Supporting Information

Highly Durable Compositionally Variant Bifunctional Tetrametallic Ni-Co-Mn-Fe Phosphide Electrocatalysts Synthesized by a Facile Electrodeposition Method for High-Performance Overall Water Splitting

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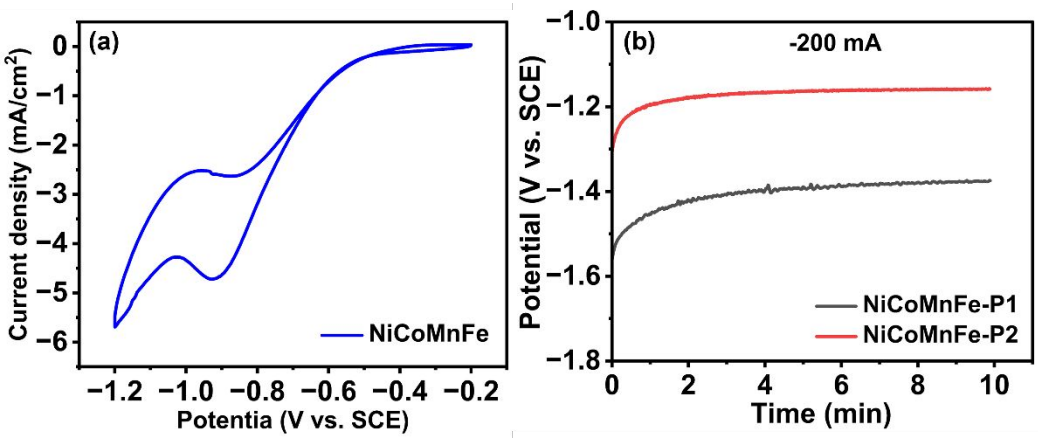

Figure S1. (a) and (b) Potential response and current response during electrodeposition for NiCoMnFe and NiCoMnFe-P based nanosheets.

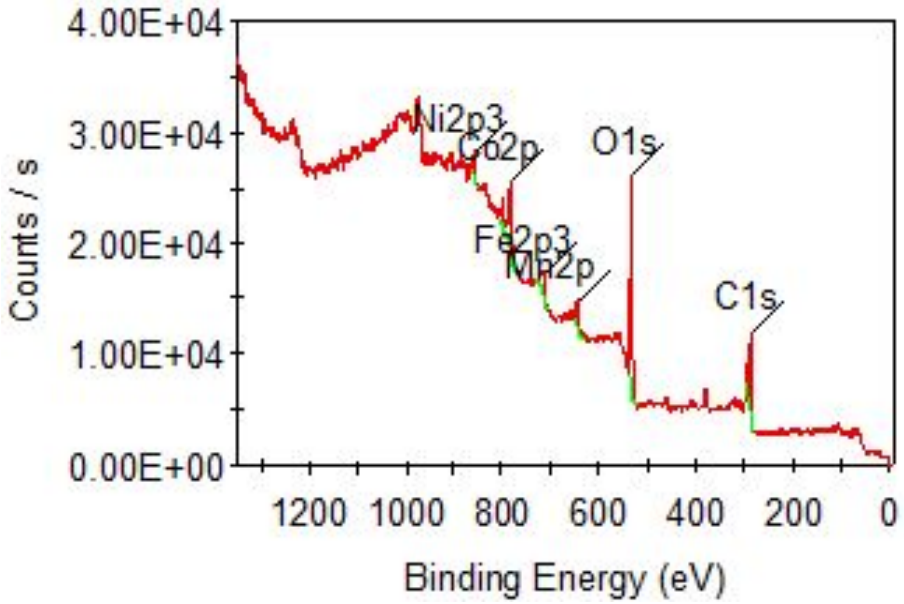

Figure S2. XPS survey scan of NiCoMnFe-P composites.

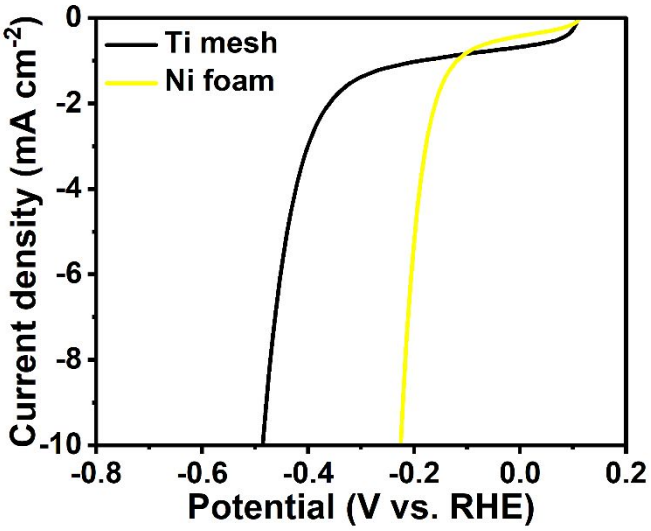

Figure S3. HER polarization curve for Ti mesh and Ni foam substrates.

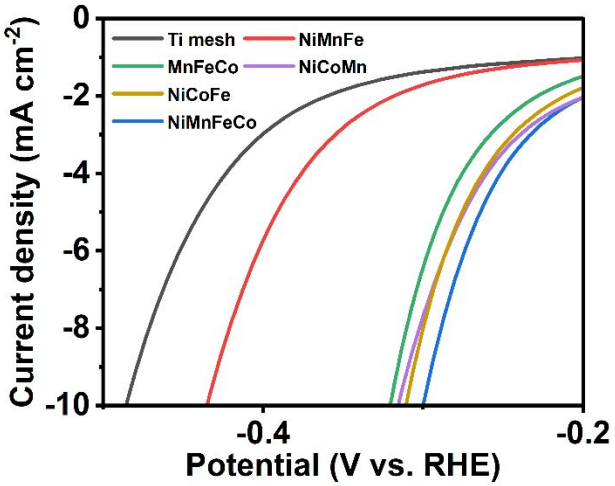

Figure S4. HER polarization curve for the fabricated composites at –10 mA.

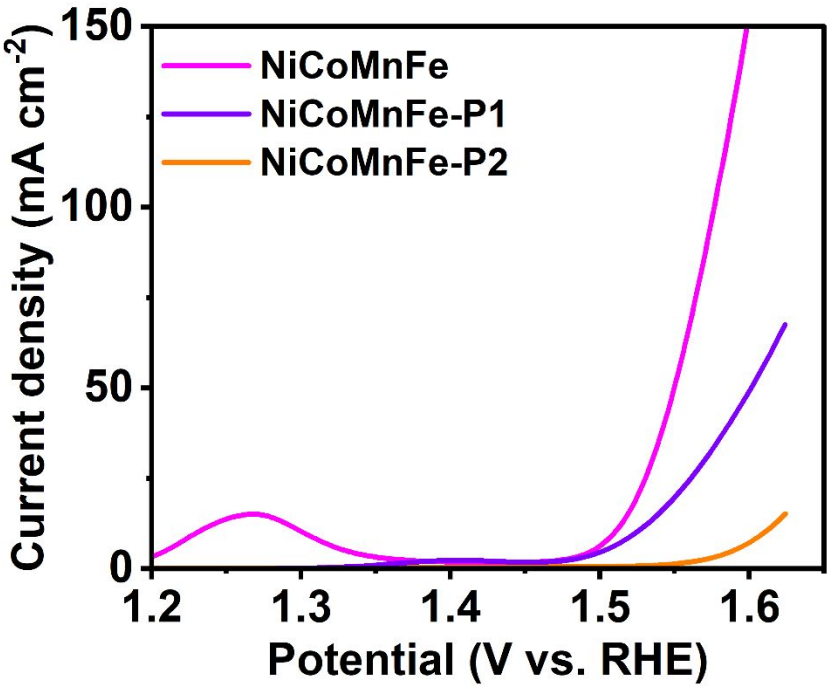

Figure S5. OER polarization curve of NiCoMnFe, NiCoMnFe-P1, and NiCoMnFe-P2.

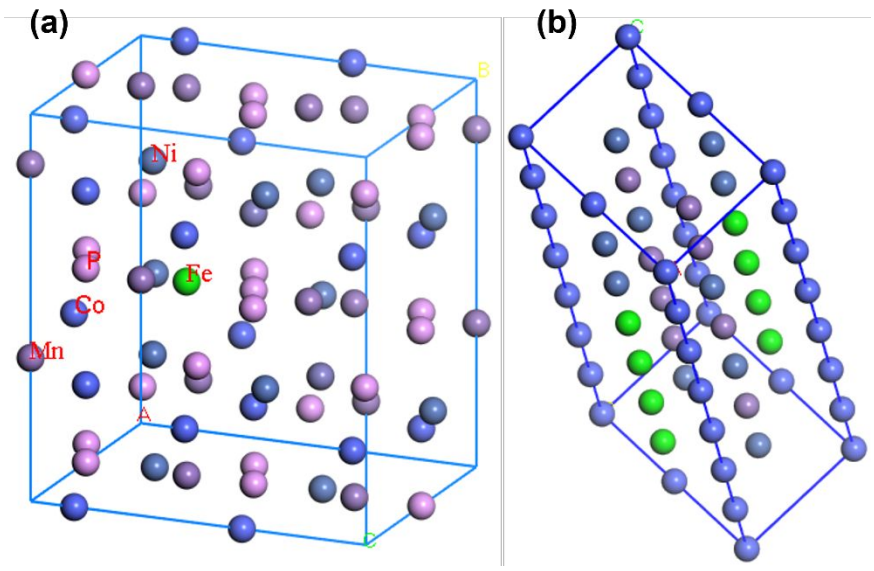

Figure S6. Geometry optimized figures of (a) MnFeNiCo-P (b) MnFeCoNi.

Theoretical Notes

The oxygen evolution reaction consists of four one-electron steps. The activity of each step is expressed by Gibbs free energy as explained in the following equations: -

$$H_2O(l) + * \rightarrow HO^* + H^+ + e^-$$

$$\Delta G_1 = E_{HO} - E_{slab} + {}^{1}/_{2}H_2 - H_2O + \Delta E_{ZPE} - T\Delta S$$

$$HO^* \rightarrow O^* + H^+ + e^-$$

$$\Delta G_2 = E_O - E_{HO} + {}^{1}/_{2}E_{H2} + \Delta E_{ZPE} - T\Delta S$$

$$O^* + H_2O(l) \rightarrow HOO^* + H^+ + e^-$$

$$\Delta G_3 = E_{HOO} - E_O + {}^{1}/_{2}E_{H2} - E_{H2O} + \Delta E_{ZPE} - T\Delta S$$

$$HOO^* \rightarrow O_2(g) + H^+ + e^-$$

$$\Delta G_4 = E_{slab} - E_{HOO} - {}^{3}/_{2}H_2 + 2H_2O + 4.92 + \Delta E_{ZPE} - T\Delta S$$

where E_{H2}, E_{HO}, E_{slab}, E_{HO}, E_H and E_{HOO} are energies of free H_2, free H_2O, clean surface, adsorbed HO, adsorbed H, adsorbed HOO on surface respectively.

Table S1. Calculated Gibbs free energy for MnFeCoNiP and MnFeCoNi during OER.

Catalyst	ΔG_1	ΔG_2	ΔG_3	ΔG_4
MnFeCoNi	1.37	0.61	2.3	0.73
MnFeCoNiP	1.62	-0.57	3.27	2.43