Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.


# Synthesis of in-situ core-shell interlink ultrathin-nanosheets $Fe@Fe_xNiO/Ni@Ni_yCoP$ nanohybrid by scalable layer-to-layer assembly strategy as an ultra-highly efficient bifunctional electrocatalyst for alkaline/neutral water reduction/oxidation

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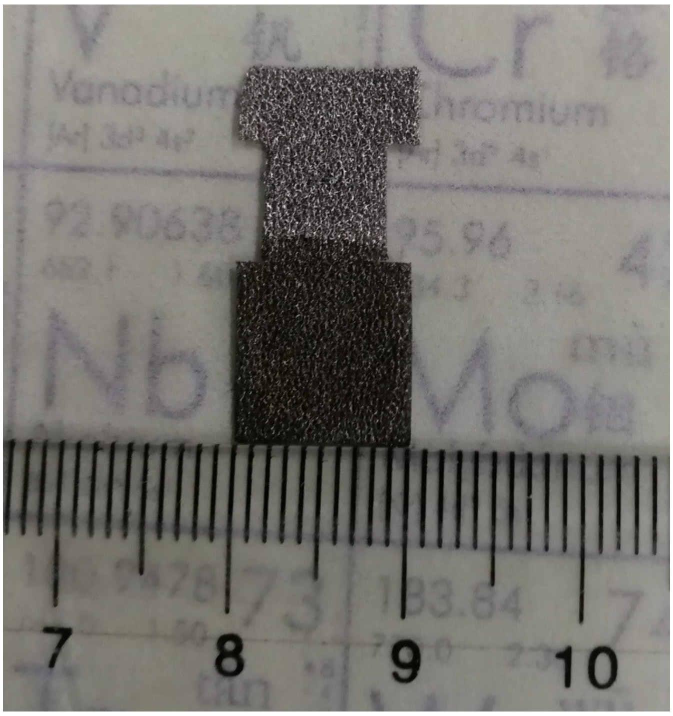
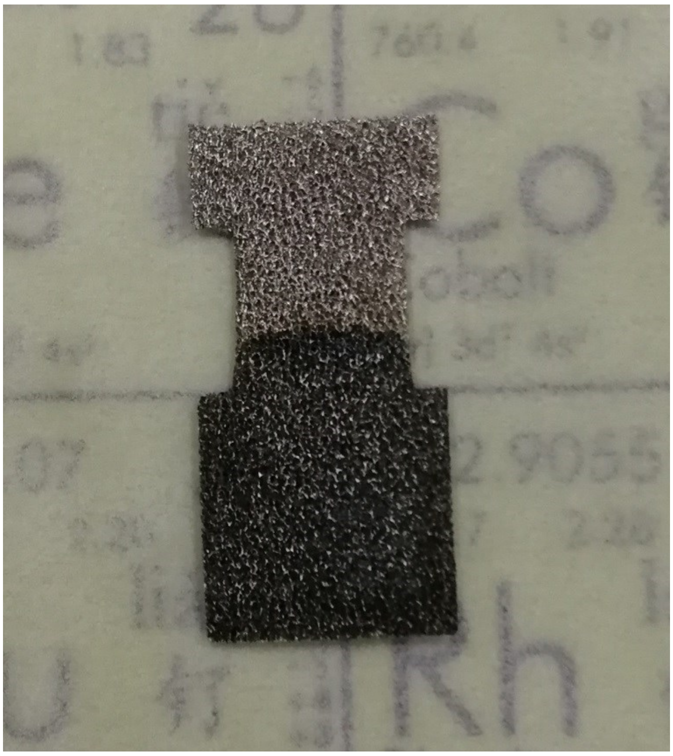
Figures and tables：




The digital photograph of $Fe@Fe_xNiO/NF$ directly as a working-electrode.



The digital photograph of $Fe@Fe_xNiO/Ni@Ni_yCoP/NF$ directly as a working-electrode.

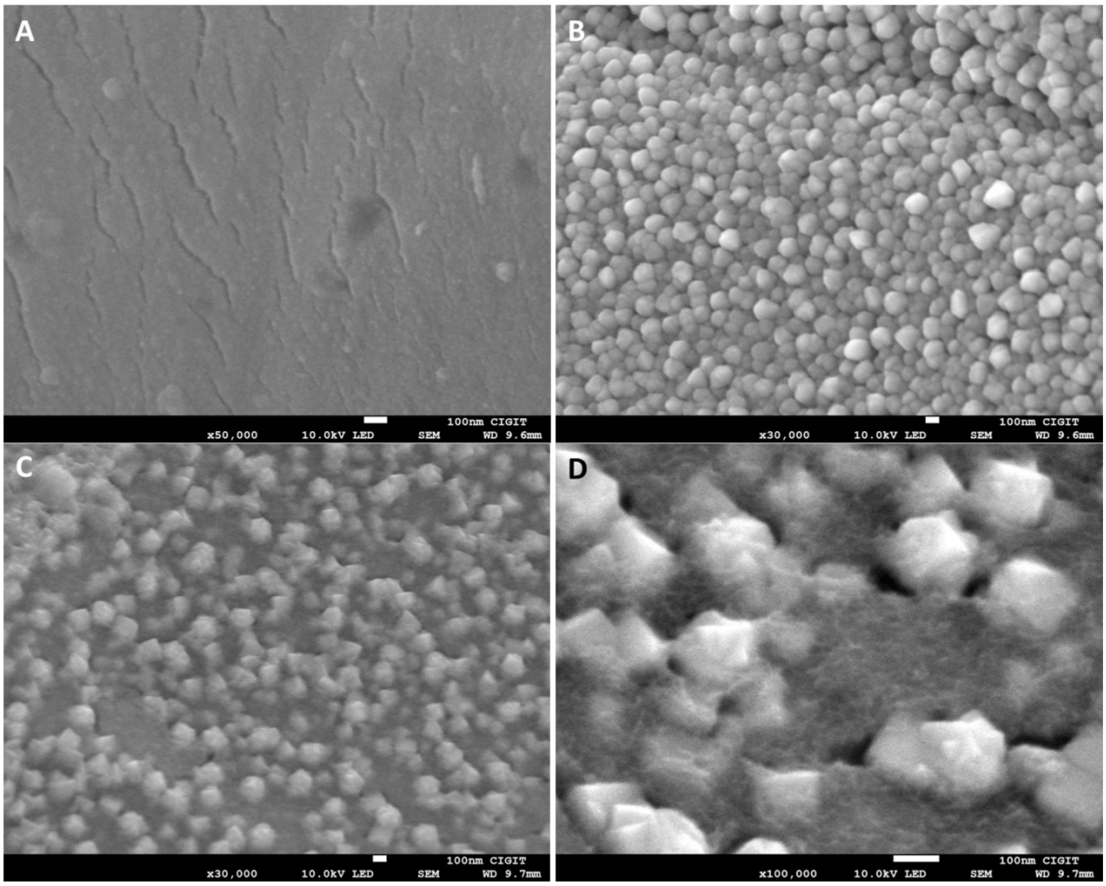



**Fig. S1** FE-SEM images of (A) without the additive of sodium citrate for ($Ni_4$-$Fe_4$)OH,

(B) $Ni_5Fe_3O$ and (C, D) $Ni_3Fe_5O$ samples.

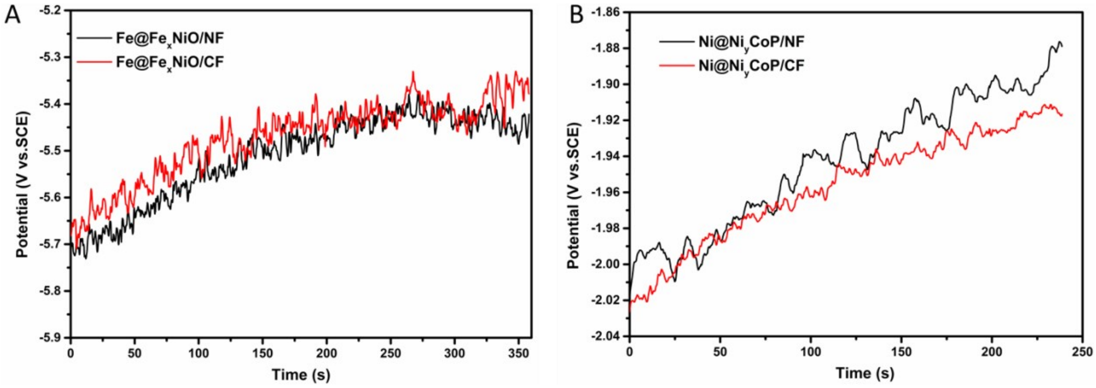



**Fig. S2** The electrodeposition process (V-t) of (A) Fe@Fe$_x$NiO at fixed current density of -45 mA·cm$^{-2}$ for 6 min and (B) Ni@Ni$_y$CoP constant current density of -200 mA·cm$^{-2}$ for 4 min on NF and CF, respectively.

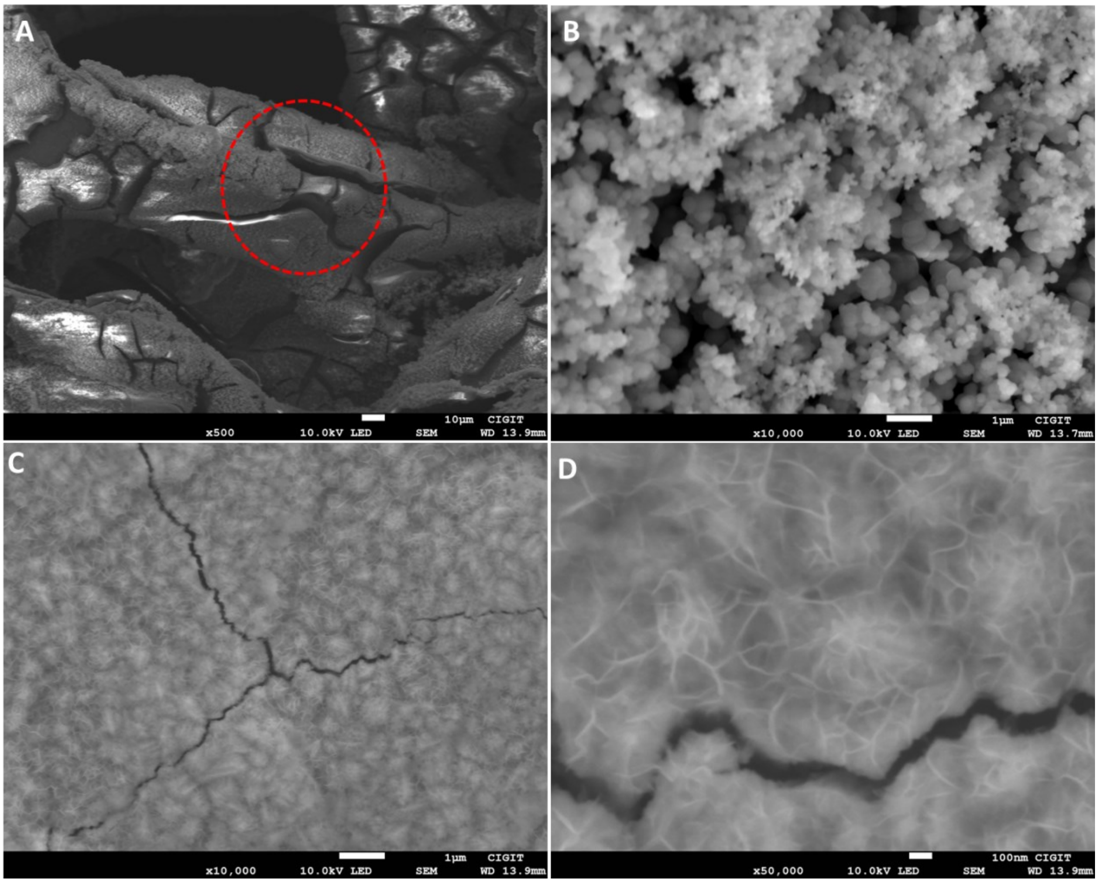



**Fig. S3** The FE-SEM images of (A, B) NiP, (C, D) CoP.

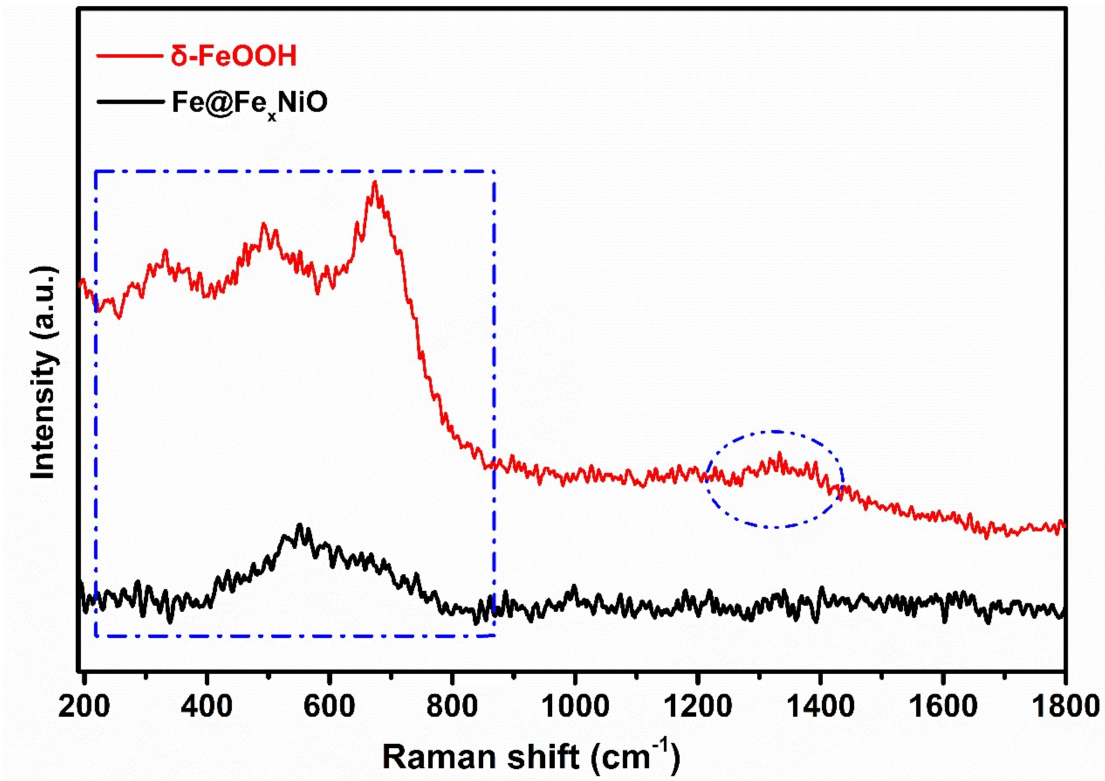



**Fig. S4** The Raman spectra of δ-FeOOH and Fe@Fe$_x$NiO. Attention! The δ-FeOOH catalyst was prepared as the same method as that of Fe@Fe$_x$NiO just without $Ni^{2+}$ precursor.

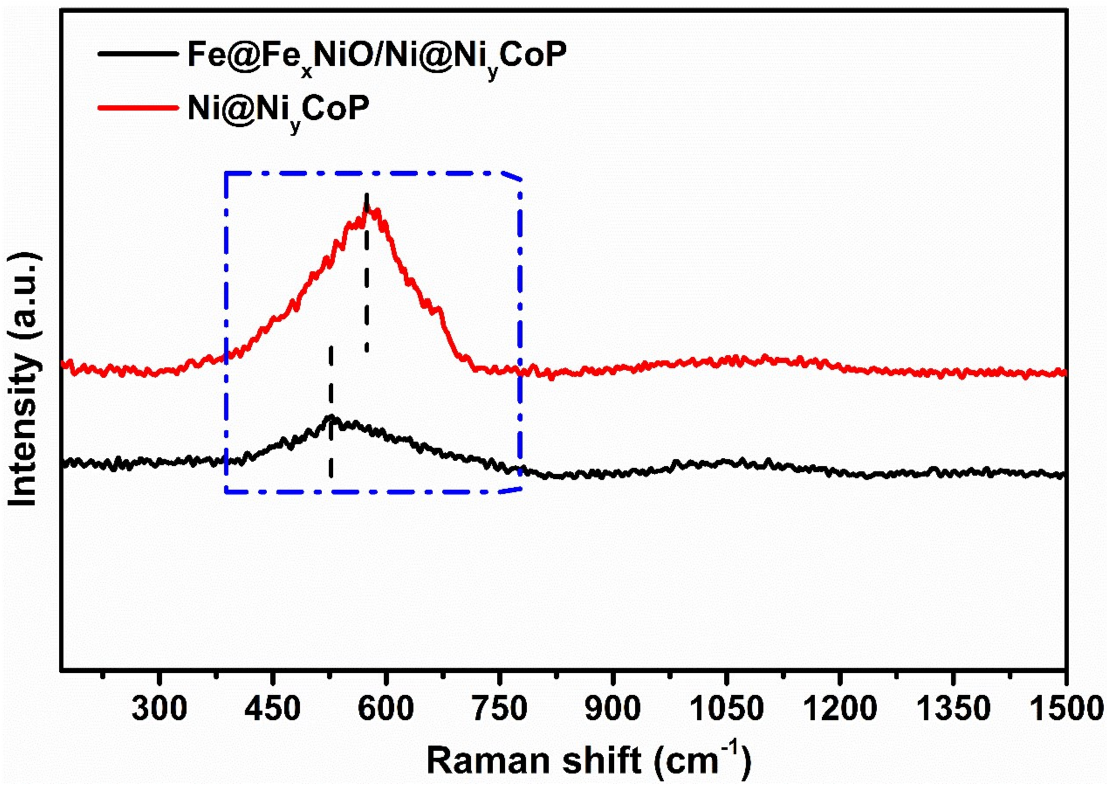



**Fig. S5** The Raman spectra of Ni@Ni$_y$CoP and Fe@Fe$_x$NiO/Ni@Ni$_y$CoP.

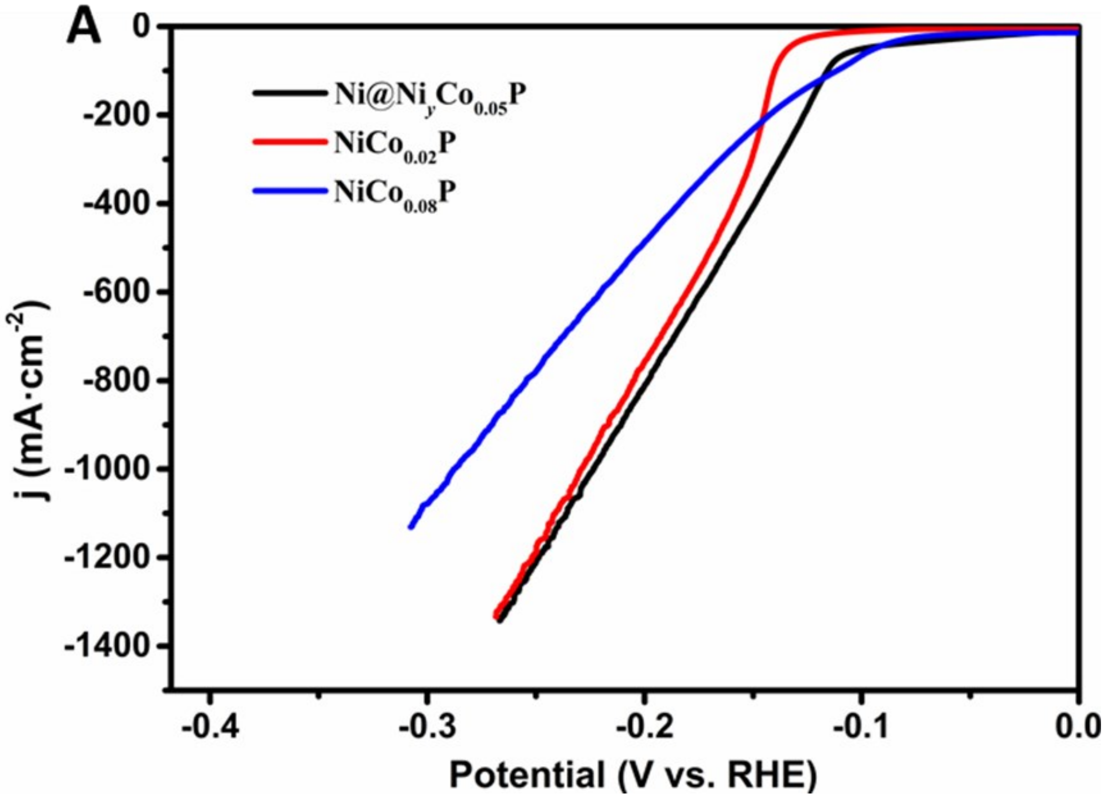



**Fig. S6** (A) The HER polarization curve of NiCo$_{0.02}$P, Ni@Ni$_y$CoP, NiCo$_{0.08}$P.

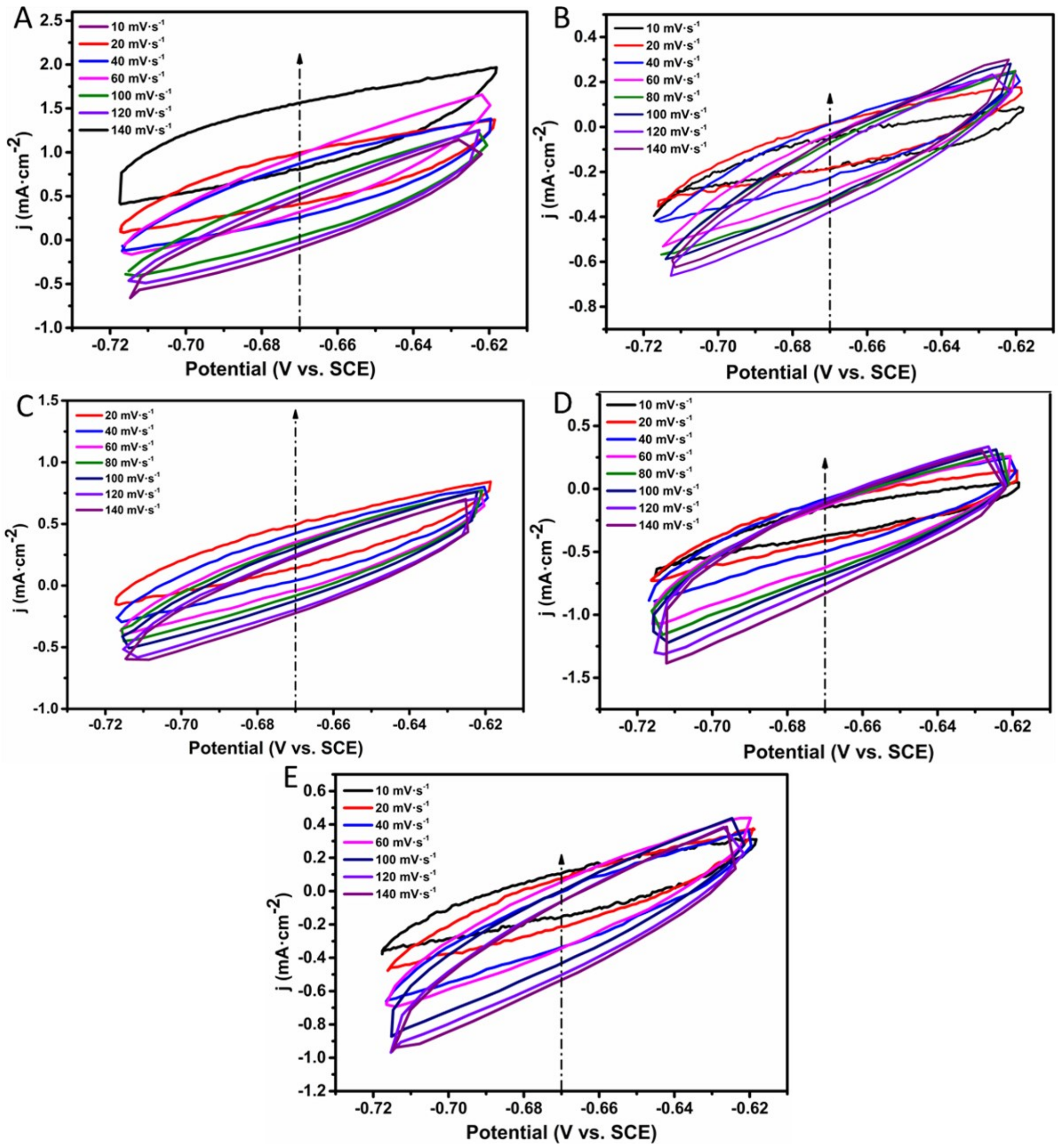



**Fig. S7** CVs of (A) CoP, (B) NiP, (C) Ni@Ni$_y$CoP, (D) Fe@Fe$_x$NiO, and (E) Fe@Fe$_x$NiO/Ni@Ni$_y$CoP at potential range from -0.62 V to -0.72 V with scan rates from 10 to 140 mV·s$^{-1}$, respectively in 1M KOH solution.

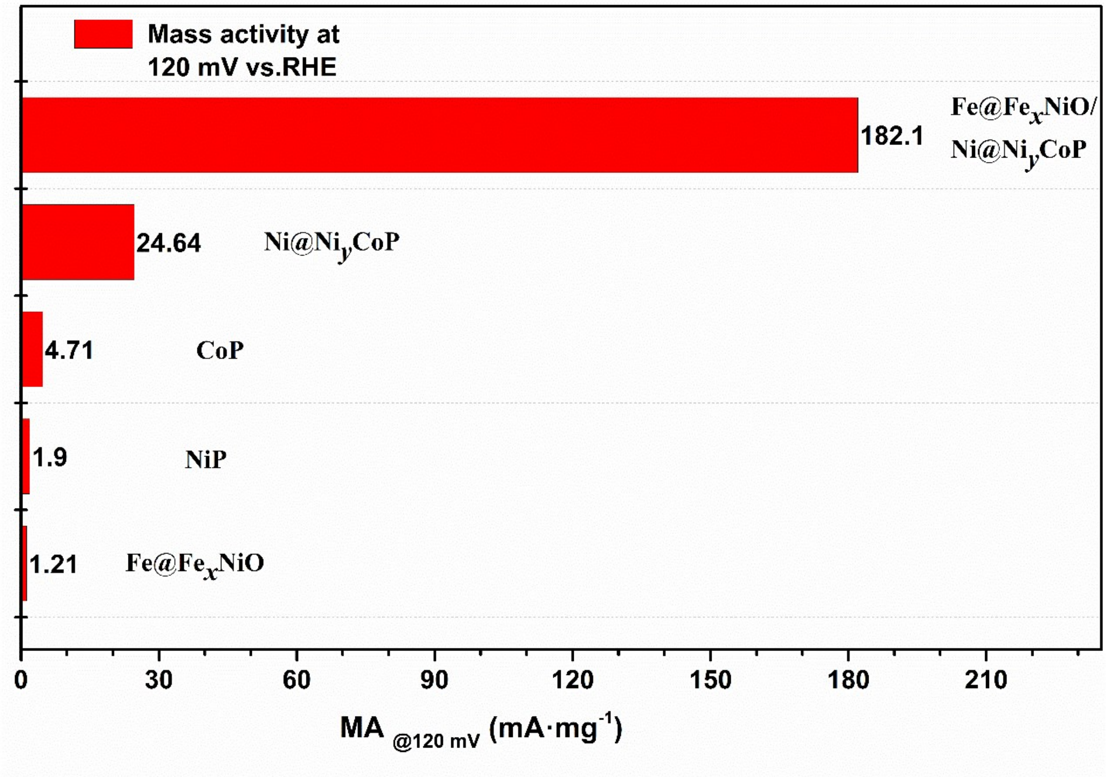



**Fig. S8** The mass activity for several keys samples at overpotential of 120 mV.

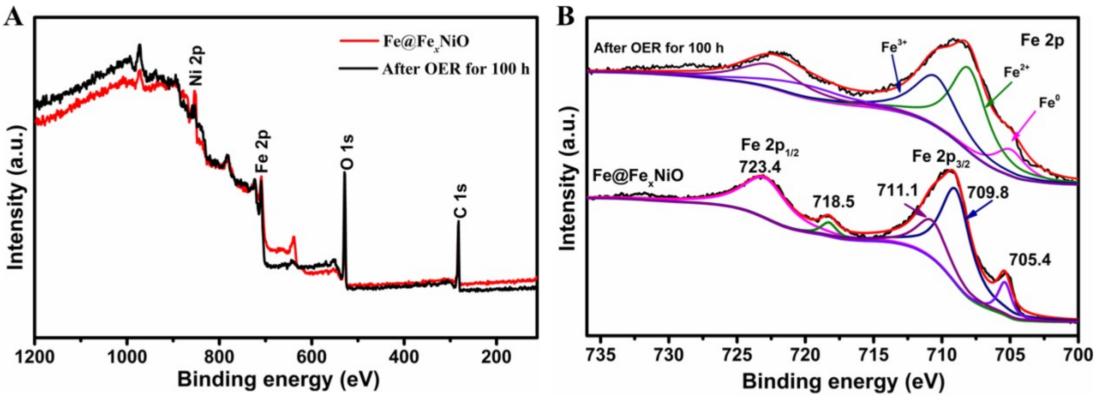



**Fig. S9.** The XPS spectrum of Fe@Fe$_x$NiO before and after OER durability at fixed 100 mA·cm$^{-2}$ for 100 h: (A) sum peaks, (B) HR-XPS for Fe 2p region.

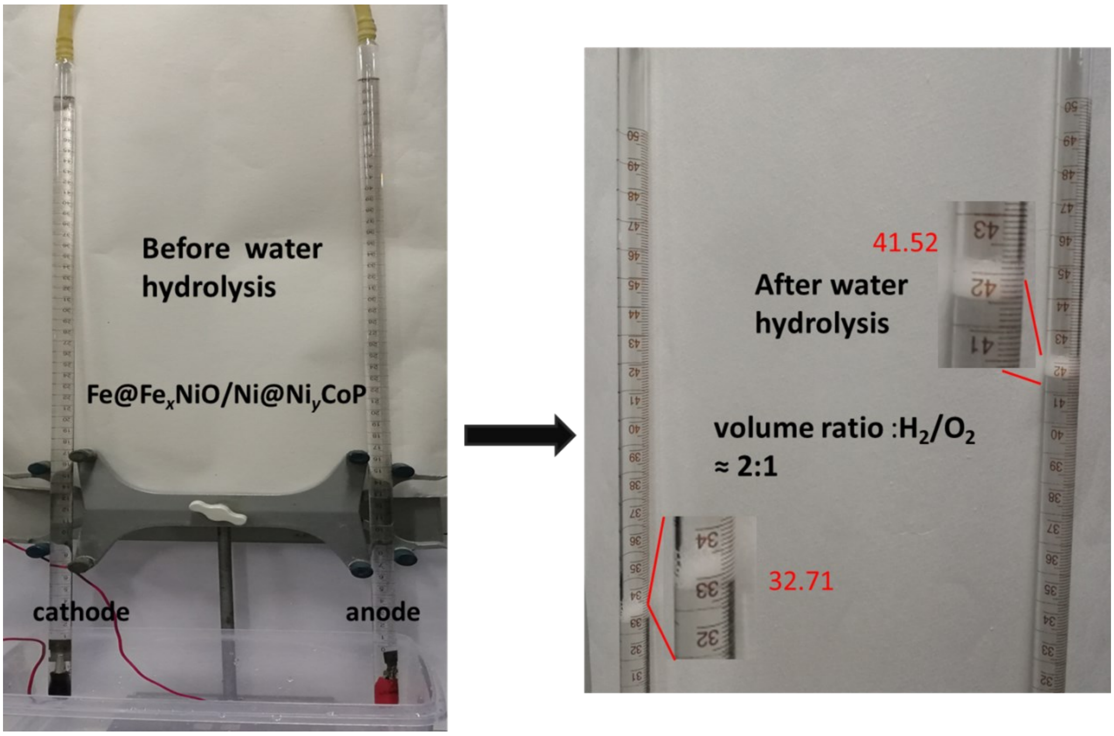



**Fig. S10** Faraday efficiency measurement based on water drainage method at 25 mA·cm$^{-2}$ for 1.5 h. Details: two 50 ml burettes is reversed-put with two same electrode of Fe@Fe$_x$NiO/Ni@Ni$_y$CoP. We recorded the data by 0 min to 90 min with 10 minute interval. E.g., at point of 90 minutes (or terminate), HER side actual volume of $H_2$ is 50.00-32.71=17.29 mL, whereas OER side actual volume of $O_2$ is 50.00-41.52=8.48 mL (Fig.S10). 17.29/8.48 (H2/ O2) ≈ 2:1.

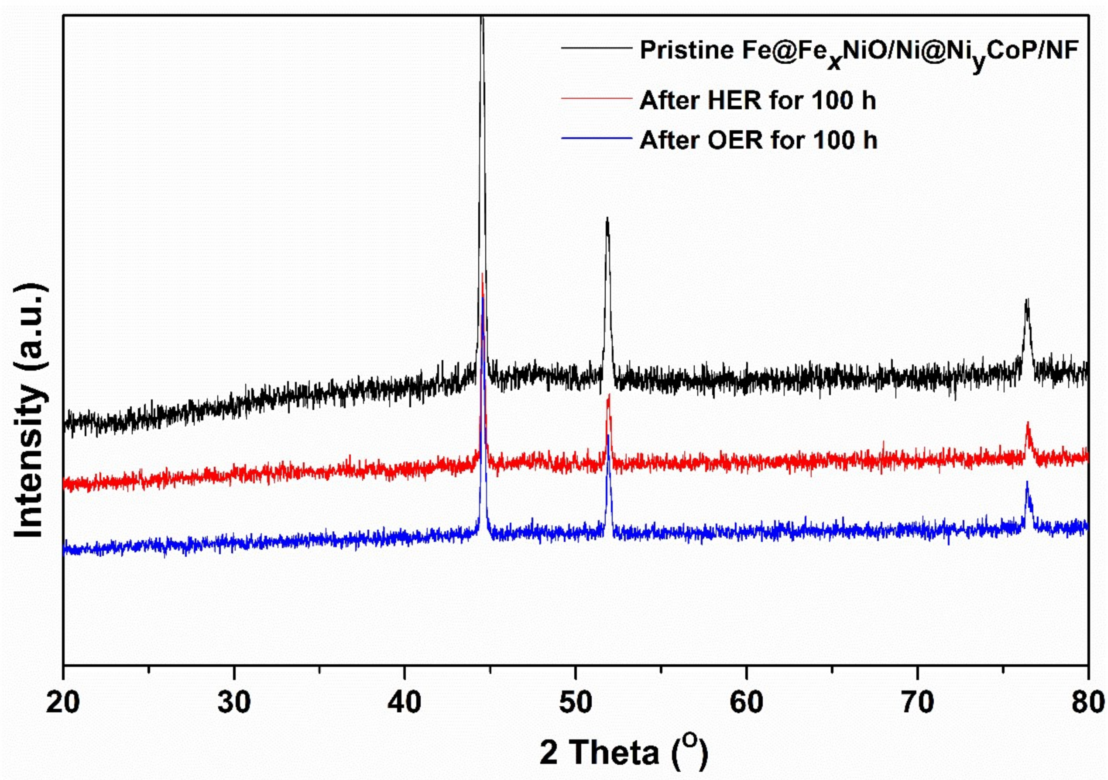



**Fig. S11** The postmortem XRD characterization for alkaline HER and OER.

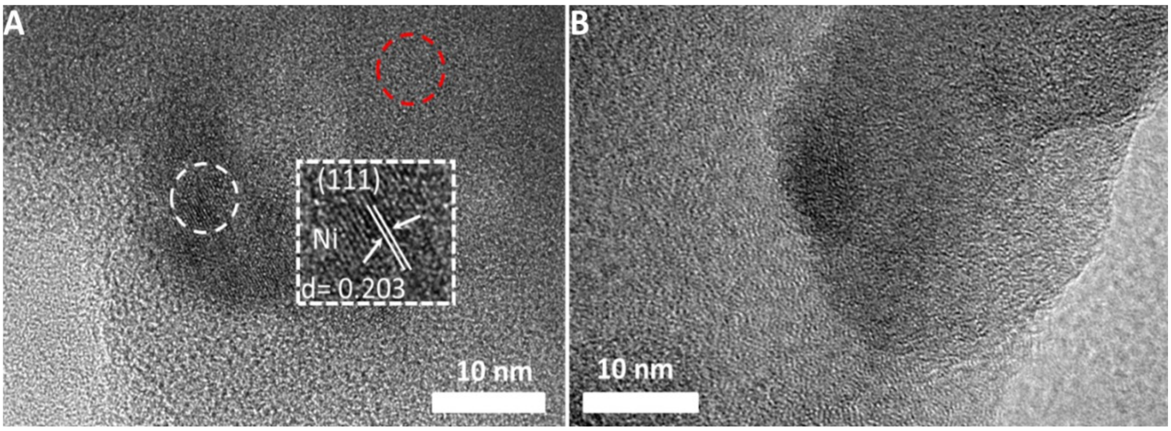



**Fig. S12** The postmortem HR-TEM images of $Fe@Fe_xNiO$/ $Ni@Ni_yCoP$ for alkaline (A) HER and (B) OER.

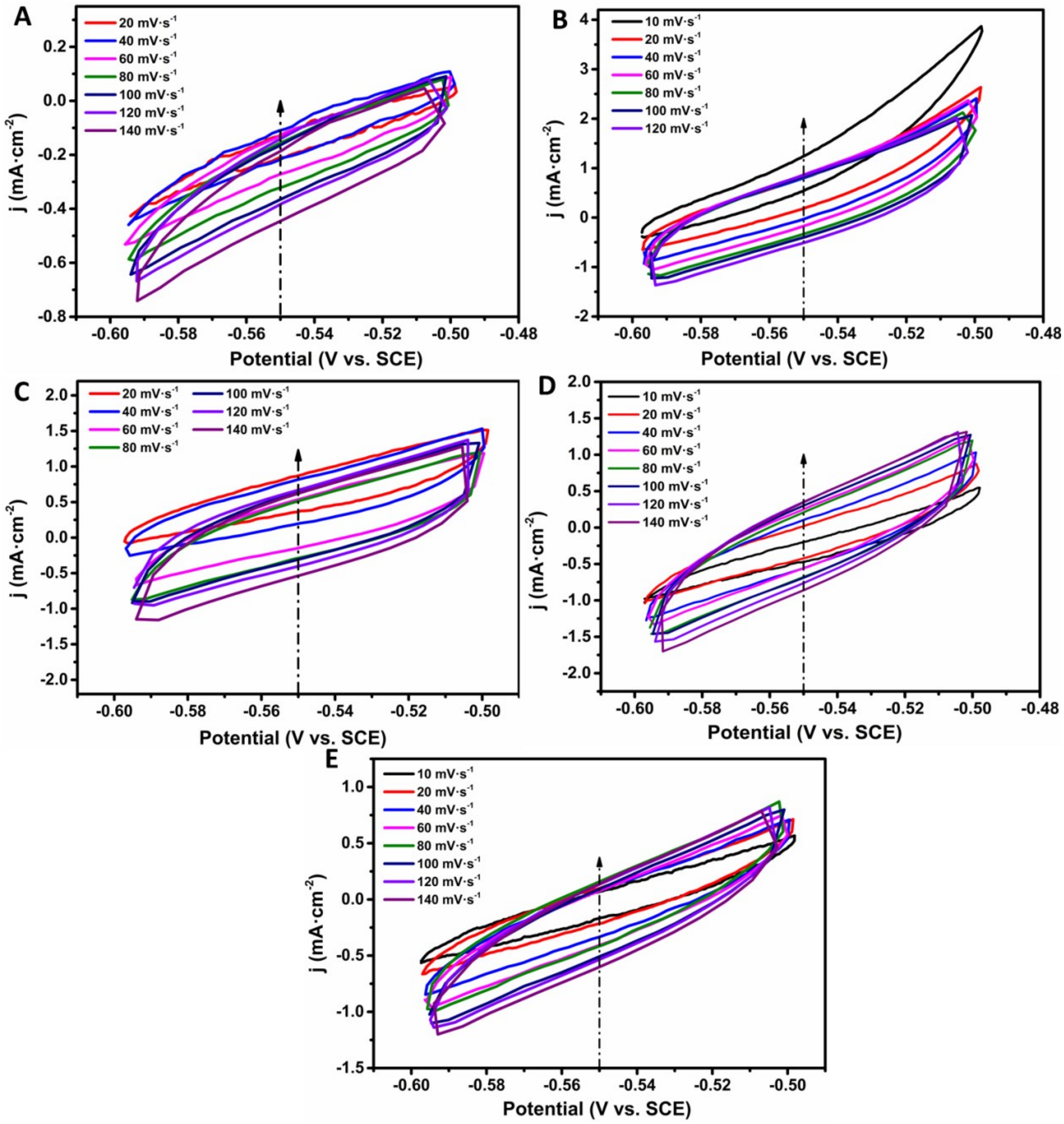



**Fig. S13** CVs of (A) NiP, (B) CoP, (C) Fe@Fe$_x$NiO, (D) Ni@Ni$_y$CoP, and (E) Fe@Fe$_x$NiO/ Ni@Ni$_y$CoP at potential range from -0.50 V to -0.60 V with scan rates from 10 to 140 mV·s$^{-1}$, respectively in PBS solution.

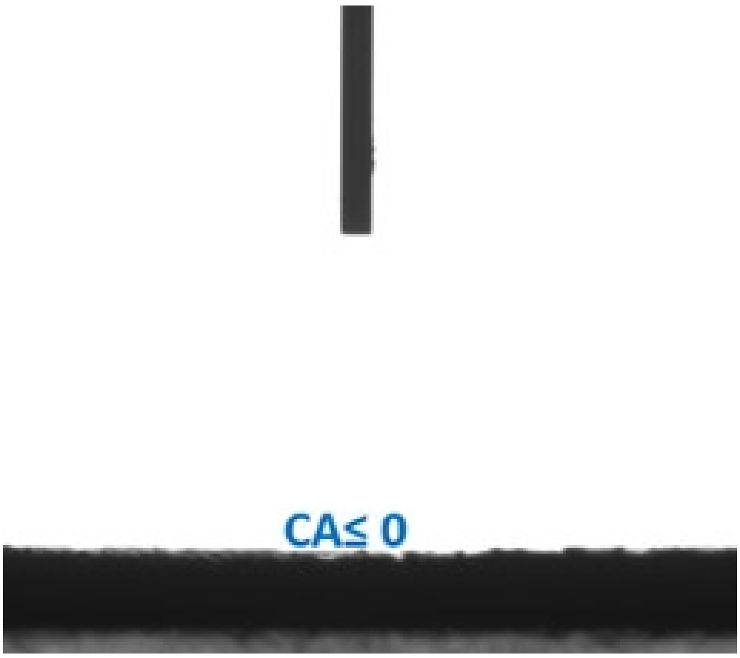



**Fig. S14** The contact angles of (CA) Fe@Fe$_x$NiO/Ni@Ni$_y$CoP catalysts.

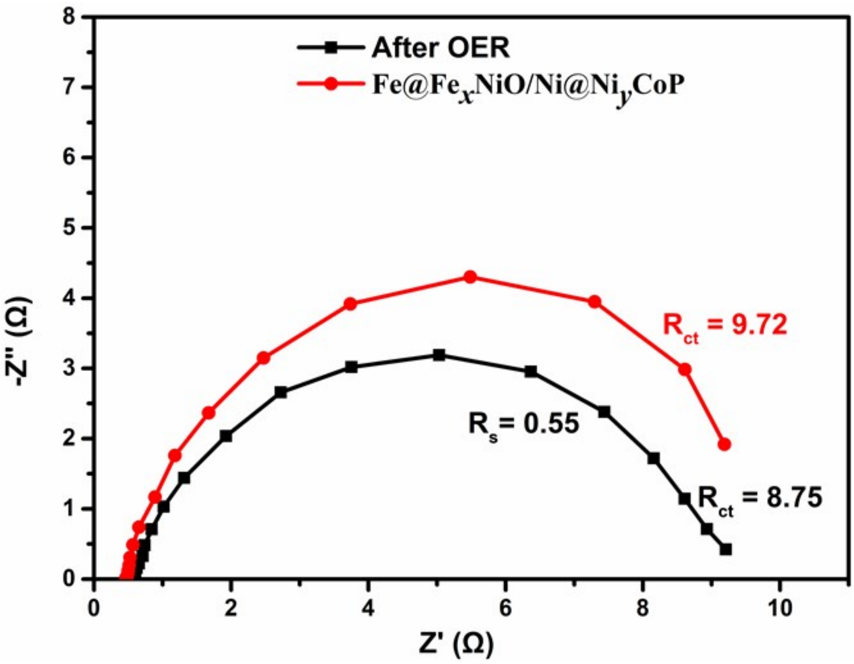



**Fig. S15** The EIS measurement before and after OER at 250 mV vs. RHE. The smaller Rct after OER indicated faster electron transformation, which is benefit for OER process.

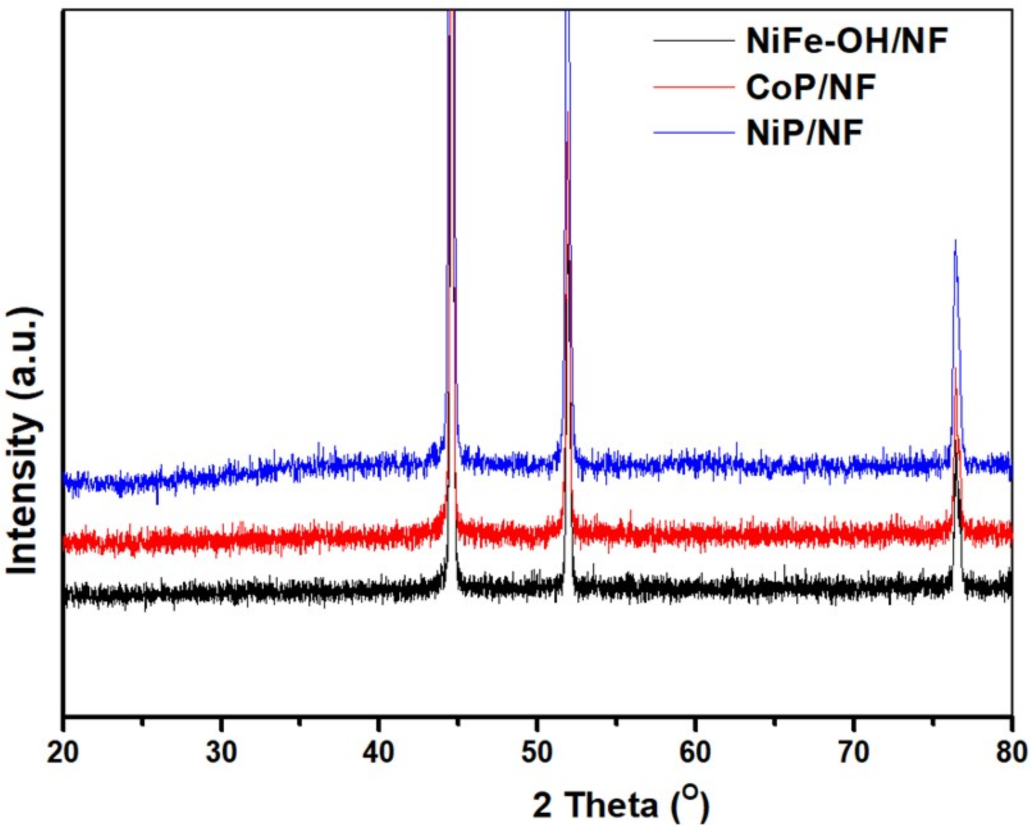



**Fig. S16** The XRD characterization of $Ni_4Fe_4$-OH/NF, CoP/NF, and NiP/NF samples.

**Table S1.** The ICP-OES results of as-prepared samples based on Cu-foam substrates.

| Samples | Atomic ratio (Fe/Ni, Ni:Co: P) |
|---|---|
| $Ni_5Fe_3O$ | 0.89: 1 |
| Fe@$Fe_x$NiO | 1.31: 1 |
| $Ni_3Fe_5O$ | 6.34: 1 |
| Ni-$Co_{0.02}$P | 5.45: 2.12: 1 |
| Ni@$Ni_y$CoP | 4.94: 4.52: 1 |
| Ni-$Co_{0.08}$P | 4.36: 5.63: 1 |

**Table S2.** HER performance comparisons with newly reported transitional metal-based phosphides electrocatalysts in alkali-electrolyte.

| Electrocatalysts | Electrolyte | $\eta_{10/20}$ (mV) | $\eta_{100}$ (mV) | Tafel plot ($mV·dec^{-1}$) | Ref. |
|---|---|---|---|---|---|
| Fe@$Fe_xNiO$/Ni @$Ni_yCoP$ | 1 M KOH | 34 | 92 ($\eta_{1500mA·cm^{-2}}$ =129) | 21 | Our work |
| Ni@$Ni_yCoP$ | 1 M KOH | 45 | 116 ($\eta_{500mA·cm^{-2}}$ =162) | 49 | |
| Ni-Co-P HNBs | 1 M KOH | 107 | ~ | 46 | Energy Environ. Sci., 2018, 11, 872-880 |
| CoP/Co-MOF | 1 M KOH | 34 | ~ | 56 | Angew. Chem. Int. Ed. 2019, 58, 1-7 |
| FeMnP | 0.1 M KOH | ~120 | ~ | 78 | Nano Energy 39 (2017) 444–453 |
| Ni-Co-P film | 1 M KOH | 30 | 185 (at 500 $mA·cm^{-2}$) | 41 | J. Mater. Chem. A,2017, 5,7564–7570 |
| CoP@NC | 1 M KOH | 129 | ~ | 58 | ACS Catal. 2017, 7, 3824-3831 |
| Ni-Fe-P Nanocubes | 1 M KOH | 182 | ~ | 85 | ACS Appl. Mater. Interfaces 2017, 9, 31, 26134-26142 |
| $Ni_5P_4$ films/ NiOOH | 1 M KOH | 150 | ~ | 53 | Angew. Chem., Int. Ed. 2015, 54, 12361-12365 |

| | | | | | |
|---|---|---|---|---|---|
| $Ni_{0.51}Co_{0.49}P$ film | 1 M KOH | 82 | - | 43 | Adv. Funct. Mater. 2016, 26, 7644-7651 |
| Nest-like NiCoP | 1 M KOH | 62 | ~ | 68.2 | ACS Catal. 2017, 7, 4131−4137 |
| $NiCo_2P_x$ Nanowires | 1 M KOH | 58 | 127 | 34.3 | Adv. Mater. 2017, 1605502 |
| CoP | 1 M KOH | 94 | ~ | 42 | Angew.Chem. 2015, 127,6349-6352 |
| O,Cu-CoP nanowire | 1 M KOH | 72 | - | 57.6 | *ACS Energy Lett.* 2018, 3, 2750-2756 |

**Table S3.** The $C_{dl}$ calculations at potential of -0.67 V vs. SCE for HER in 1 M KOH.

| Samples | $C_{dl}$ ($mF \cdot cm^{-2}$) |
|---|---|
| Fe@$Fe_x$NiO/Ni@$Ni_y$CoP | 0.835 |
| Ni@$Ni_y$CoP | 0.369 |
| Fe@$Fe_x$NiO | 1.61 |
| CoP | 0.395 |
| NiP | 0.285 |

**Table S4.** The EIS parameters at overpotential of -90 mV for HER measurements based on *Zview 2* software fitting in 1 M KOH.

| Samples | Rs (Ω $cm^{-2}$) | Rct (Ω $cm^{-2}$) | CPE-T | CPE-P |
|---|---|---|---|---|
| $Fe@Fe_xNiO/Ni@Ni_yCoP$ | 0.5162 | 0.658 | 0.28744 | 0.9029 |
| $Ni@Ni_yCoP$ | 0.48424 | 0.740 | 0.32192 | 0.88564 |
| $Fe@Fe_xNiO$ | 0.52142 | 36.380 | 0.018447 | 0.83922 |
| CoP | 0.52176 | 2.707 | 0.16651 | 0.89937 |
| NiP | 0.41986 | 5.920<br>Rmt, 14.050 | CPE-T1, 0.001034<br>CPE-T2, 0.014911 | CPE-P1, 0.90056<br>CPE-P2, 0.86714 |

**Table S5.** The EIS parameters at overpotential of 250 mV for OER measurements *via Zview 2* software fitting in 1 M KOH.

| Samples | Rs (Ω $cm^{-2}$) | Rct (Ω $cm^{-2}$) | CPE-T | CPE-P |
|---|---|---|---|---|
| $Fe@Fe_xNiO/Ni@Ni_yCoP$ | 0.47385 | 9.723 | 0.1386 | 0.89857 |
| $Ni@Ni_yCoP$ | 0.3735 | 41.87 | 0.12045 | 0.90532 |
| $Fe@Fe_xNiO$ | 0.5786 | 11.070 | 0.06512 | 0.80766 |
| CoP | 0.45498 | 51.920 | 0.23276 | 0.92782 |
| NiP | 0.41346 | 108.200 | 0.056707 | 0.90835 |

79 **Table S6.** The cell-voltage for overall water splitting recent newly reported
80 bifuntional electrocatalysts in alkaline solution & ~25 °C.

| electrocatalysts | Electrolyte | $Voltage_{10}$ (V) | $Voltage_{1200}$(V) | Ref. |
|---|---|---|---|---|
| $Fe@Fe_xNiO/Ni@Ni_yCoP$ \|\| $Fe@Fe_xNiO/Ni@Ni_yCoP$ | 1 M KOH | 1.43 | 1.76 | Our work |
| $(Co_{1-x}Ni_x)(S_{1y}P_y)_2/G$ \|\| $(Co_{1-x}Ni_x)(S_{1-y}P_y)_2/G$ | 1 M KOH | 1.65 | - | Adv. Energy Mater. 2018, 1802319 |
| $Ni/Mo_2C$(1:2)-NCNFs \|\| $Ni/Mo_2C$(1:2)-NCNFs | 1 M KOH | 1.64 | - | Adv. Energy Mater. 2019, 1803185 |
| $Ni_2P@FePO_x$ \|\| $Ni_2P@FePO_x$ | 1 M KOH | 1.51 | - | Chem. Sci.,2018, 9,1375-1384 |
| LiCoBPO \|\| LiCoBPO | 1 M KOH | 1.53 | 1.73 (100 $mA\cdot cm^{-2}$) | Energy Environ. Sci., 2019,12, 988-999. |
| NiFeMo \|\| NiFeMo | 1 M KOH | 1.45 | ~1.82 (100 $mA\cdot cm^{-2}$) | ACS Energy Lett. 2018, 3, 546-554 |
| Nest-like NiCoP \|\| Nest-like NiCoP | 1 M KOH | 1.52 | 1.77 | ACS Catal. 2017, 7, 4131−4137 |
| FeMnP \|\| FeMnP | 1 M KOH | 1.55 | - | Nano Energy 39 (2017) 444-453 |
| NiFeSP/NF \|\| NiFeSP/NF | 1 M KOH | 1.58 | - | ACS Nano 2017, 10, 10303-10312 |
| NiCoP \|\| NiCoP | 1 M KOH | 1.58 | - | Nano Lett. 2016, 16, 7718-7725 |
| $FeCoNiP_{0.5}S_{0.5}$ \|\| | 1 M KOH | 1.46 | - | ACS Catal. 2018, |

| | | | | |
|---|---|---|---|---|
| $FeCoNiP_0S_1$ | | | | 8, 9926-9935 |
| Cu@NiFe LDH ‖ Cu@NiFe LDH | 1 M KOH | 1.54 | 1.69 (100 $mA{\cdot}cm^{-2}$) | Energy Environ. Sci., 2017, 10, 1820-1827 |
| Ni-Fe LDH@NiCu ‖ $NiFeO_x$@NiCu | 1 M KOH | 1.51 | - | Adv. Mater. 2018, 1806769 |
| $MoP/Ni_2P$ ‖ MoP/Ni2P | 1 M KOH | 1.55 | - | J. Mater. Chem. A,2017, 5, 15940 |
| Ni-Co-P HNBs ‖ Ni-Co-P HNBs | 1 M KOH | 1.62 | - | Energy Environ. Sci., 2018, 11, 872-880 |
| FeMnP ‖ FeMnP | 1 M KOH | 1.55 | - | Nano Energy 39 (2017) 444-453 |

81 **Table S7.** The HER performance of as-prepared samples in 1 M PBS.

| As-prepared catalysts | $\eta_{100\ mA \cdot cm^{-2}}$ |
|---|---|
| $Fe@Fe_xNiO/Ni@Ni_yCoP$ | 386 |
| $Ni@Ni_yCoP$ | 448 |
| $Fe@Fe_xNiO$ | 548 |
| CoP | 499 |
| NiP | 679 |

82 **Table S8.** The $C_{dl}$ calculations at potential of -0.55 V vs. SCE for HER in 1 M PBS.

| Samples | $C_{dl}$ ($mF{\cdot}cm^{-2}$) |
|---|---|

| | |
|---|---|
| Fe@Fe$_x$NiO/Ni@Ni$_y$CoP | 1.71 |
| Ni@Ni$_y$CoP | 2.60 |
| Fe@Fe$_x$NiO | 2.77 |
| CoP | 3.44 |
| NiP | 0.76 |

**Table S9.** The EIS parameters at overpotential of -250 mV for HER measurements from *Zview 2* software fitting in 1 M PBS.

| Samples | Rs (Ω $cm^{-2}$) | Rct (Ω $cm^{-2}$) | CPE-T | CPE-P |
|---|---|---|---|---|
| Fe@Fe$_x$NiO/Ni@Ni$_y$CoP | 1.043 | 9.887 | 0.00754 | 0.74925 |
| Ni@Ni$_y$CoP | 0.730 | 14.450 | 0.16762 | 0.65253 |
| Fe@Fe$_x$NiO | 0.851 | 23.600 | 0.13843 | 0.68061 |
| CoP | 1.093 | 18.510 | 0.001474 | 0.71561 |
| NiP | 1.314 | 36.130 | 0.001517 | 0.81993 |

**Table S10.** The OER performance of as-prepared samples in 1 M PBS.

| Catalysts | $\eta_{100\ mA\cdot cm^{-2}}$ |
|---|---|
| Fe@Fe$_x$NiO/Ni@Ni$_y$CoP | 422 |

| | |
|---|---|
| $Ni@Ni_yCoP$ | 628 |
| $Fe@Fe_xNiO$ | 668 |
| CoP | 708 |
| NiP | 770 |

**Table S11.** The cell-voltage for overall water splitting recent reported bifuntional electrocatalysts in 1 M PBS & ~25 $^{o}$C.

| electrocatalysts | Electrolyte | $Voltage_{10}$ (V) | Ref. |
|---|---|---|---|
| $Fe@Fe_xNiO/Ni@Ni_yCoP$ \|\| $Fe@Fe_xNiO/Ni@Ni_yCoP$ | 1 M PBS | 1.86 | Our work |
| S-$NiFe_2O_4$/NF \|\| S-$NiFe_2O_4$/NF | 1 M PBS | 1.95 | Nano energy, 40, 264-273 |
| CoP NA/CC \|\| CoP NA/CC | 1 M PBS | 1.6 (2 $mA\cdot cm^{-2}$) | ChemElectroChem, 4(8), 1840-1845. |
| $Ni_{0.1}Co_{0.9}P$ \|\| $Ni_{0.1}Co_{0.9}P$ | 1 M PBS | 1.89 | Angew. Chem. 2018, 130, 15671 - 15675 |
| $CoO/CoSe_2$ | 1 M PBS | 2.18 | Adv. Sci. 2016, 3, 1500426 |
| $Ni_3N$@Ni-Bi NS/Ti \|\| $Ni_3N$@Ni-Bi NS | 1 M PBS | 1.95 | J. Mater. Chem. A, 2017,5, 7806-7810 |
| $NiS_{2(1-x)}Se_2x$ \|\| $NiS_{2(1-x)}Se_2x$ | 1 M PBS | 1.87 | J. Mater. Chem. A, 2019,7, 16793- |

| | |
|---|---|
| | 16802 |

**Table S12.** The EIS fitting parameters at open potential for water splitting based on *Zview 2* software in 1 M PBS.

| Electrode | Rs (Ω cm$^{-2}$) | Rct (Ω cm$^{-2}$) | CPE-T | CPE-P |
|---|---|---|---|---|
| Fe@$Fe_x$NiO/Ni@$Ni_y$CoP | 1.006 | 298.5 | 0.041832 | 0.78042 |
| After durability for 100 h | 1.061 | 336.7 | 0.04032 | 0.85017 |