

# Hierarchical NiFeV Hydroxide Nanotubes: Synthesis, Topotactic Transformation and Electrocatalysis towards Oxygen Evolution Reaction

Qingying Li,<sup>a</sup> Xiaohe Liu,<sup>\*a,b</sup> Zhicheng Zheng,<sup>a</sup> Gen Chen,<sup>a</sup> Renzhi Ma,<sup>c</sup> Hao Wan<sup>\*b</sup>

<sup>a</sup> State Key Laboratory of Powder Metallurgy and School of Materials Science and Engineering, Central South University, Changsha, Hunan 410083, P.R. China.

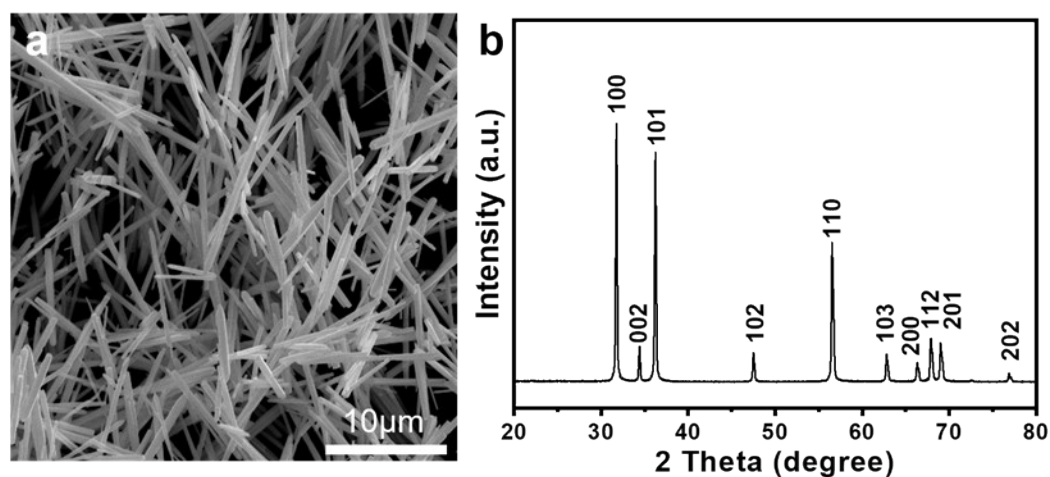
<sup>b</sup> School of Chemical Engineering, Zhengzhou University, Zhengzhou 450001, P.R. China.

<sup>c</sup> World Premier International Center for Materials Nanoarchitectonics (WPI-MANA), National Institute for Materials Science (NIMS), Namiki 1-1, Tsukuba, Ibaraki 305-0044, Japan.

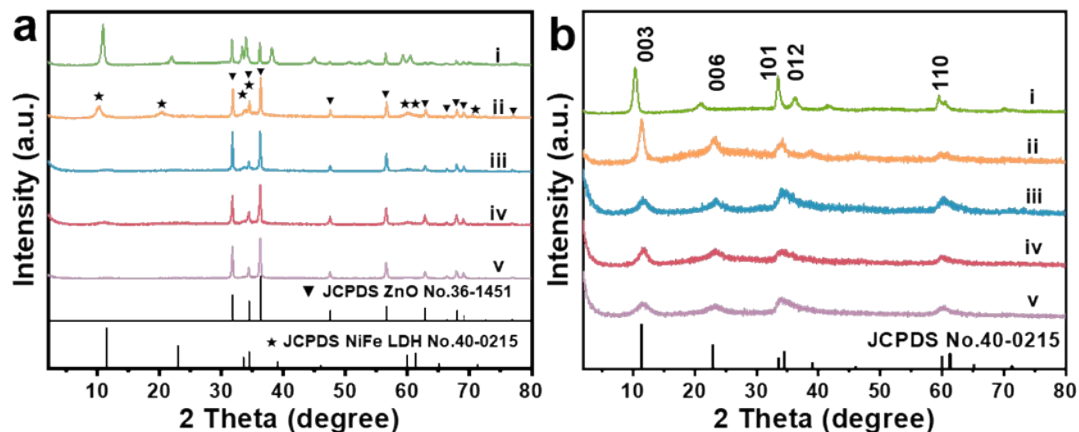
## Corresponding Author

\*E-mail: liuxh@csu.edu.cn (Xiaohe Liu).

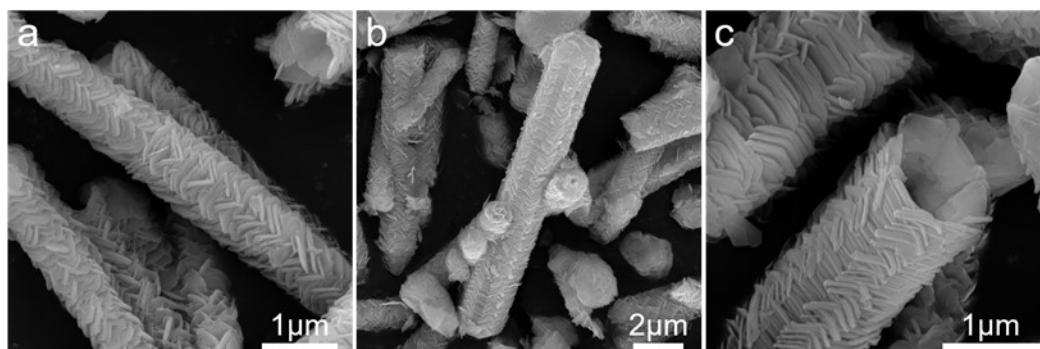
\*E-mail: wanhao@zzu.edu.cn (Hao Wan).



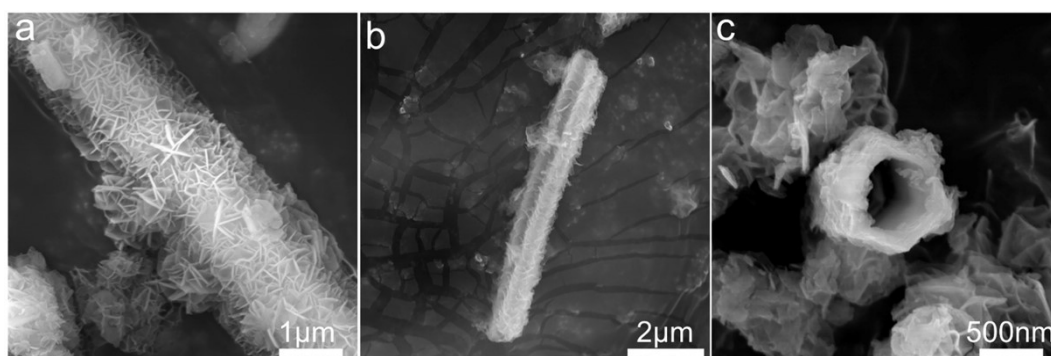
**Fig. S1.** (a) SEM image and (b) XRD pattern of ZnO nanorods.



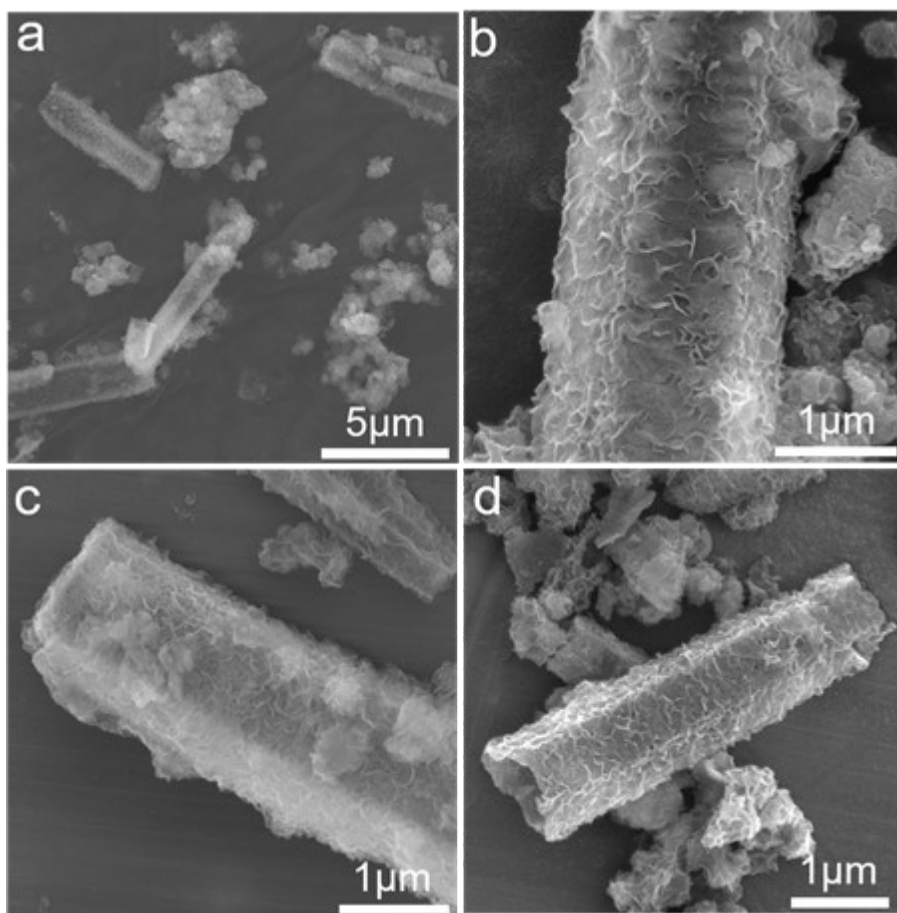
**Fig. S2.** (a) XRD pattern of i)  $\text{Ni}(\text{OH})_2\text{-CST}$ , ii)  $\text{NiFe-82 LDHs-CST}$ , iii)  $\text{NiFeV-611 LDHs-CST}$ , iv)  $\text{NiFeV-811 LDHs-CST}$ , v)  $\text{NiFeV-1011 LDHs-CST}$ ; (b) XRD pattern of i)  $\text{Ni}(\text{OH})_2\text{-HNT}$ , ii)  $\text{NiFe-82 LDHs-HNT}$ , iii)  $\text{NiFeV-611 LDHs-HNT}$ , iv)  $\text{NiFeV-811 LDHs-HNT}$ , v)  $\text{NiFeV-1011 LDHs-HNT}$ .



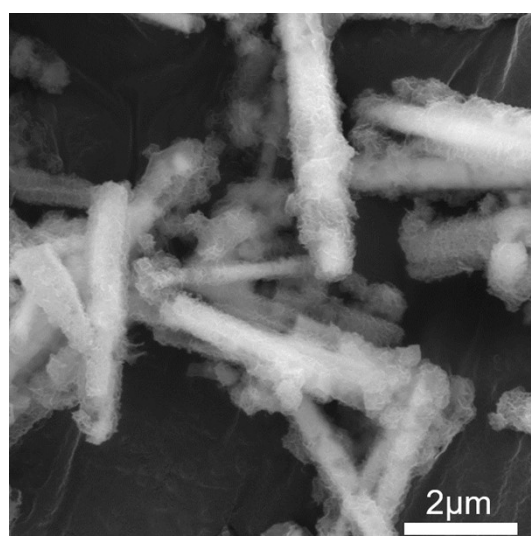
**Fig. S3.** (a) SEM image of  $\text{Ni}(\text{OH})_2\text{-CST}$ ; (b) and (c) SEM image of  $\text{Ni}(\text{OH})_2\text{-HNT}$  with different magnification.



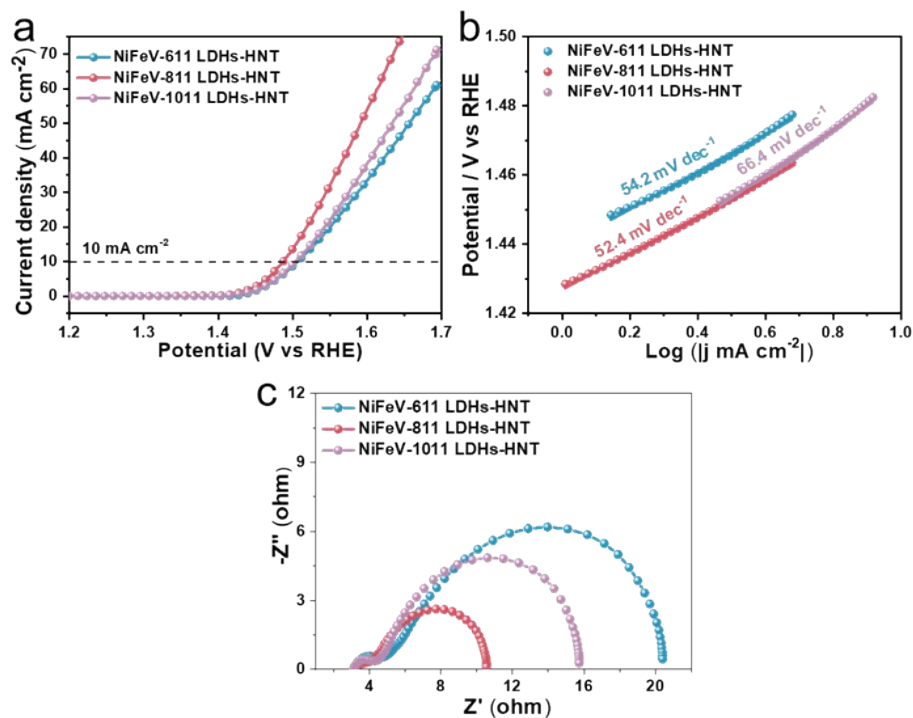
**Fig. S4.** (a) SEM image of  $\text{NiFe-82 LDHs-CST}$ ; (b) and (c) SEM image of  $\text{NiFe-82 LDHs-HNT}$  with different magnification.



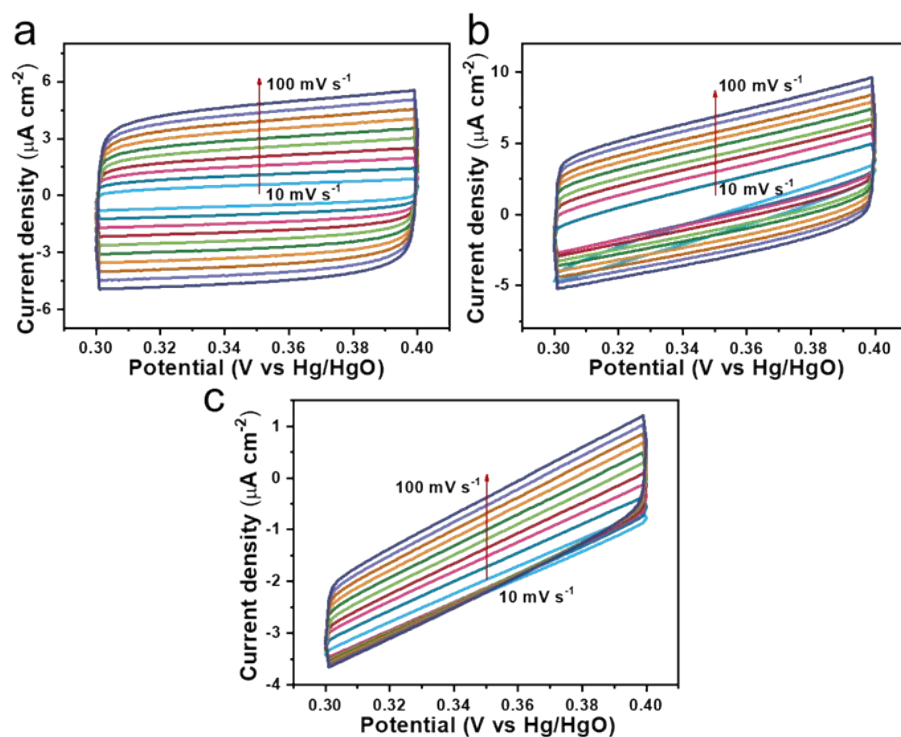
**Fig. S5.** SEM image of (a) NiFeV-811 LDHs-HNT with low magnification; (b) NiFeV-811 LDHs-HNT with high magnification (c) NiFeV-611 LDHs-HNT and (d) SEM image of NiFeV-1011 LDHs-HNT.



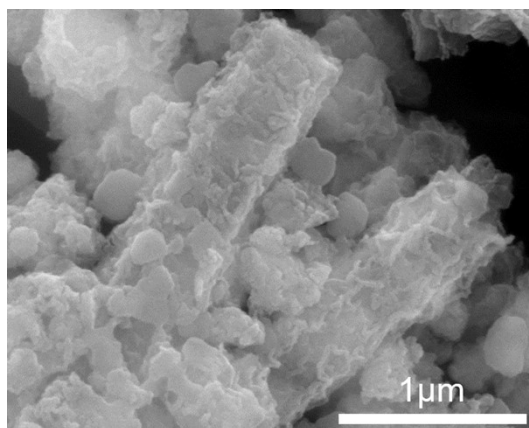
**Fig. S6.** SEM image of NiFeV-811 LDHs-CST.



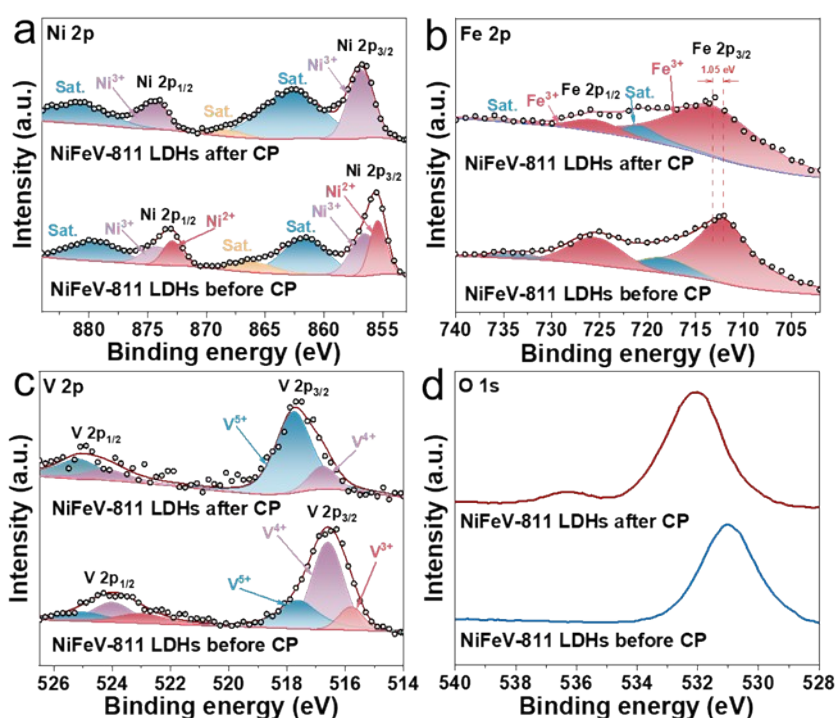
**Fig. S7.** Electrochemical measurement results of NiFe-611 LDHs-HNT, NiFeV-811 LDHs-HNT and NiFeV-1011 LDHs-HNT (a) LSV plots, (b) Tafel plots, (c) Nyquist plots measured at 0.55 V vs Hg/HgO.



**Fig. S8.** The Cycle voltammograms (CV) curves of (a) NiFe-82 LDHs-HNT, (b) NiFeV-811 LDHs-HNT, (c) NiFeV-811 LDHs-CST.

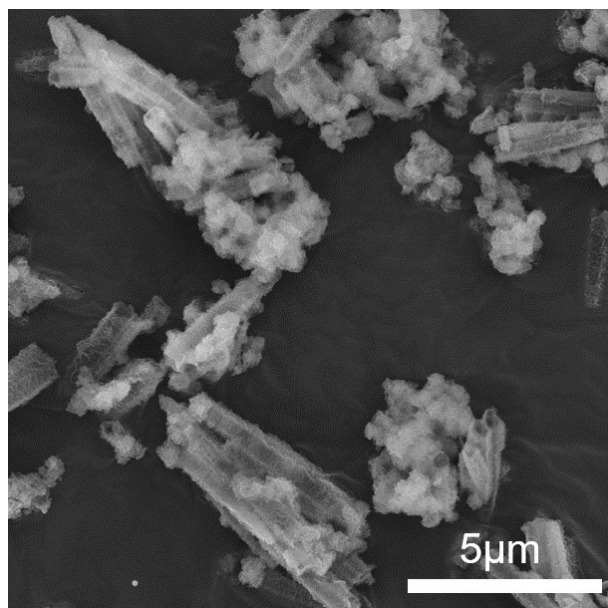


**Fig. S9.** SEM image of NiFeV-811 LDHs-HNT after 45h CP.

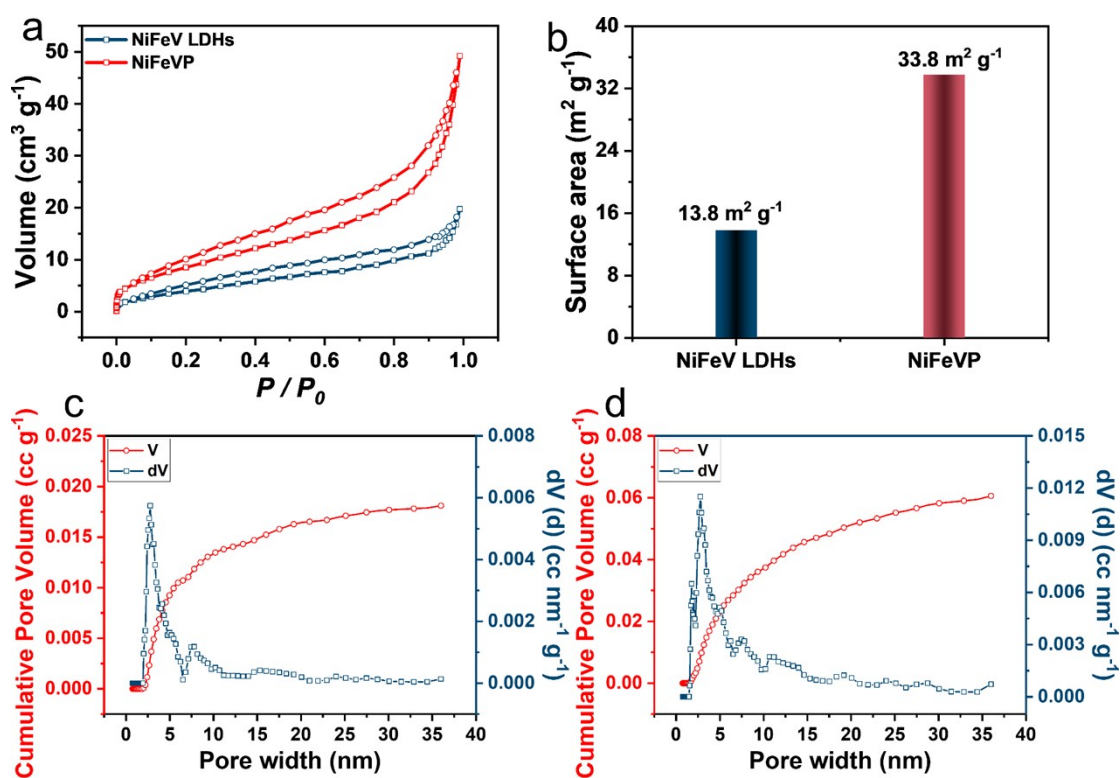


**Fig. S10.** High-resolution XPS spectra of NiFeV-811 LDHs HNT before and after CP measurement: (a) Ni 2p; (b) Fe 2p; (c) V 2p; (d) O 1s spectra. It can be observed that after a long time of OER process, due to the oxidation during the testing, Ni<sup>2+</sup> was completely oxidized to Ni<sup>3+</sup>, while the peaks of Fe 2p also shift to higher binding energy. The content of V<sup>5+</sup> in V 2p shows a higher peak area after OER than the initial NiFeV-811 LDHs-HNT. In the O 1s spectra, the main peak for O 1s is shifted from 530.9 eV to 532.1 eV, which indicate that the hydroxyl group in the hydroxide is converted into peroxide group (-OOH). Meanwhile, compared to the NiFeV-811 LDHs-HNT before CP a new peak is generated at 536.2eV, which is ascribed to the oxidation of carbon fiber paper.





**Fig. S11.** SEM image of NiFeVP hollow nanotubes with low magnification.



**Fig. S12.** Porosity analysis of NiFeV-811 LDHs HNT and NiFeVP samples. (a) N<sub>2</sub> sorption isotherm and (b) specific surface area. Pore structures of (c) NiFeV-811 LDHs HNT and (d) NiFeVP samples. Pore volume was estimated as 0.024 and 0.061 cc g<sup>-1</sup> for NiFeV-811 LDHs-HNT and NiFeVP hollow nanotubes using DFT analysis, respectively.

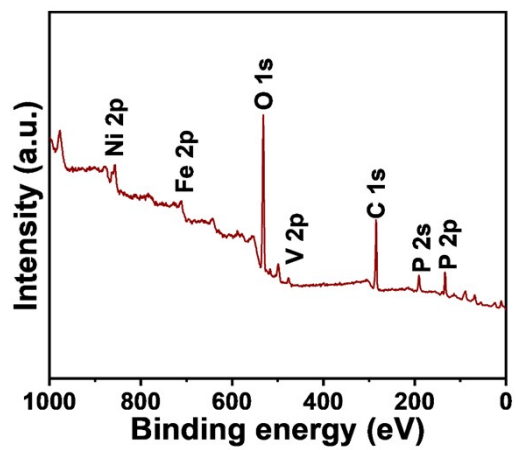


Fig. S13. Full XPS spectrum of NiFeVP hollow nanotubes.

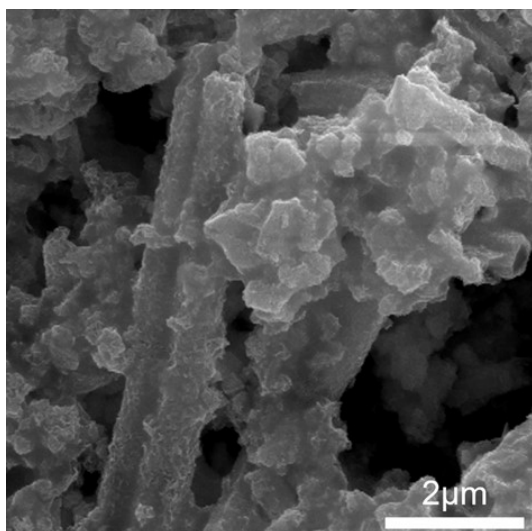
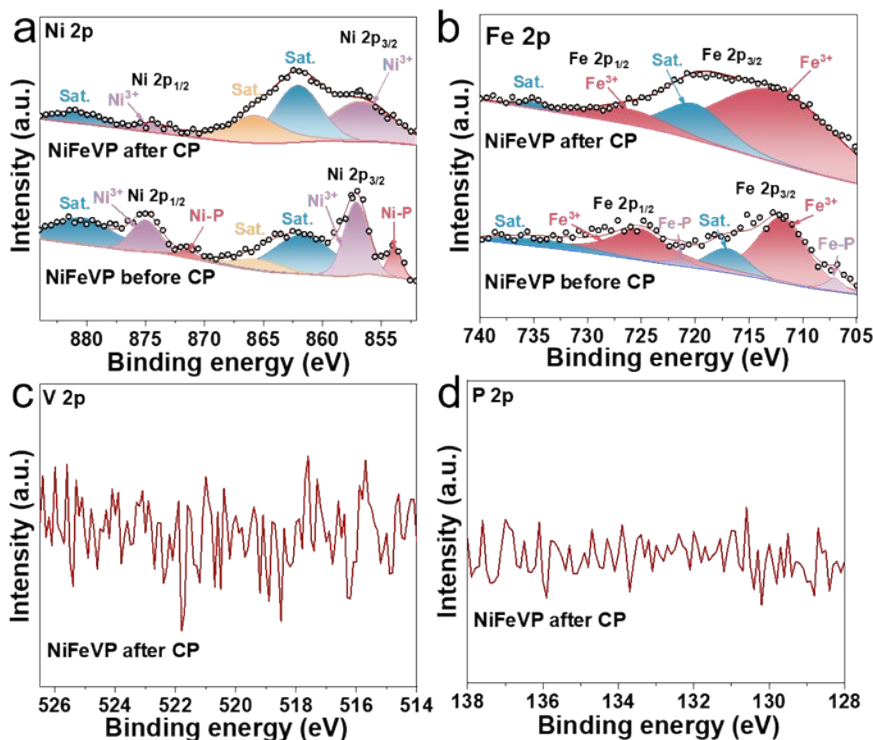


Fig. S14. SEM image of NiFeVP hollow nanotubes after 50h CP.



**Fig. S15.** High-resolution XPS spectra of NiFeVP hollow nanotubes before and after CP measurement. (a) Ni 2p, (b) Fe 2p, (c) V 2p and (d) P 2p.

**Table S1.** Calculated values based on the fitted equivalent circuit.

Product	Rs ( $\Omega$ )	Rct ( $\Omega$ )	Rp ( $\Omega$ )
NiFe-82 LDHs-HNT	3.182	50.42	7.284
NiFeV-811 LDHs-HNT	3.252	6.31	1.215
NiFeV-811 LDHs-CST	2.942	51.94	16.04
NiFeVP	2.696	3.649	0.915

**Table S2.** Electrochemical analysis of NiFeV-811 LDHs-HNT, NiFe-82 LDHs-HNT, NiFeV-811 LDHs-CST and their intrinsic activities toward OER.

Product	Double-layer Capacitance ( $C_{dl}$ ) ( $mF\ cm^{-2}$ )	Rough Factor ( $R_f$ )	J @ 1.5 V <sub>RHE</sub> ( $mA\ cm^{-2}$ )	J <sub>specific</sub> @ 1.5 V <sub>RHE</sub> ( $mA\ cm^{-2}$ )
NiFeV-811 LDHs HNT	96.28	1.60	13.84	8.62
NiFe-82 LDHs HNT	91.96	1.53	6.32	4.13
NiFeV-811 LDHs CST	17.66	0.30	2.21	7.52



**Table S3.** Comparison of electrocatalytic performances of some representative Ni-based catalysts for OER in 1.0 M KOH.

Catalysts	Current density (mA cm <sup>-2</sup> )	Tafel slop (mV dec <sup>-1</sup> )	Overpotential (mV)	Reference
NiFeVP hollow nanotubes	10	30.3	209.5	This work
NiFeVP	10	34.4	249.0	[1]
Ni <sub>1.5</sub> Fe <sub>0.5</sub> P	10	125.0	264.0	[2]
D-Ni <sub>5</sub> P <sub>4</sub>  Fe	10	45.7	217.3	[3]
NiFeP	10	60.0	270.0	[4]
NiFePi/P	10	57.0	230.0	[5]
NiFe LDH @NiCoP/NF	10	48.6	220.0	[6]
V-Ni <sub>2</sub> P/NF-AC	10	66.0	221.0	[7]
P-NiFe-800 NPs	10	39.0	270.1	[8]

## References

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