Mo doped Ni$_2$P Nanowire Arrays: An Efficient Electrocatalyst for Hydrogen Evolution Reaction with Enhanced Activity at All pH Values

Yiqiang Sun[a,b], Lifeng Hang[a,b], Qi Shen[c], Tao Zhang[a,b], Huilin Li[a,b], Xiaomin Zhang[d], Xianjun Lyu[e], Yue Li[a]*

a Key Lab of Materials Physics, Anhui Key Lab of Nanomaterials and Nanotechnology, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei, 230031, P. R. China

b University of Science and Technology of China, Hefei, 230026, P. R. China
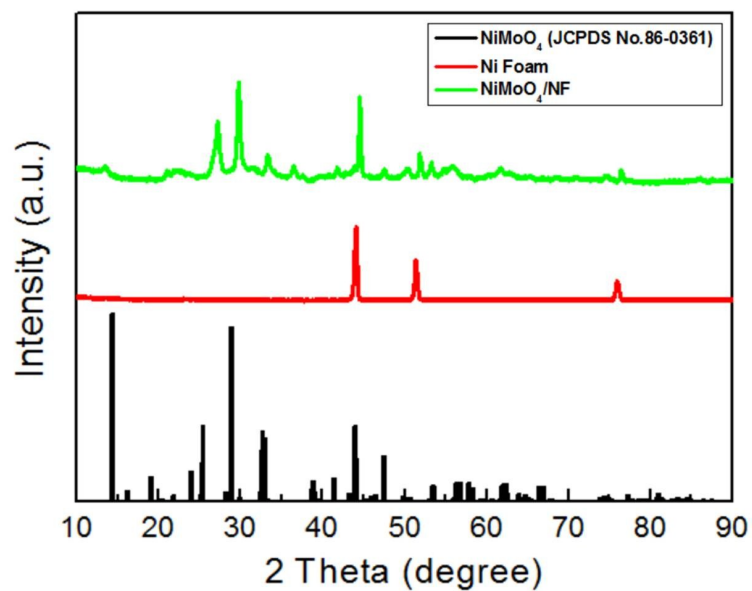
c Shandong Product Quality Inspection Research Institute, Jinan, 250102, Shandong, P. R. China

d Xi'an University of Architecture and Technology, Xi' an, 710055, P.R. China
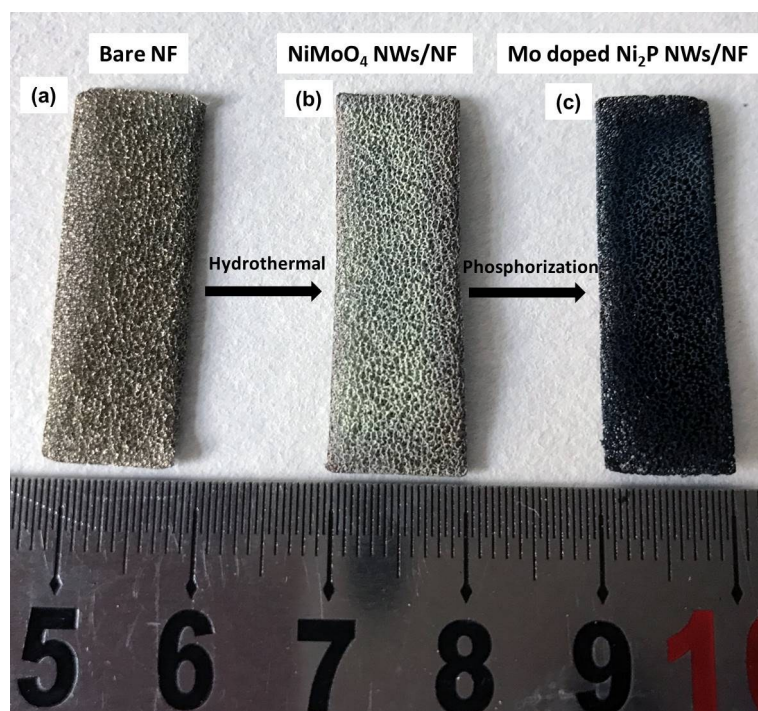
e College of Chemical and Environmental Engineering, Shandong University of Science and Technology, Qingdao, 266590, P.R. China
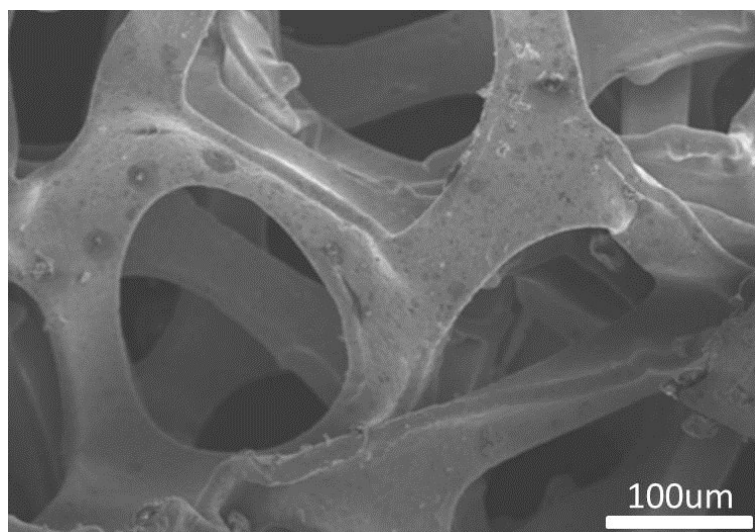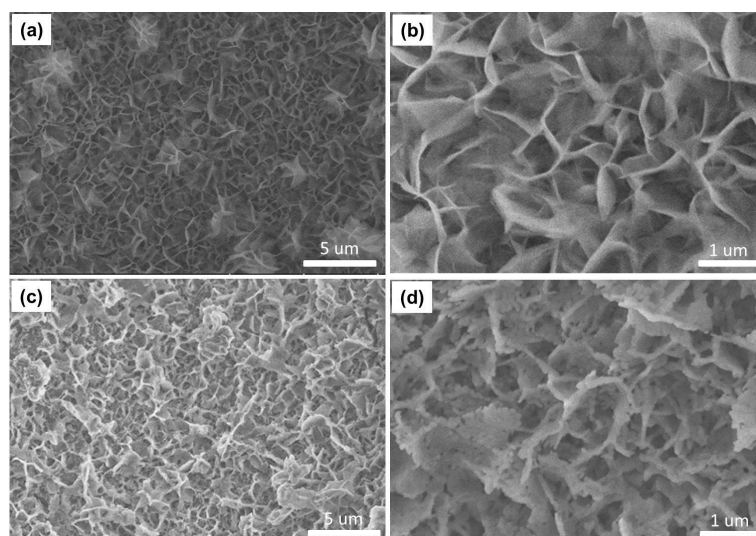
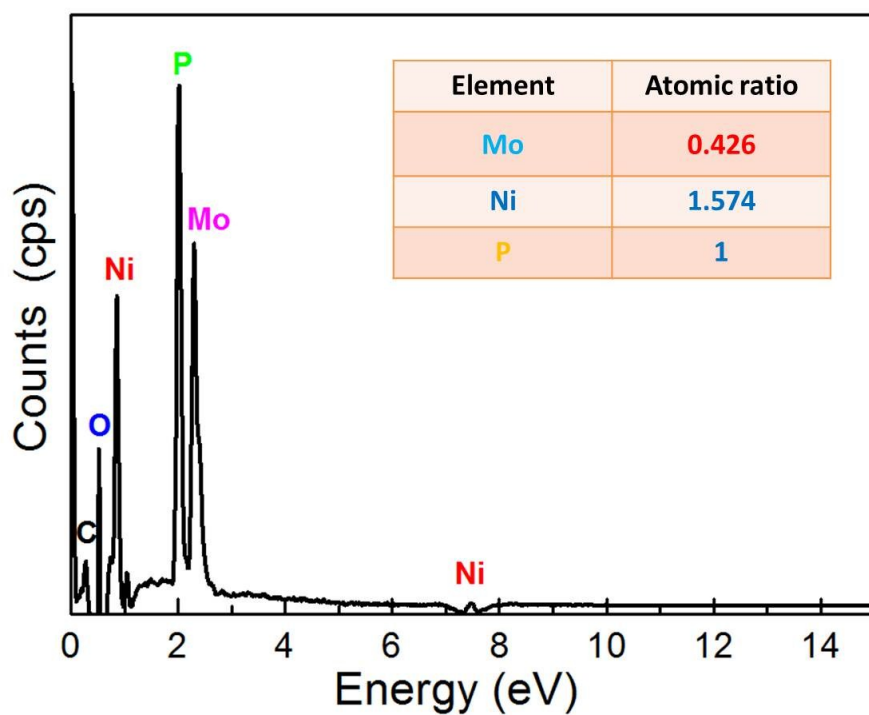**Figure S1.** The SEM image of bare Ni foam.

Figure S2. XRD pattern of Ni foam and as-prepared NiMoO$_4$ nanowires on Ni foam..
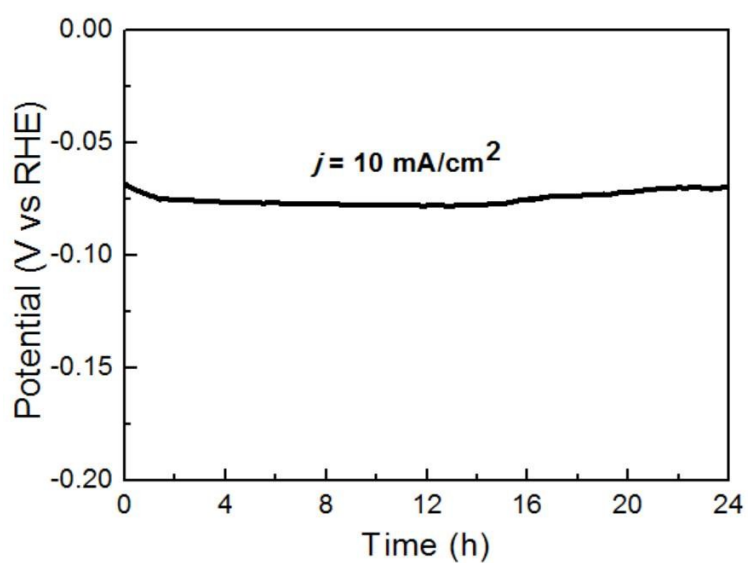
Figure S3. The photographic images of (a) Ni foam (NF), (b) NiMoO$_4$ MWs /NF, and (c) Mo doped Ni$_2$P MWs/NF.

Figure S4. SEM images for hydroxide precursor sheets on NF and SEM images (c, d) for Ni$_2$P porous sheets/NF.

Element	Atomic ratio
Mo	0.426
Ni	1.574
P	1

Figure S5. EDS spectrum of Mo-Ni$_2$P nanowires peeled off from the integrated electrode.

Figure S6. Chronopotentiometric curve for Mo-Ni$_2$P/NF with a constant current density of 10 mA cm^{-2} for 24 h.
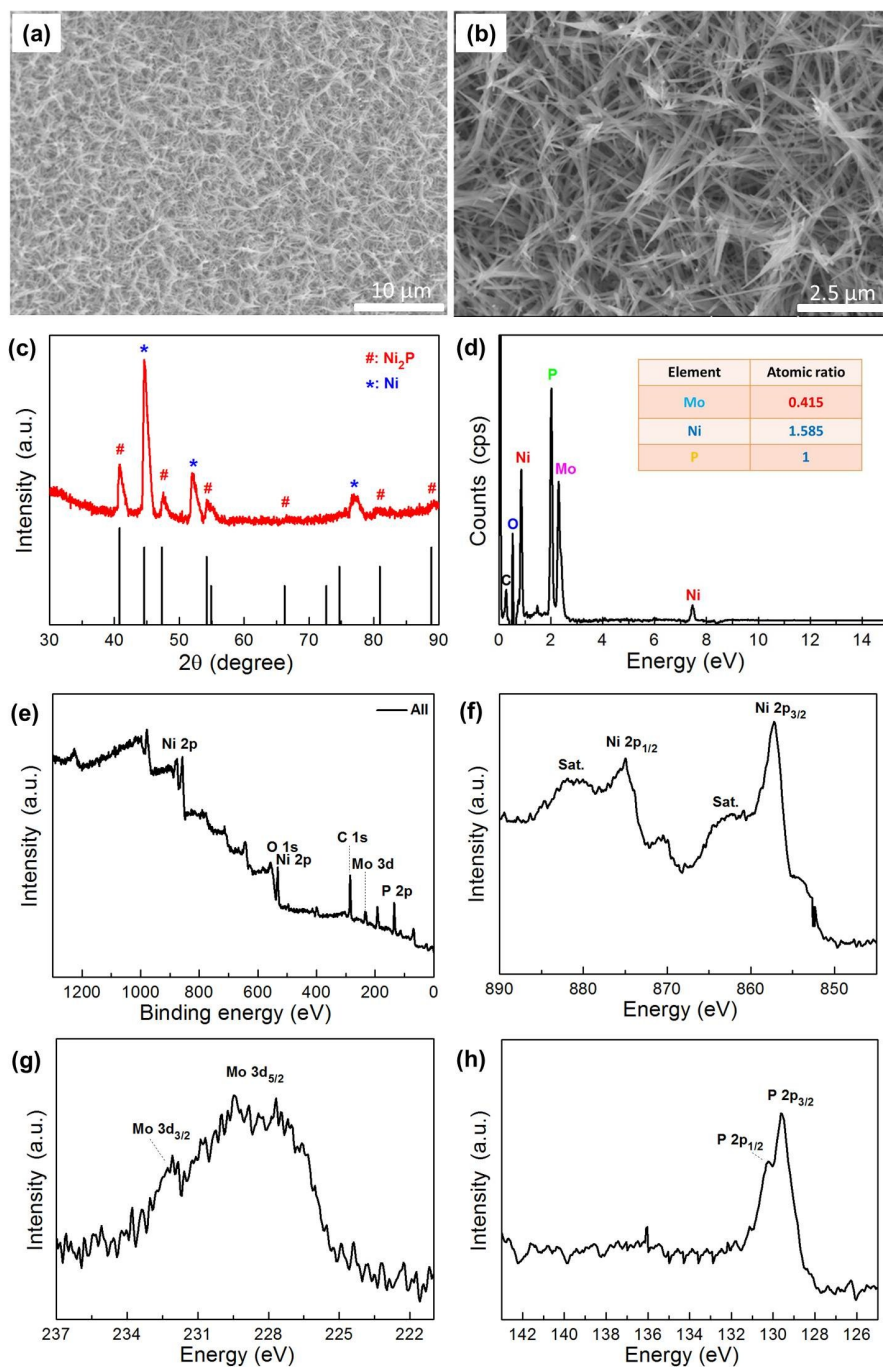
Figure S7. (a, b) SEM images, (c) XRD pattern, (d) EDS spectrum, (e-h) XPS spectra of Mo-Ni$_2$P/NF after HER electrolysis in basic condition.
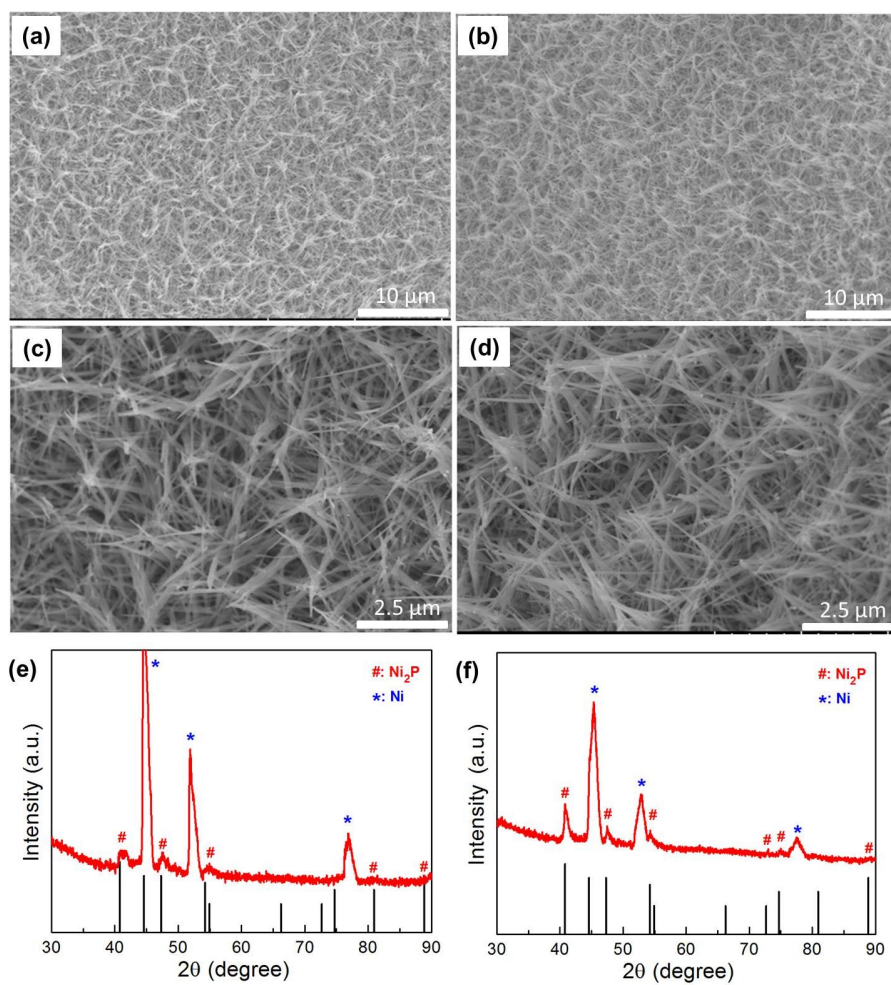
Figure S8. (a, c) SEM images, (e) XRD pattern of Mo-Ni$_2$P/NF after HER electrolysis in acidic condition. (b, d) SEM images, (f) XRD pattern of Mo-Ni$_2$P/NF after HER electrolysis in neutral solution.

Table S1. Comparison of the HER performance of Mo-Ni$_2$P/NF with other reported non-precious HER electrocatalysts in basic electrolyte.

Catalyst	Water electrolysis test	Overpential (10mA cm^{-2})	Electrolyte	Reference
Mo-Ni$_2$P	HER	78	1M KOH	This work
Ni$_3$S$_2$/NF	HER	223	1M KOH	J. Am. Chem. Soc. 2015, 137,14023
NiSe/NF	HER	96	1 M KOH	Angew. Chem. Int. Ed. 2015, 54,1
Ni-Mn$_3$O$_4$/NF	HER	91	1 M KOH	Chem. Commun. 2016, 52, 10566
Ni$_5$P$_4$/nanosheets	HER	150	1M KOH	Angew. Chem., 2015, 127, 12538.
Ni-P/films	HER	93	1M KOH	ChemCatChem, 2016, 8, 106.
NiSe$_2$ NPs	HER	96	1 M KOH	ACS Appl. Mater. Inter., 2016, 8, 4718.
Ni-Fe/nanocarbon	HER	219	1 M KOH	ACS Catal. 2016, 6, 580.
Ni$_2$P nanoparticles	HER	230	1 M KOH	Phys. Chem. Chem. Phys. 2014, 16, 5917.
Ni$_1$Mn$_1$ porous materials	HER	360	1 M KOH	Adv. Funct. Mater. 2015, 25, 393.
NiSe nanowire/NF	HER	96	1 M KOH	Angew. Chem. Int. Ed. 2015, 54, 9351

Table S2. Comparison of the HER performance of Mo-Ni$_2$P/NF with other reported non-precious HER electrocatalysts in acidic electrolyte.

Catalyst	Water electrolysis test	Overpential (10mA cm^{-2})	Electrolyte	Reference
Mo-Ni$_2$P	HER	67	0.5M H$_2$SO$_4$	This work
NiSe$_2$/Ni hybridfoam	HER	143	0.5M H$_2$SO$_4$	Nano Energy 2016, 20, 29.
Ni$_2$P	HER	75	0.5M H$_2$SO$_4$	Journal of Catalysis 2015, 326, 92.
Ni/NiO/CoSe$_2$	HER	88	0.5M H$_2$SO$_4$	Angew. Chem. Int. Ed. 2013, 52, 8546.
NiSe$_2$/carbon paper	HER	135	0.5M H$_2$SO$_4$	Chem. Mater. 2015, 27, 5702.
Se-enriched NiSe$_2$ nanosheets	HER	117	0.5M H$_2$SO$_4$	Angew. Chem. Int. Ed. 2016, 128, 7033.
MoP	HER	117	0.5M H$_2$SO$_4$	Angew. Chem. Int. Ed. 2014, 53, 14433.
Mo$_2$C-NC	HER	124	0.5M H$_2$SO$_4$	Angew. Chem. Int. Ed. 2015, 54, 10752.
MoCNs@carbon	HER	78	0.5M H$_2$SO$_4$	Angew. Chem. Int. Ed. 2015, 54, 14723.
CoMoN$_x$ nanosheets	HER	190	0.5M H$_2$SO$_4$	J. Am. Chem. Soc. 2013, 135, 19186.
Ni-Mo-S nanosheets	HER	200	0.5M H$_2$SO$_4$	Science Advances. 2015, 1, e1500259

Table S3. Comparison of the HER performance of Mo-Ni$_2$P/NF with other reported non-precious HER electrocatalysts in netural electrolyte.

Catalyst	Water electrolysis test	Overpential (10mA cm^{-2})	Electrolyte	Reference
Mo-Ni$_2$P	HER	84	1M PBS	This work
Ni-C-N nanosheets	HER	92.1	1M PBS	J. Am. Chem. Soc. 2014, 136,7587.
Ni$_3$S$_2$/NF	HER	170	1M KPi	J. Am. Chem. Soc. 2015, 137, 14023.
Amorphous MoS$_X$	HER	280 (at 2 mA cm^{-2})	PBS	Chem. Sci. 2011, 2, 1262.
CoNiP/NF	HER	120	1M KPi	J. Mater. Chem. A 2016, 4, 10195.
Fe, Co, or Ni-doped amorphous MoS$_2$	HER	200-300(at 1 mA cm^{-2})	PBS	Chem. Sci. 2012, 3, 2515.
Mo$_2$C@NC	HER	156	0.1M PBS	Angew. Chem., Int. Ed. 2015, 54, 10752.
NiS$_2$/CC	HER	243	1M PBS	Electrochim. Acta 2015, 153, 508.
MoS$_2$/Ti plate	HER	200	1M PBS	Electrochim. Acta 2015, 168, 256.
MoS$_2$-NS	HER	400	1M PBS	J. Mater. Chem. A 2014, 2, 13795.