Supporting information for:

Hierarchical Ni-Co-O-C-P hollow tetragonal microtubes grown on Ni foam for efficient overall water splitting in alkaline media

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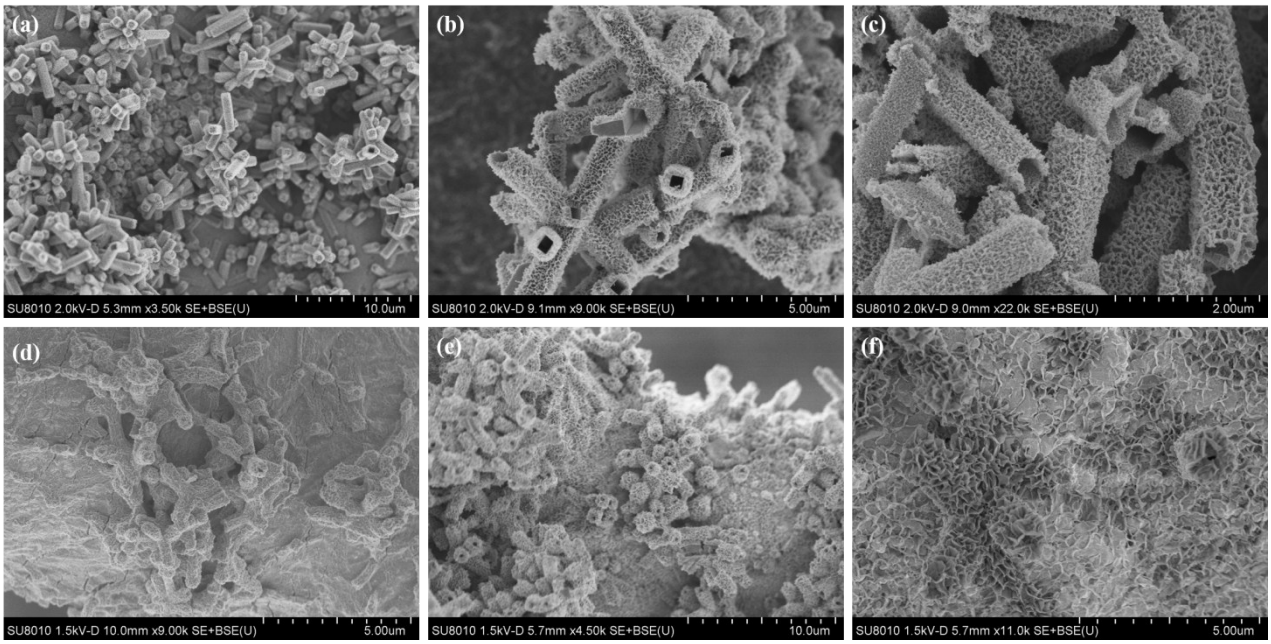

Fig. S1. SEM images of (a, b) $NiCo_2O_4$ power, (c) $NiCo_2O_4$ power after in-situ in-situ phosphorization process, (d) Ni-Co-O-C/NF with the increasing of carbon coating, (e) double the concentration of precursor, (f) Ni-Co-O-C-P/NF with the increasing of P content.

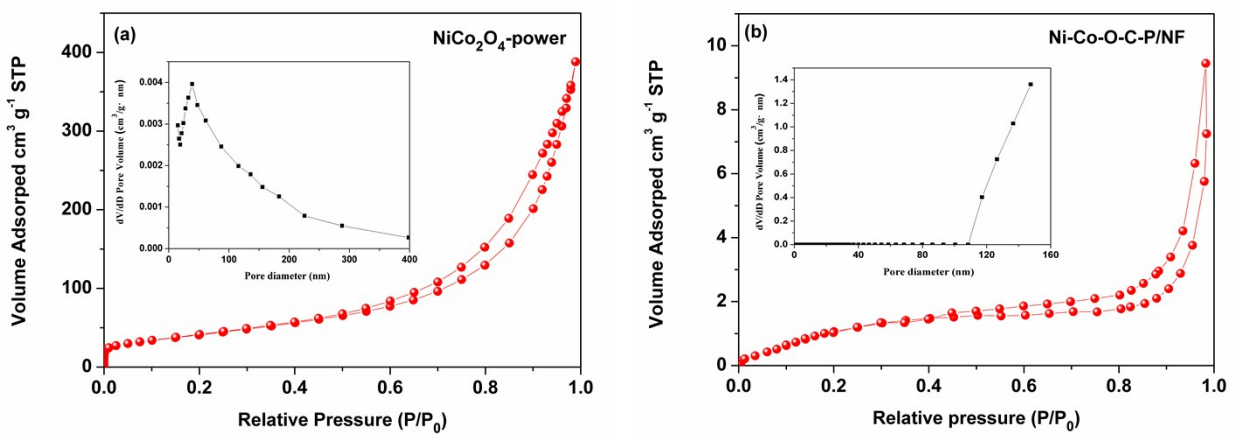

Fig. S2. N_2 adsorption-desorption isotherms and the corresponding pore size distribution of (a) $NiCo_2O_4$ powder, (b) Ni-Co-O-C-P/NF.

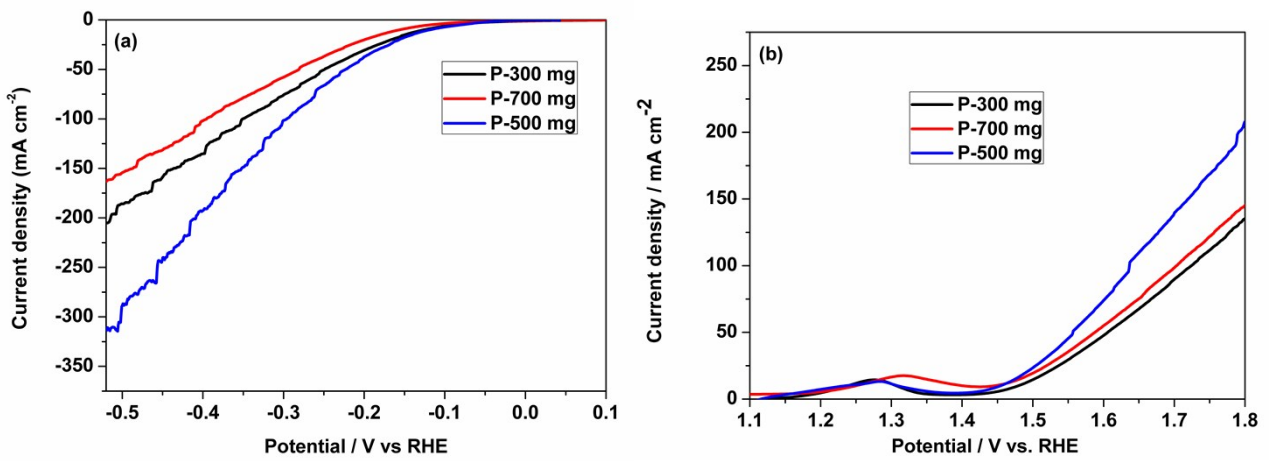

Fig. S3. Polarization curves of the hierarchical Ni-Co-O-C-P/NF with different P content for (a) HER and (b) OER.

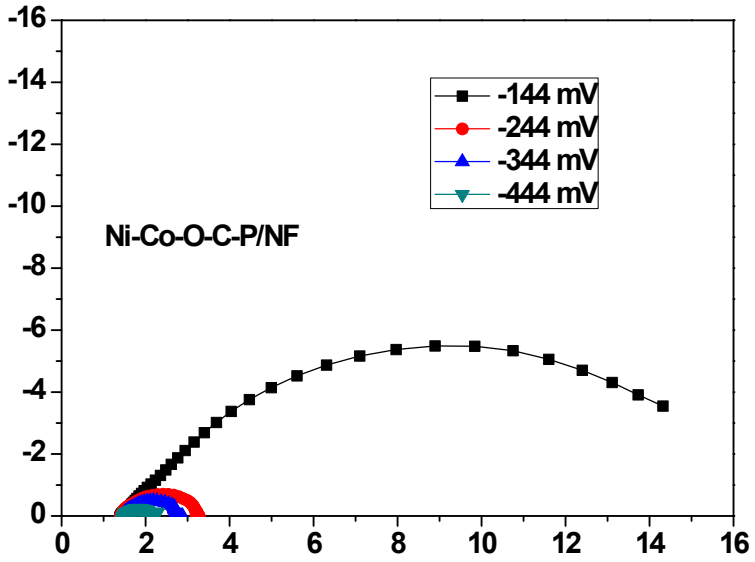

Fig. S4. Nyquist plots of the Ni-Co-O-C-P/NF measured under different potentials (mV vs. RHE) in the frequency range of 10^5 to 1 Hz.

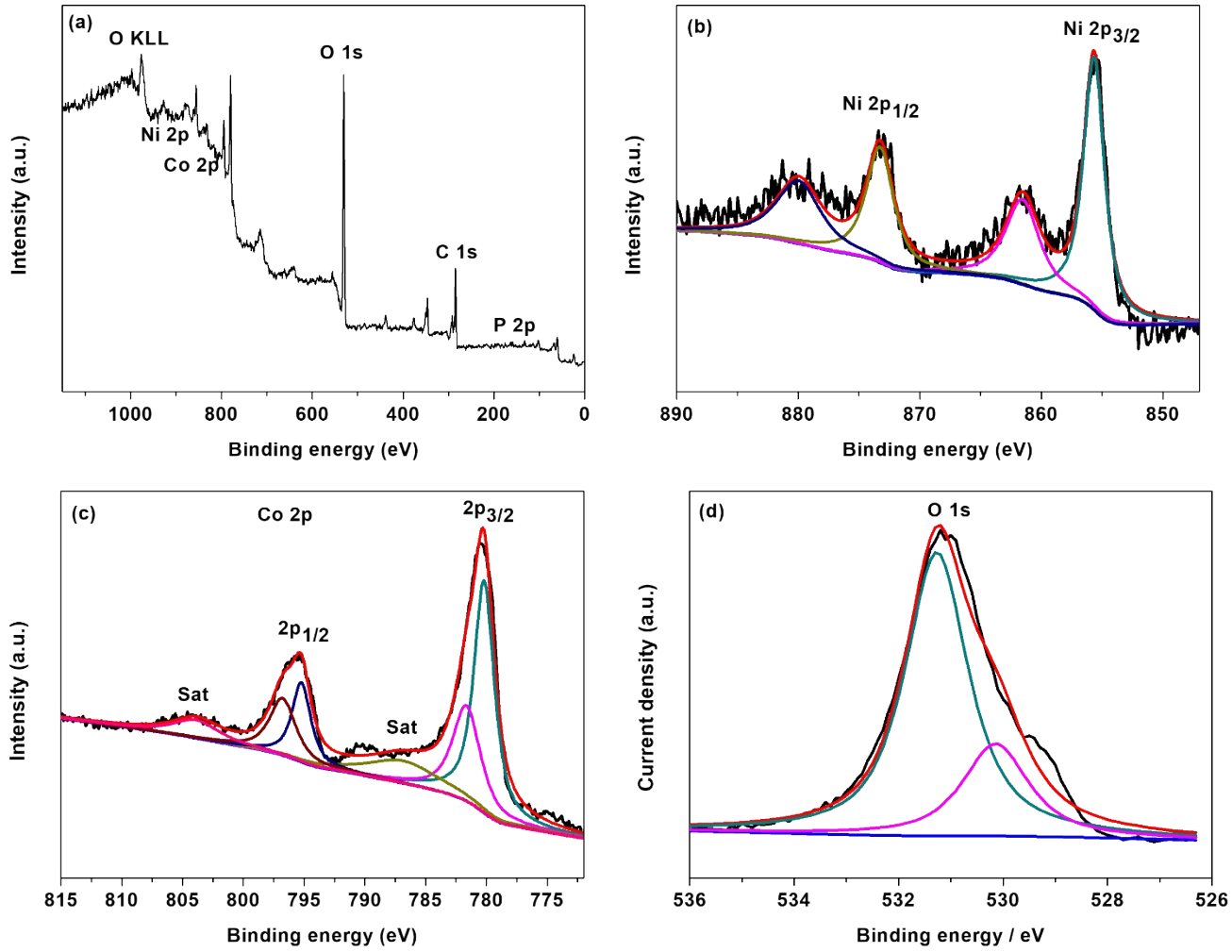

Fig. S5: The XPS spectrum of Ni-Co-O-C-P/NF after OER reaction. XPS spectra of (a) survey spectrum, (b) Ni 2p, (c) Co 2p and (d) O 1s.

As shown in Fig. S5, XPS analysis of Ni-Co-O-C-P/NF after OER reaction were given. The survey XPS spectrum confirms the presence of Ni, Co, O, C and P elements (Fig. S5a). For the Ni 2p region (Fig. S5b), the peaks at 855.6 eV and 873.1 eV along with two satellite peaks at 861.3 and 880.2 are attributed to Ni $2p_{3/2}$ and Ni $2p_{1/2}$ of the oxidized nickel species, respectively. For Co 2p spectrum (Fig. S5c), the peak at 781.8 eV in the Co $2p_{3/2}$ region and 797.5 eV in the Co $2p_{1/2}$ region are assigned to oxidized Co species ($Co^{2+/3+}$). The peaks at 787.9 and 804.1 eV are according to the corresponding satellite peaks of Co $2p_{3/2}$ and Co $2p_{1/2}$. For O 1s spectrum (Figure S5d), the peak at 531.4 eV is usually related to OH- groups, which indicates that the surface of the Ni-Co-O-C-P/NF is partially hydroxylated; and the characteristic peak located at 529.9 eV corresponds to Ni-Co-O.

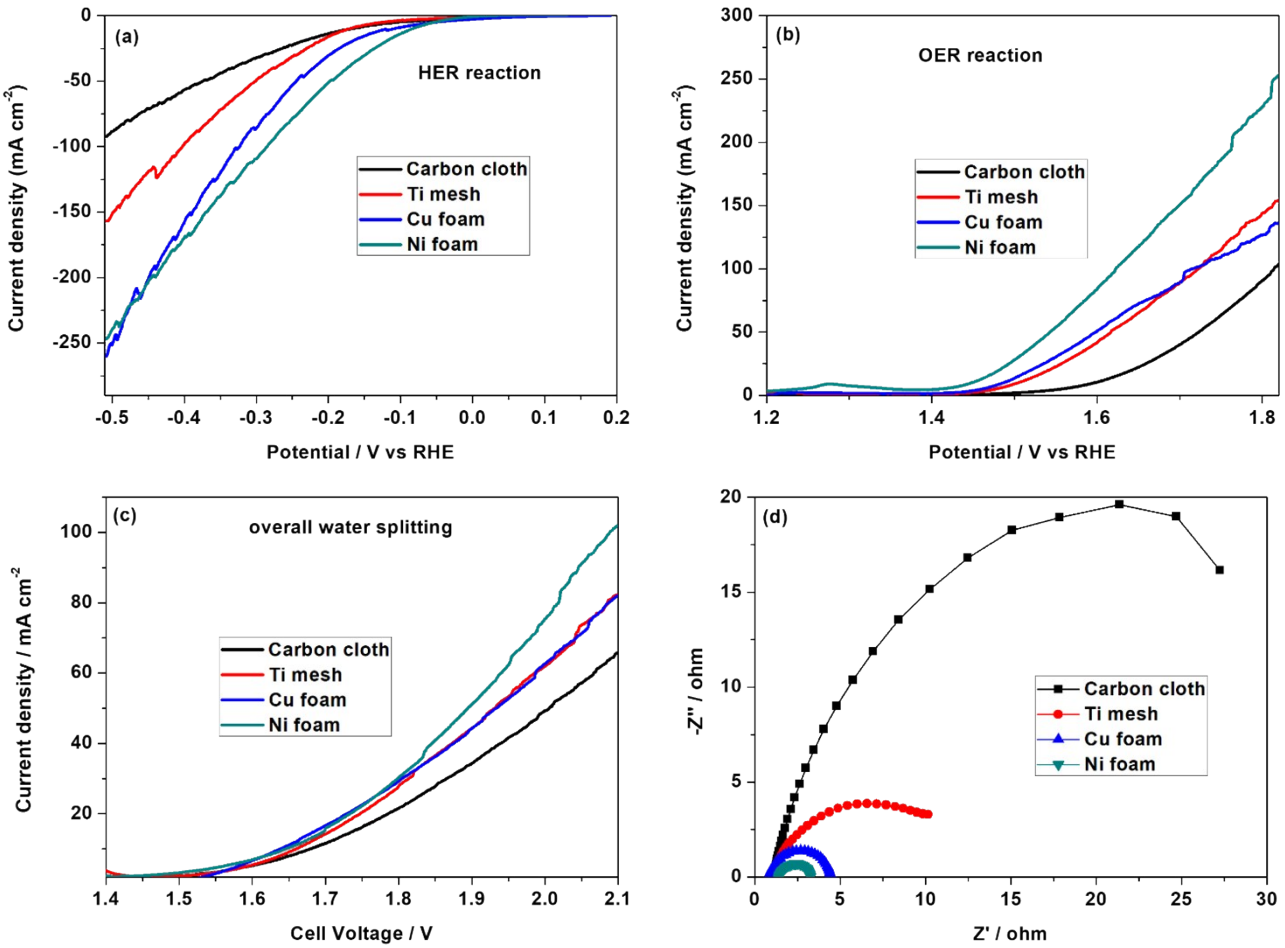

Fig. S6. *iR*-corrected polarization curve of the Ni-Co-O-C-P grown on different support for (a)HER, (b) OER, (c) overall water splitting reaction and (d) Nyquist plots of the Ni-Co-O-C-P grown on different support measured under -244 mV (vs. RHE) in the frequency range of 10^5 to 1 Hz.

The electrochemical reaction performance of Ni-Co-O-C-P grown on different supports are presented in Fig. S6. The Ni foam shows the best electrochemical activity for HER, OER and overall water splitting reaction, therefore, we chose Ni foam as the support. Fig. S6(d) shows the Nyquist plots of the Ni-Co-O-C-P grown on different support. The smaller diameter of the semicircle of the Ni-Co-O-C-P/NF suggests transfer impedance of contact and charge smaller than other samples. This may be one important reason for the different catalytic performance with different support.

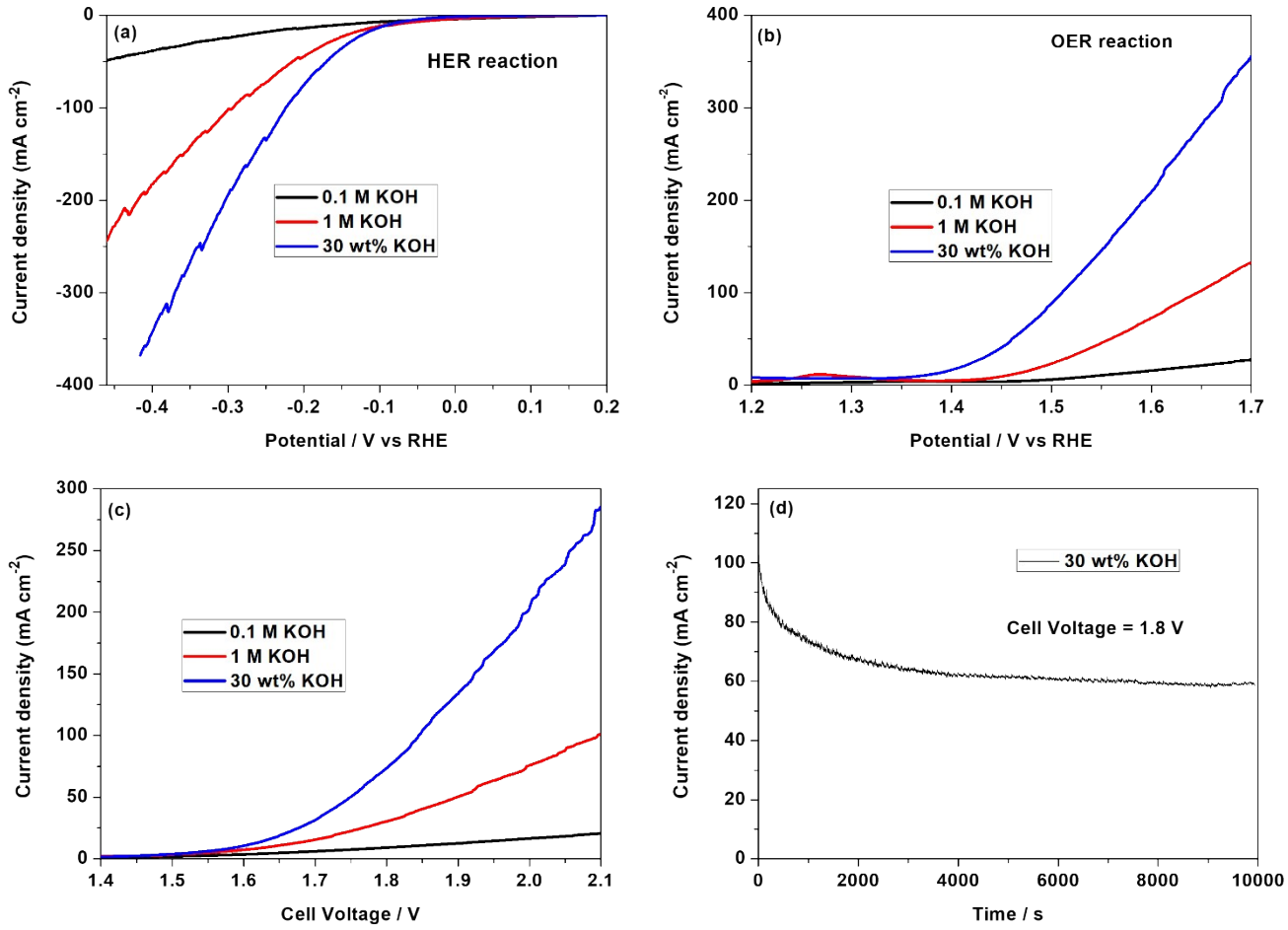

Fig. S7. The performance of Ni-Co-O-C-P/NF in 0.1 M and 30wt% KOH. iR-corrected polarization curve of the as prepared Ni-Co-O-C-P/NF for (a)HER, (b) OER and overall water splitting reaction; (d) the i-t curve of the hierarchical Ni-Co-O-C-P/NF for overall water splitting at a voltage of 1.80 V in 30 wt% KOH.

Table S1: Comparison of HER performance of NiCoP-based catalysts in 1.0 M KOH

Catalysts	η_{-10} (mV)	Tafel slope	Reference
Ni-Co-O-C-P hollow tetragonal microtubes	-119	90	This work
hierarchical Ni-Co-P hollow nanobricks	-107	-	1
CoNiP@NF	-155	-	2
Ni_5P_4@$NiCo_2O_4$	-27	27	3
$NiCo_2P_x$	-58	34	4
CoP	-209	129	5
CoP@NC	-78	49	6
Ni_2P/CNT	-124	41	7

Table S2: Comparison of OER performance of NiCoP-based catalysts in 1.0 M KOH

Catalysts	η_{100} (mV)	Tafel slope (mV dec^{-1})	Reference
Ni-Co-O-C-P hollow tetragonal microtubes	340	30	This work
CoP	413	47	8
CoP2/rGO	400	96	9
NiCoP@NF	360	87	10
NiCoP nanoparticle	370	52	11
hierarchical Ni-Co-P hollow nanobricks	320	76	1
Ni_2P nanoparticles	350	-	12

Table S3: Comparison of overall water splitting performance of NiCoP-based catalysts in 1.0 M KOH

Catalysts	$\eta_{10,overall}$ (mV)	$j_{1.7,overall}$	Reference
Ni-Co-O-C-P hollow tetragonal microtubes	1.54	23	This work
Ni_2P	1.63	20	12
NiCoP	1.68	16	10
NiS/NF	1.50	500	13
hierarchical Ni-Co-P hollow nanobricks	1.62	25	1

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