Supporting Information

Hierarchical Mn-Ni_2P/NiFe LDH nanosheets arrays as an efficient bifunctional electrocatalyst for energy-saving hydrogen production *via* urea electrolysis

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1. Experimental

1.1. Chemicals reagents

$Ni(NO_3)_2 \cdot 6H_2O$, $MnCl_2 \cdot 4H_2O$, NH_4F, $Fe(NO_3)_3 \cdot 9H_2O$, urea and NaH_2PO_2 were obtained from Sinopharm Chemical Reagent Co. Ltd. KOH was obtained from Adamas-beta®. NF was obtained from Taiyuan source of power company.

1.2. Samples preparation

1.2.1 Preparation of $Mn\text{-}Ni_2P$

NF (3 cm × 1 cm) was ultrasonically treated for 30 min in HCl aqueous solution followed by subsequent washing of water and ethanol to eliminate impurities and oxides on the surface. The $Mn\text{-}Ni_2P$ was synthetized through following process. Firstly, 1.9 mmol $Ni(NO_3)_2$, 0.1 mmol $MnCl_2$, 6 mmol NH_4F and 10 mmol urea were mixed in 35 mL distilled water. Then, NF was added into above solution, which was heated at 120 ℃ for 6 h. After that, Mn-NiOH precursor was washed, and heated in air at 70 ℃. Secondly, the Mn-NiOH was further baked to 320 ℃ for 2h in N_2 with 0.9g NaH_2PO_2 as P source to prepare the $Mn\text{-}Ni_2P$.

1.2.2 Preparation of the $Mn\text{-}Ni_2P$/NiFe LDH

Typically, 0.25 mmol $Ni(NO_3)_2$, 0.25 mmol $Fe(NO_3)_3$, 3 mmol NH_4F and 5 mmol urea were added in water with stirring to get a uniform solution. Then, the $Mn\text{-}Ni_2P$ was submerged in above solution and shifted into 50 mL autoclave, which was maintained for 6 h at 120 °C. After that, the $Mn\text{-}Ni_2P$/NiFe LDH was prepared after washing and placed at 70 °C for 12 h.

1.3. Samples characterization

Phases and components of obtained products was recorded by powder X-ray diffraction (XRD, Bruker D8). The morphology was visualized by scanning electron microscopy (SEM, S-4800) and transmission electron microscopy (TEM, FEI Talos F200X). The surface formation and element valence of products was determined by X-ray photo-electron spectrometer (XPS, Thermo ESCALAB 250).

1.4. Electrochemical measurements

Electrochemical tests were implemented in standard three-electrode system by biologic VMP3 electrochemical workstation, and obtained materials was employed as working electrodes. The catalytic behavior was measured at a scan rate of 2 mV s^{-1} in alkaline electrolyte without and with 0.5 M urea. All potentials were rectified. Electrocatalytic active area (ECSA) was tested at diverse scan rates in non-Faradaic region. Electrochemical impedance spectroscopy (EIS) was performed at a frequency from 100 kHz to 0.01 Hz with a 5 mV AC amplitude.

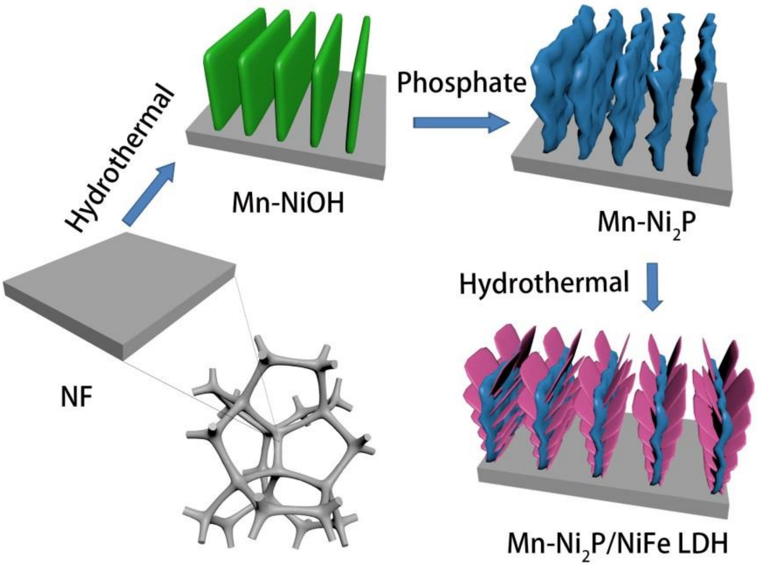

Fig. S1. Schematic diagram for synthesizing Mn-Ni_2P/NiFe LDH.

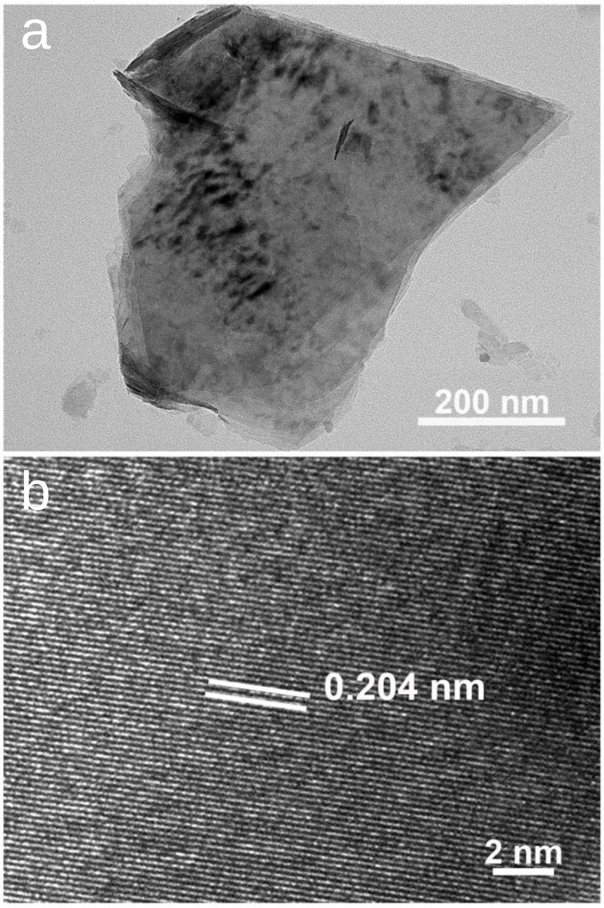

Fig. S2. (a) TEM and (b) HRTEM images of Mn-NiOH and Mn-Ni_2P.

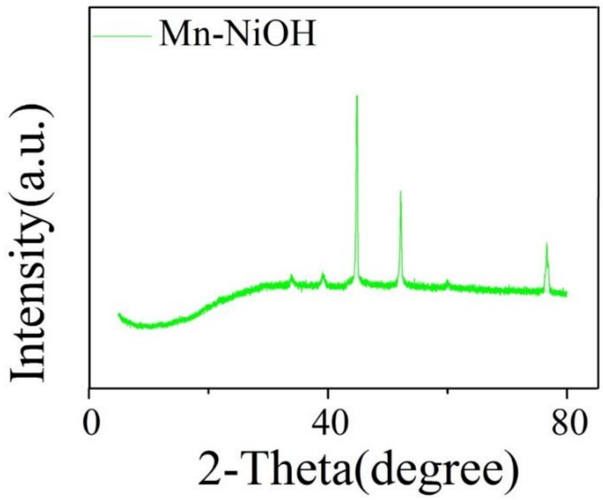

Fig. S3. XRD pattern of Mn-NiOH.

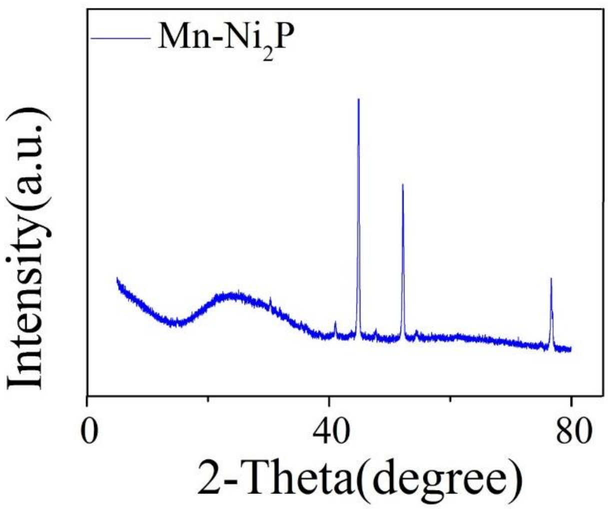

Fig. S4. XRD pattern of Mn-Ni_2P.

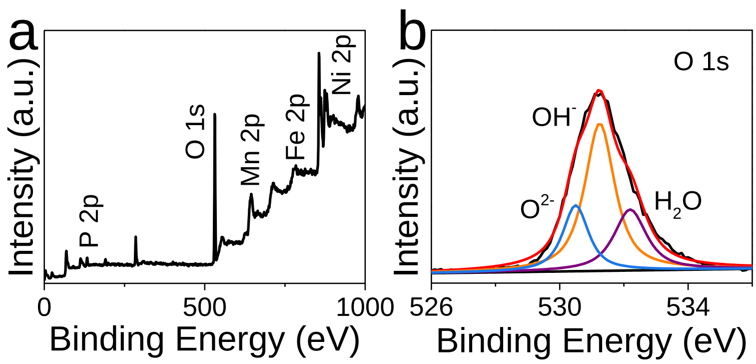

Fig. S5. XPS spectra of (a) survey scan and (b) O 1s for Mn-Ni_2P/NiFe LDH.

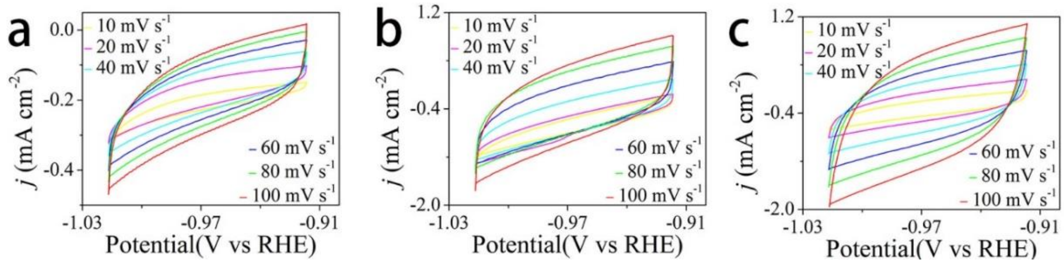

Fig. S6. CV curves of Ni_2P (a), Mn-Ni_2P (b), and Mn-Ni_2P/NiFe LDH (c).

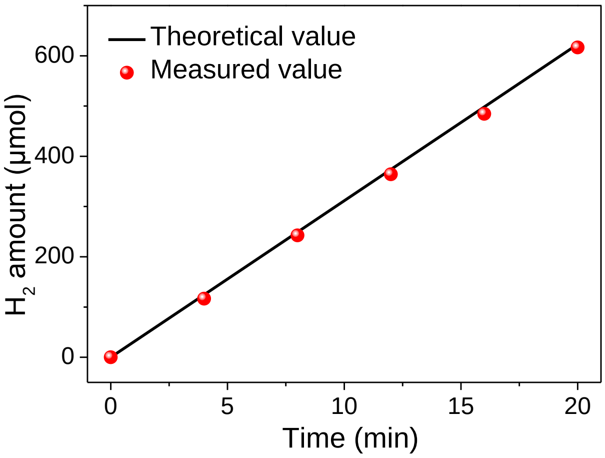

Fig. S7. Experimental and theoretical calculated amount of evolved H_2 over the Mn-Ni_2P/NiFe LDH.

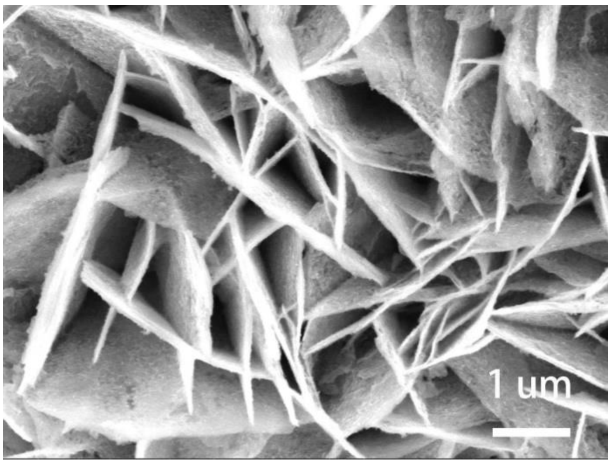

Fig. S8. SEM image of Mn-Ni_2P/NiFe LDH after HER stability.

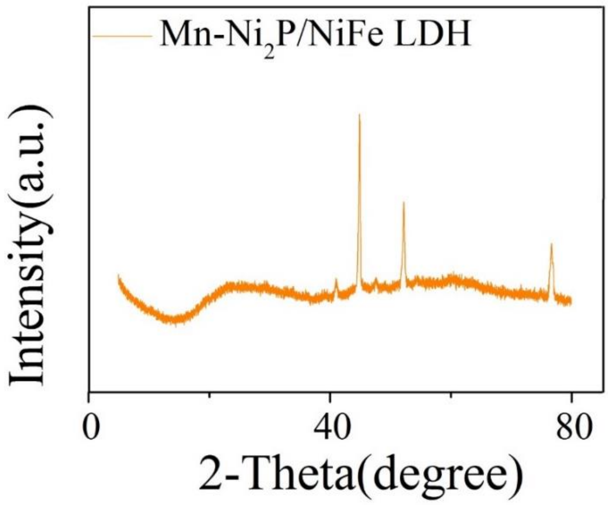

Fig. S9. XRD pattern of the Mn-Ni_2P/NiFe LDH after HER stability.

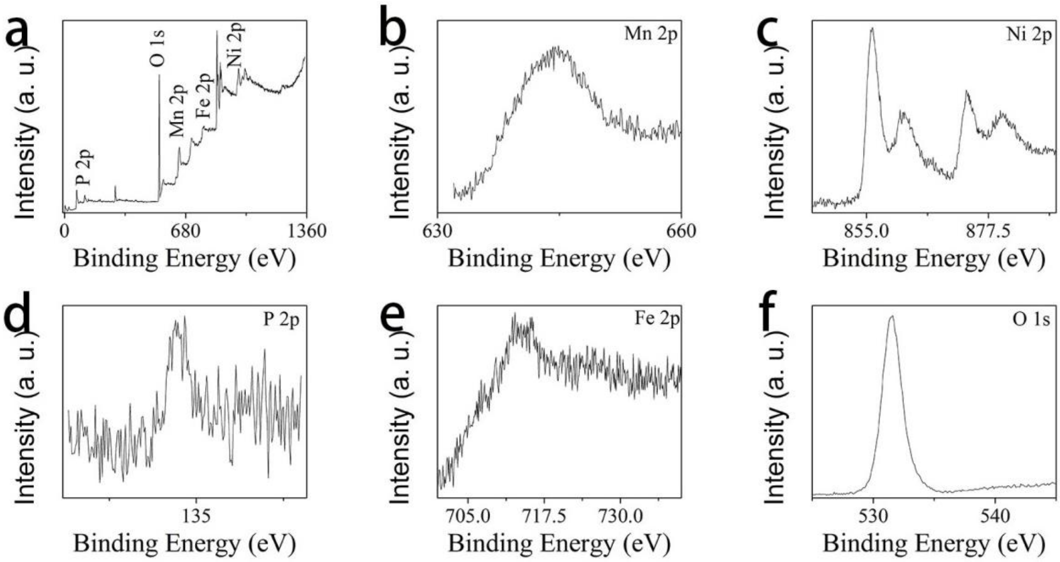

Fig. S10. XPS spectra of (a) survey scan, (b) Mn 2p, (c) Ni 2p, (d) P 2p, (e) Fe 2p and (f) O 1s for the Mn-Ni_2P/NiFe LDH after HER stability.

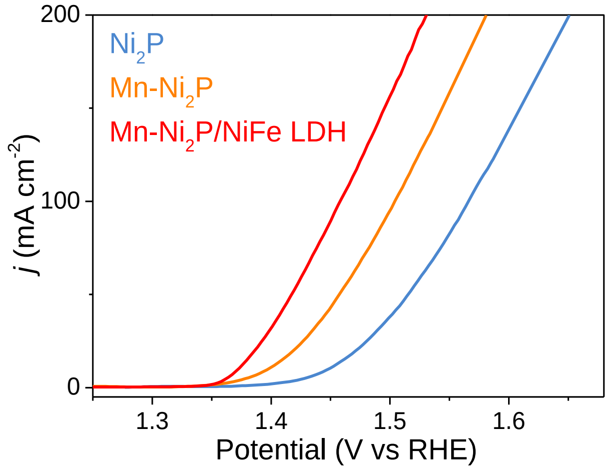

Fig. S11. LSV curves of Ni_2P, Mn-Ni_2P and Mn-Ni_2P/NiFe LDH in 1.0 M KOH with 0.5 M urea.

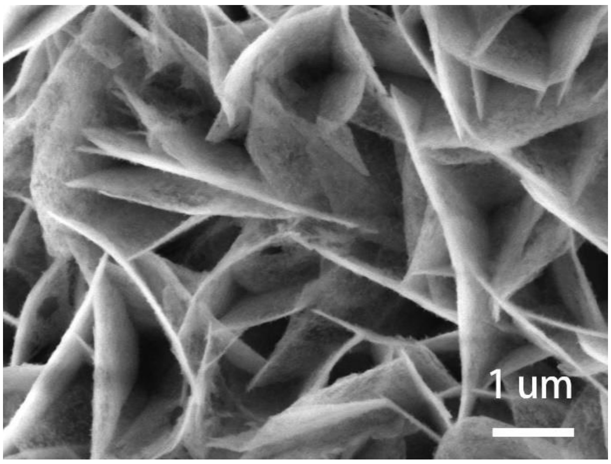

Fig. S12. SEM image of Mn-Ni_2P/NiFe LDH after UOR stability.

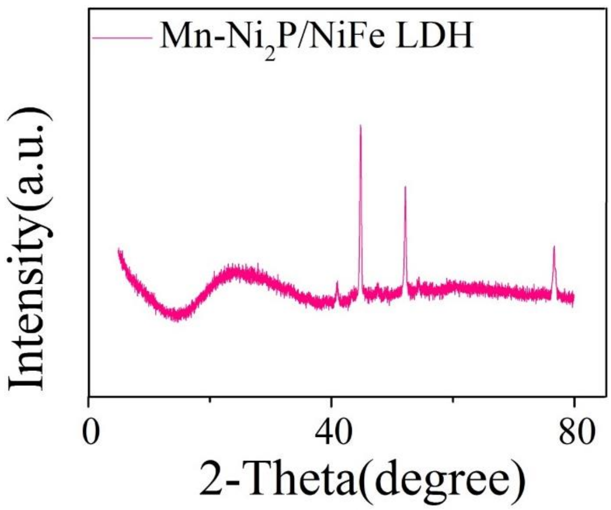

Fig. S13. XRD pattern of the Mn-Ni_2P/NiFe LDH after UOR stability.

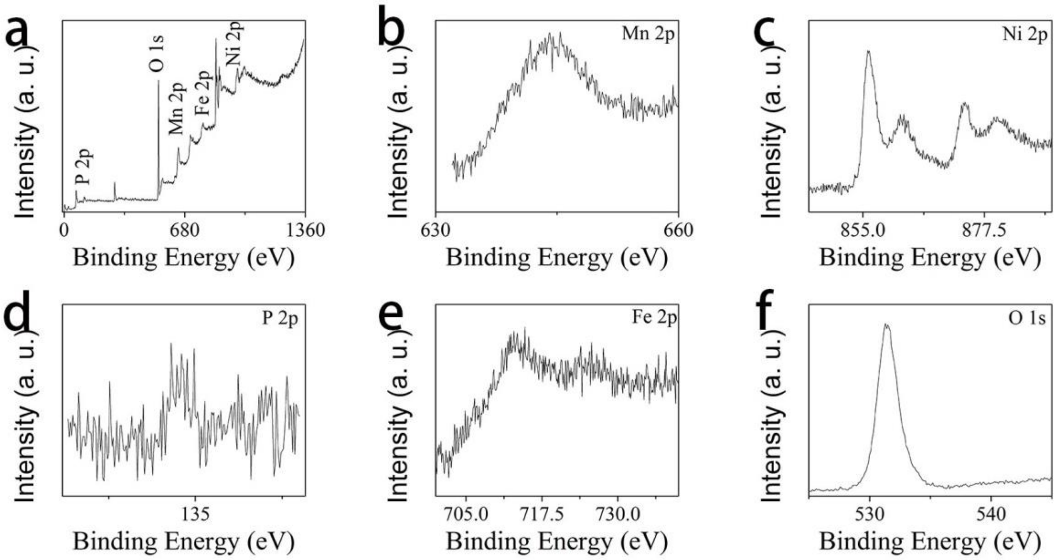

Fig. S14. XPS spectra of (a) survey scan, (b) Mn 2p, (c) Ni 2p, (d) P 2p, (e) Fe 2p and (f) O 1s for Mn-Ni_2P/NiFe LDH after UOR stability.

Table S1. Comparison of UOR performance of Mn-Ni_2P/NiFe LDH with other reported catalysts.

Catalysts	Overpotential (V) at 10 mA cm^{-2}	References
Mn-Ni_2P/NiFe LDH	**1.372**	**This work**
Fe_3O_4@FeOOH-NF	1.38	[S1]
Fe_2O_3/NF	1.41	[S1]
Ni/SiO_x/N-C	1.38	[S2]
NiMoSe	1.39	[S3]
Ce-Ni_2P/NF	1.4	[S4]
NiMo@ZnO/NF	1.4	[S5]
Fe-Ni_3S_2@$FeNi_3$	1.4	[S6]
Ni_2P/NiF_3/CC	1.4	[S7]
Mo-Ni_2P	1.41	[S8]
Ni_2P/CFC	1.42	[S9]
P-CoS_2	1.51	[S10]

Table S2. Comparison of water splitting performances of Mn-Ni_2P/NiFe LDH with recently reported catalysts.

Catalysts	Voltage (V) at 10 mA cm^{-2}	References
Mn-Ni_2P/NiFe LDH	**1.632**	**This work**
NiMo-PVP/NiFe-PVP	1.66	[S11]
Ni/Mo_2C-PC	1.66	[S12]
NiFe/$NiCo_2O_4$/Ni foam	1.67	[S13]
$SrNb_{0.1}Co_{0.7}Fe_{0.2}O_{3-\delta}$ perovskite	1.68	[S14]
Ni_5P_4/Ni foil	1.7	[S15]
Co_xP@NC	1.71	[S16]
$Co_2B/CoSe_2$	1.73	[S17]
V/Ni foam	1.74	[S18]
CoPS/Al_2O_3-3	1.75	[S19]
Co/CeO_2/Co_2P/CoP@NC	1.76	[S20]

Table S3. Comparison of urea electrolysis performances of Mn-Ni_2P/NiFe LDH with recently reported catalysts.

Catalysts	Voltage (V) at 10 mA cm^{-2}	References
Mn-Ni_2P/NiFe LDH	**1.494**	**This work**
CoMn/$CoMn_2O_4$	1.51	[S21]
$NiTe_2$/$Ni(OH)_2$	1.52	[S22]
Ni-MOF	1.52	[S23]
Fe_7Se_8@Fe_2O_3	1.55	[S24]
Bulk MnO_2	1.55	[S25]
Ni@NCNT-3	1.56	[S26]
MnO_2/$MnCo_2O_4$/Ni	1.58	[S27]
FQD/CoNi LDH/NF	1.59	[S28]
HC-NiMoS/Ti	1.59	[S29]
$Ni(OH)_2$NS@NW/NF	1.68	[S30]

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