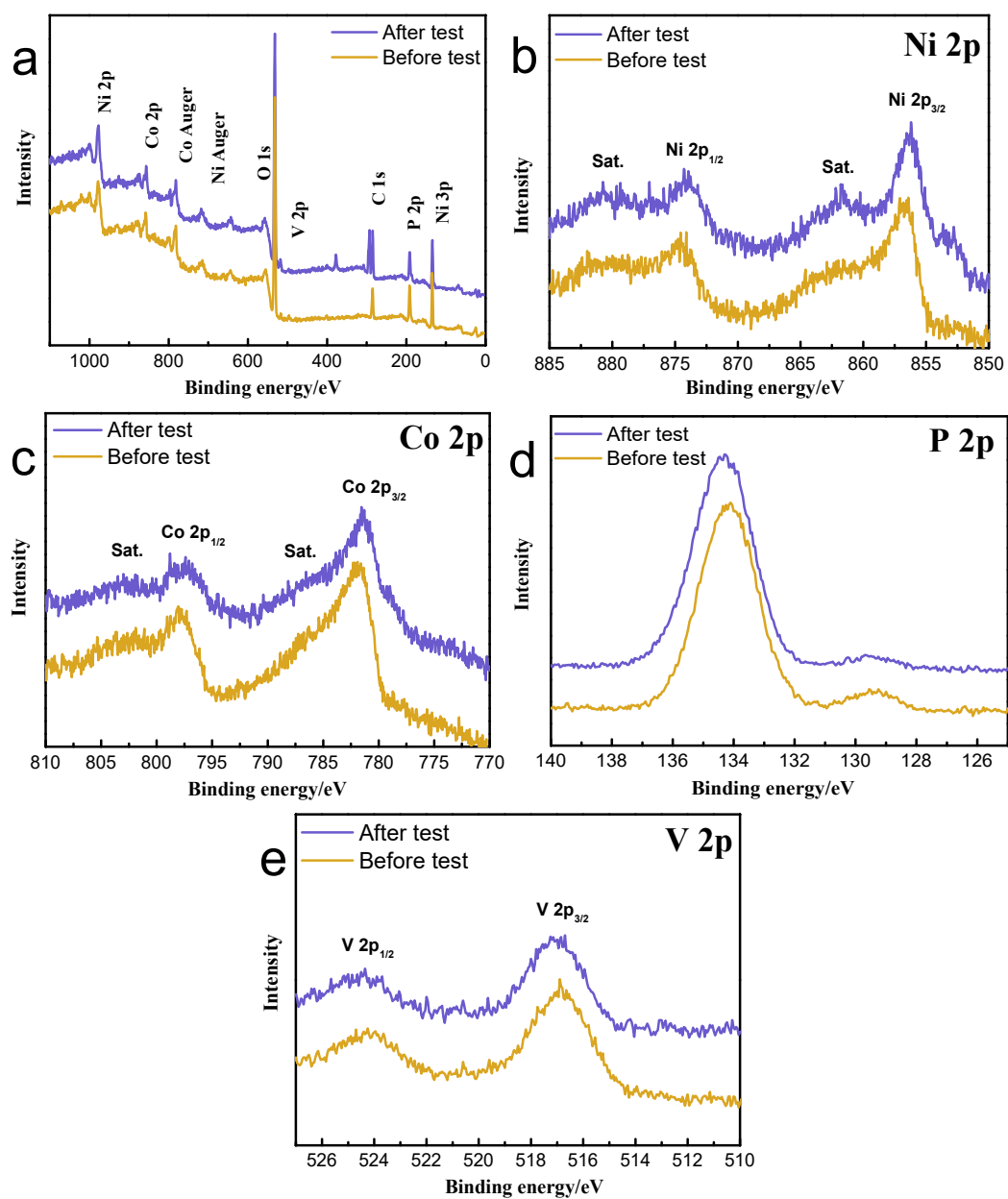
**Fig. S14** (a) Multi-current process obtained with the  $V_{15}$ -NiCoP/CFP electrode in 1 M PBS. The current density started at  $10 \text{ mA} \cdot \text{cm}^{-2}$  and finished at  $120 \text{ mA} \cdot \text{cm}^{-2}$ , with an increment of  $10 \text{ mA} \cdot \text{cm}^{-2}$  per 500 s. (b) Chronopotentiometry curves of  $V_{15}$ -NiCoP/CFP in 1 M PBS.



**Fig. S15** XRD pattern of the V<sub>15</sub>-NiCoP/CFP electrocatalyst after 48 h durability tests (1 M PBS).



**Fig. S16** (a, b) SEM images of V<sub>15</sub>-NiCoP/CFP after 48h stability test (1 M PBS) and (c) EDX elemental mapping.



**Fig. S17** XPS data of  $V_{15}$ -NiCoP/CFP sample after 48h stability test (1 M PBS): (a) survey, (b) Ni 2p, (c) Co 2p, (d) P 2p, and (e) V 2p.

**Table S1** Comparison of the HER activities of the V<sub>15</sub>-NiCoP/CFP composite with other reported catalysts in alkaline medium (1 M KOH).

Electrode	$\eta$ (mV)	Reference
V <sub>15</sub> -NiCoP/CFP	46.5 mV@ 10 mA·cm <sup>-2</sup> 132.2 mV@ 100 mA·cm <sup>-2</sup>	This work
NiCoP/CFP	99.6 mV@ 10 mA·cm <sup>-2</sup> 171.2 mV@ 100 mA·cm <sup>-2</sup>	This work
Pt-C/CFP	30.0 mV@ 10 mA·cm <sup>-2</sup> 105.6 mV@ 100 mA·cm <sup>-2</sup>	This work
Ni <sub>2</sub> P nanoparticles	225 mV@ 10 mA·cm <sup>-2</sup>	<i>Phys. Chem. Chem. Phys.</i> <b>2014</b> , 16, 5917-5921.
Co <sub>9</sub> S <sub>8</sub> /NC@MoS <sub>2</sub>	67 mV@ 10 mA·cm <sup>-2</sup>	<i>ACS Appl. Mater. Interfaces</i> <b>2017</b> , 9, 28394-28405
CoS <sub>2</sub> /CoSe <sub>2</sub>	80 mV@ 10 mA·cm <sup>-2</sup>	<i>J. Mater. Chem. A</i> <b>2017</b> , 5, 2504-2507.
CoNiP@NF	155 mV@ 10 mA·cm <sup>-2</sup>	<i>J. Mater. Chem. A</i> <b>2016</b> , 4, 10195-10202.
MoP NA/CC	80 mV@ 10 mA·cm <sup>-2</sup>	<i>Appl. Catal. B-Environ.</i> <b>2016</b> , 196, 193.
NiCo <sub>2</sub> P <sub>x</sub> nanowires	58 mV@ 10 mA·cm <sup>-2</sup>	<i>Adv. Mater.</i> <b>2016</b> , 29, 1605502.
NiN <sub>3</sub> on Ni foam	150 mV@ 100 mA·cm <sup>-2</sup>	<i>Adv. Energy Mater.</i> <b>2016</b> , 7, 1601735.
Ni(OH) <sub>2</sub> @Fe <sub>2</sub> P/Ti mesh	94 mV@ 10 mA·cm <sup>-2</sup>	<i>Chem. Commun.</i> <b>2018</b> , 54, 1201-1204.
Ni <sub>0.89</sub> -Co <sub>0.11</sub> Se <sub>2</sub> /NF	85mV@ 10 mA·cm <sup>-2</sup>	<i>Adv. Mater.</i> <b>2017</b> , 29, 1606521.
CoP/CC	209 mV@ 10 mA·cm <sup>-2</sup>	<i>J. Am. Chem. Soc.</i> <b>2014</b> , 136, 7587-7590.
Ni-Co-P HNBS	107 mV@ 10 mA·cm <sup>-2</sup>	<i>Energy Environ. Sci.</i> <b>2018</b> , 11, 872.

**Table S2** Comparison of the HER activities of the V<sub>15</sub>-NiCoP/CFP composite with other reported catalysts in acidic medium (0.5 M H<sub>2</sub>SO<sub>4</sub>).

Electrode	$\eta$ (mV)	Reference
V <sub>15</sub> -NiCoP/CFP	52.4 mV@ 10 mA·cm <sup>-2</sup>	This work
	118.2 mV@ 100 mA·cm <sup>-2</sup>	
NiCoP/CFP	89.2 mV@ 10 mA·cm <sup>-2</sup>	This work
	157.8 mV@ 100 mA·cm <sup>-2</sup>	
Pt-C/CFP	28.0 mV@ 10 mA·cm <sup>-2</sup>	This work
	91.7 mV@ 100 mA·cm <sup>-2</sup>	
MoS <sub>2</sub> /CPs	80 mV@ 10 mA·cm <sup>-2</sup>	<i>Nano Energy</i> <b>2015</b> , 15, 335.
CoP/CC	67 mV@ 10 mA·cm <sup>-2</sup>	<i>J. Am. Chem. Soc.</i> <b>2014</b> , 136, 7587.
Ir/GF	7 mV@ 10 mA·cm <sup>-2</sup>	<i>Nano Energy</i> 2017, 40, 27
Co <sub>9</sub> S <sub>8</sub> /NC@MoS <sub>2</sub>	117 mV@ 10 mA·cm <sup>-2</sup>	<i>ACS Appl. Mater. Interfaces</i> <b>2017</b> , 9, 28394-28405
WO <sub>3</sub> ·2H <sub>2</sub> O/WS <sub>2</sub>	152 mV@ 100 mA·cm <sup>-2</sup>	<i>ACS Appl. Mater. Interfaces</i> <b>2016</b> , 8, 13966-13972.
Ni-Mo nanopowders	80 mV@ 20 mA·cm <sup>-2</sup>	<i>ACS Catal.</i> <b>2013</b> , 3, 166-169.
Ni <sub>0.89</sub> -Co <sub>0.11</sub> Se <sub>2</sub> /NF	52 mV@ 10 mA·cm <sup>-2</sup>	<i>Adv. Mater.</i> <b>2017</b> , 29, 1606521
Mn-Co-P/Ti	49 mV@ 10 mA·cm <sup>-2</sup>	<i>ACS Catal.</i> <b>2017</b> , 7, 98-102.
CC@N-CoP/CFP	42 mV@ 10 mA·cm <sup>-2</sup>	<i>Adv. Mater.</i> <b>2018</b> , 30, 1800140.
np-Co <sub>2</sub> P	80 mV@ 10 mA·cm <sup>-2</sup>	<i>Adv. Mater.</i> <b>2016</b> , 28, 2951.
V <sub>8</sub> C <sub>7</sub> /NF	38 mV@ 10 mA·cm <sup>-2</sup>	<i>Adv. Energy Mater.</i> <b>2018</b> , 8, 1800575.
CoPS NPIs/CFP	48 mV@ 10 mA·cm <sup>-2</sup>	<i>Nat. Mater.</i> <b>2015</b> , 14, 1245.
Ni <sub>2</sub> P@NPCNFs/CFP	63 mV@ 10 mA·cm <sup>-2</sup>	<i>Angew. Chem. Int. Ed.</i> <b>2018</b> , 130, 1981-1985.

**Table S3** Comparison of the HER activities of the V<sub>15</sub>-NiCoP/CFP composite with other reported catalysts in neutral medium (1 M PBS).

Electrode	$\eta$ (mV)	Reference
V <sub>15</sub> -NiCoP/CFP	85.3 mV@ 10 mA·cm <sup>-2</sup> 184.7 mV@ 100 mA·cm <sup>-2</sup>	This work
NiCoP/CFP	181.8 mV@ 10 mA·cm <sup>-2</sup>	This work
Pt-C/CFP	34.0 mV@ 10 mA·cm <sup>-2</sup>	This work
CoP nanowires	106 mV@ 10 mA·cm <sup>-2</sup>	<i>J. Am. Chem. Soc.</i> <b>2014</b> , 136, 7587-7590.
FeP/CC	115 mV@ 10 mA·cm <sup>-2</sup>	<i>ACS Appl. Mater. Interfaces</i> <b>2014</b> , 6, 20579-20584.
NiCo <sub>2</sub> P <sub>x</sub> /CFP	63 mV@ 10 mA·cm <sup>-2</sup>	<i>Adv. Mater.</i> <b>2017</b> , 29, 1605502.
Ni <sub>2</sub> P@NPCNFs	185 mV@ 10 mA·cm <sup>-2</sup>	<i>Angew. Chem. Int. Ed.</i> <b>2018</b> , 130, 1981-1985.
Co <sub>9</sub> S <sub>8</sub> /NC@MoS <sub>2</sub>	261 mV@ 10 mA·cm <sup>-2</sup>	<i>ACS Appl. Mater. Interfaces</i> <b>2017</b> , 9, 28394-28405
Mn-Co-P/Ti	86 mV@ 10 mA·cm <sup>-2</sup>	<i>ACS Catal.</i> <b>2017</b> , 7, 98-102.
CoW(OH) <sub>x</sub> /NF	74 mV@ 10 mA·cm <sup>-2</sup>	<i>ACS Catal.</i> <b>2018</b> , 8, 5200-5205.
FLNPC@MoP-NC/ MoP-C	106 mV@ 10 mA·cm <sup>-2</sup>	<i>Adv. Funct. Mater.</i> <b>2018</b> , 28, 1801527.
CoS film	160 mV@ 10 mA·cm <sup>-2</sup>	<i>J. Am. Chem. Soc.</i> <b>2013</b> , 135, 17699-17702.
Co <sub>9</sub> S <sub>8</sub> /CC	175 mV@ 10 mA·cm <sup>-2</sup>	<i>J. Mater. Chem. A</i> <b>2016</b> , 4, 6860-6867.
Ni <sub>3</sub> S <sub>2</sub> /Ni foam	170 mV@ 10 mA·cm <sup>-2</sup>	<i>J. Am. Chem. Soc.</i> <b>2015</b> , 137, 14023-14026.
FeP nanoparticles on Ti	102 mV@ 10 mA·cm <sup>-2</sup>	<i>ACS Nano</i> <b>2014</b> , 8, 11101-11107.