

## Electronic supplementary information

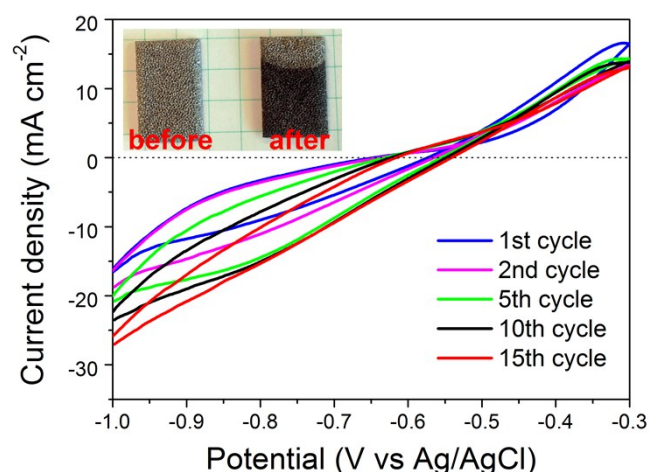
### Electro-synthesis of 3D porous hierarchical Ni-Fe phosphate film/Ni foam as high-efficiency bifunctional electrocatalyst for overall water splitting

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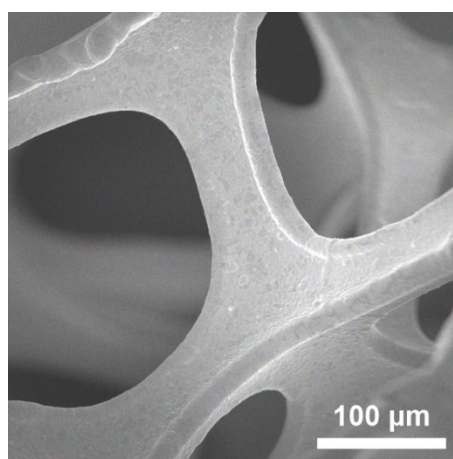
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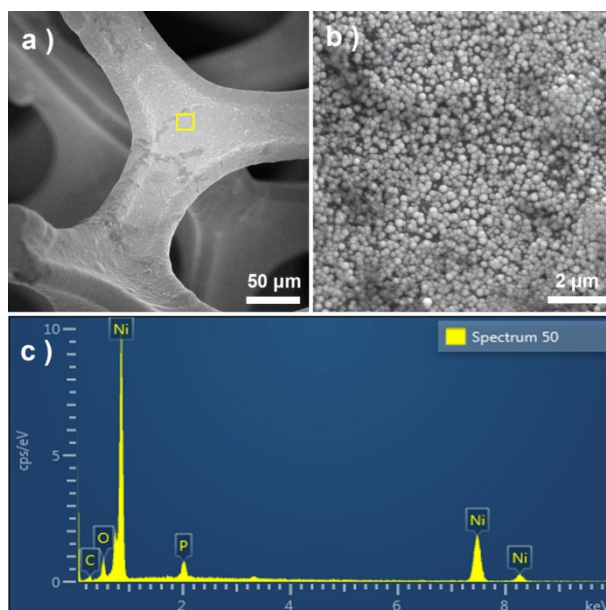
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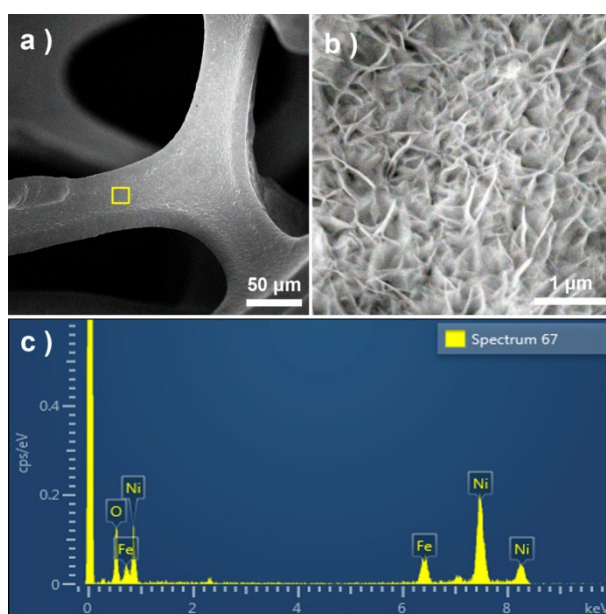
**Figure S1** Electrodeposition of NiFe-P catalysts at CV mode for 15 cycles, inset shows the photograph of Ni foam before and after deposition.



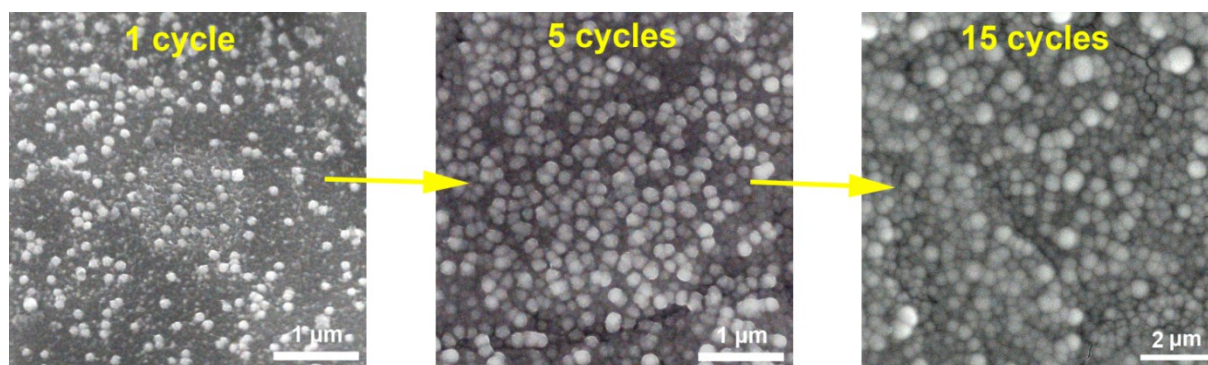
**Figure S2** SEM image of pristine Ni foam.



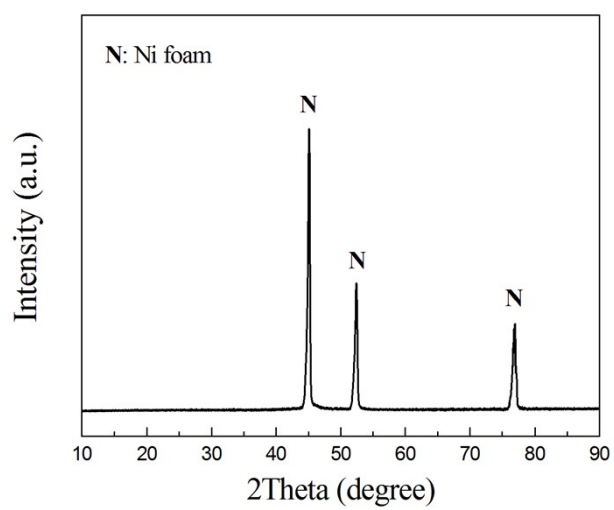
**Figure S3** (a) Low and (b) high magnification SEM images and (c) EDX spectrum of as-deposited Ni-P on Ni foam.



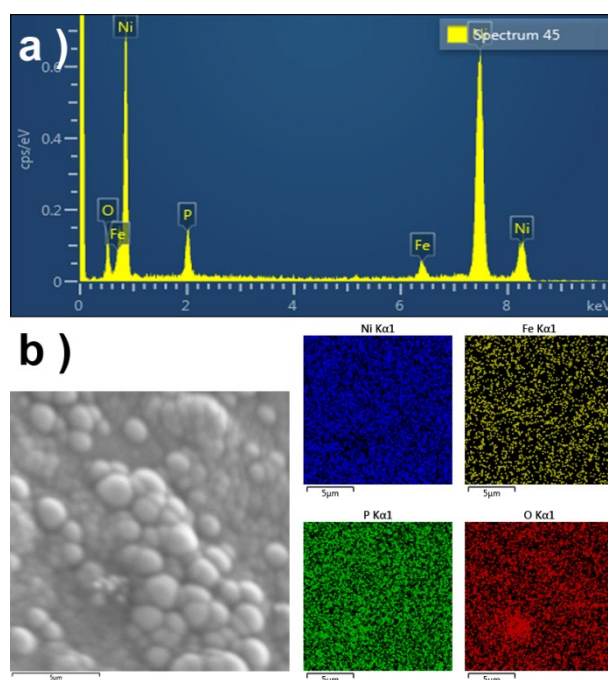
**Figure S4** (a) Low and (b) high magnification SEM images and (c) EDX spectrum of as-deposited NiFe-OH on Ni foam.



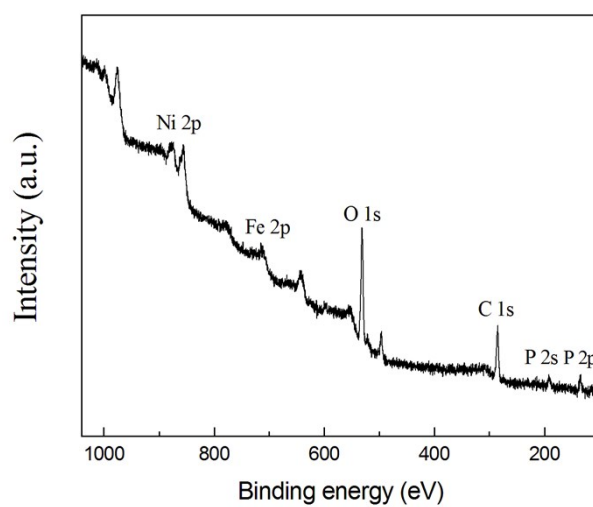
**Figure S5** Surface morphology evolution of NiFe-P during electrodeposition at CV mode.



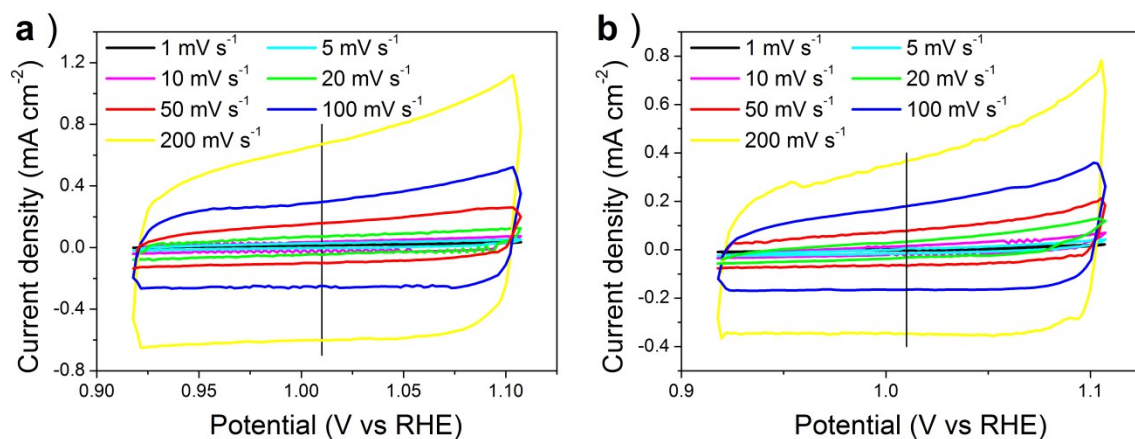
**Figure S6** XRD spectra of as-obtained NiFe-P.



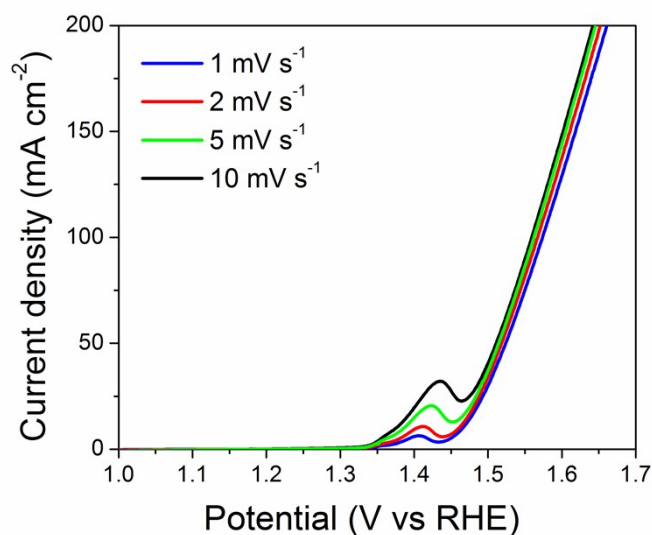
**Figure S7** (a) EDX spectrum and (b) EDX mapping images of the as-prepared NiFe-P.



**Figure S8** XPS survey spectrum of as-prepared NiFe-P.



**Figure S9** CV curves of (a) NiFe-P and (b) Ni-P obtained at 0.917~1.107 V vs RHE with different potential scanning rates.



**Figure S10** Polarization curves of NiFe-P catalyst obtained in 1 M KOH under various potential scanning rates.



**Figure S11** Photograph of two-electrode electrochemical cell for overall water splitting

**Table S1** Comparison of various bifunctional electrocatalysts for overall water splitting

Catalyst	$j$ (mA cm <sup>-2</sup> )	$\eta_j$ (mV)	Reference
NiFe phosphates	<b>10</b> <b>20</b>	<b>326</b> <b>385</b>	<b>This work</b>
NiFe LDHs	10	470	<i>Science</i> <b>2014</b> , 345, 1593
Ni phosphorous nanoparticles	10	450	<i>J. Power Sources</i> <b>2015</b> , 299, 342
Ni <sub>5</sub> P <sub>4</sub> films	10	470	<i>Angew. Chem. Int. Ed.</i> <b>2015</b> , 54, 12361
NiCo <sub>2</sub> S <sub>4</sub> nanowires	10	450	<i>Nanoscale</i> <b>2015</b> , 7, 15122
Fe phosphide nanotubes	10	460	<i>Chemistry—A European Journal</i> <b>2015</b> , 21, 18062
Co phosphorous films	10	420	<i>Angew. Chem. Int. Ed.</i> <b>2015</b> , 54, 6251
CoO <sub>x</sub> /N-doped Carbon	20	320	<i>J. Am. Chem. Soc.</i> , <b>2015</b> , 137, 2688
Ni phosphorous films	10	440	<i>ChemCatChem</i> <b>2016</b> , 8, 106
CoMn phosphide nanoparticles	10	330	<i>J. Am. Chem. Soc.</i> <b>2016</b> , 138, 4006
Nanoporous CoFe phosphides	10	300	<i>Energy Environ. Sci.</i> <b>2016</b> , 9, 2257
CoO <sub>x</sub> -CoSe films	20	430	<i>J. Mater. Chem. A</i> <b>2016</b> , 4, 10933