Supplementary Materials

Paired electrolysis of acrylonitrile and 5-hydroxymethylfurfural for simultaneous generation of adiponitrile and 2,5-furandicarboxylic acid

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I: Formulas and calculation procedures

1.1 The calculation formulas

1.1.1   Cathode reaction (AN→ADN+PN+Others):

The reactant conversion was quantified by external standard method. A series different concentration of standard samples were detected by gas chromatography (GC). The GC peak area can make a standard curve that reflects the relationship between peak area and concentration. After analysis, the area of AN in the samples was substituted into the curve (**Figure S17a**), and the corresponding chemicals concentration of the samples could be obtained. It should be noted that the ADN and PN selectivity were calculated by the method of peak area percent, since the toxic PN standard sample could not be purchased.

$$\text{Conversion(AN,\%)} = \frac{\Delta \text{ mole of AN}}{\text{initial mole of AN}} \times 100\% \tag{1}$$

$$\text{Selectivity(ADN,\%)} = \frac{\text{The GC area of ADN}}{\text{The GC area of all products}} \times 100\% \tag{2}$$

$$\text{Selectivity(PN,\%)} = \frac{\text{The GC area of PN}}{\text{The GC area of all products}} \times 100\% \tag{3}$$

$$\text{Yield(ADN,\%)} = S(ADN) \times C(AN) \times 100\% \tag{4}$$

$$\text{Charge(C)} = \Sigma j \times A \times t \tag{5}$$

$$\text{FE(ADN, \%)} = \frac{n(ADN)}{(\text{Charge}/ne \times F)} \times 100\% \tag{6}$$

j is the current density, A is the surface area of the working electrode and t is the time period of electrolysis, F is the Faraday constant (96485 $C \cdot mol^{-1}$), ne is the number of electrons, the value is 2 in this reaction.

$$\text{Areal production rate (kg}_{ADN} \cdot h^{-1} \cdot m^{-2}) = \frac{\text{ADN production (kg)}}{t(h) \times a(m^2)} \tag{7}$$

$$W(J) = \Sigma U \times t \times i \tag{8}$$

$$\text{Energy productivity(kg}_{ADN} \cdot kWh^{-1}) = \frac{\text{ADN production（kg）}}{W(kWh)} \tag{9}$$

For formula Eq.8, i is the working current, the area of "U-t" can be integral from the reaction curve. The unit of the value that "U-t" area multiply i is Joule (J). 1 kWh = 3600000 J.

1.1.2 Anode reaction (HMF→FDCA+HMFCA+FFCA):

The products were quantified by ESTD, and a series different concentration of standard samples were detected by HPLC. The HPLC peak area can make a curve that

reflects the relationship between peak area and concentration. After dececting, the area of HMF and FDCA in the samples were substituted into the curve (**Figure S17c-d**), and the corresponding chemicals concentration of the samples could be obtained.

$$\text{Conversion(HMF, \%)}=\frac{\Delta \text{ mole of HMF}}{\text{initial mole of HMF}} \times 100\% \tag{10}$$

$$\text{Selectivity(FDCA, \%)}=\frac{\text{The mole of FDCA}}{\Delta \text{ mole of HMF}} \times 100\% \tag{11}$$

$$\text{Yield(FDCA, \%)}=\text{S(FDCA)} \times \text{C(HMF)} \times 100\% \tag{12}$$

$$\text{Charge(C)}=\Sigma j \times A \times t \tag{13}$$

$$\text{FE(FDCA, \%)}=\frac{\text{n(FDCA)}}{(\text{Charge/ne} \times F)} \times 100\% \tag{14}$$

j is the current density, A is the surface area of the working electrode, t is the time period of electrolysis, F being the Faraday constant (96485 $C \cdot mol^{-1}$), ne is the number of electrons, the value is 6 in this reaction.

1.2 The formulas of reference electrode converse

1.2.1 Cathode

The reference electrode SCE is calibrated by measuring the RHE potential. The potential was converted to RHE by the Nernst formula:

$$E_{RHE} = E_{SCE} + 0.059 \times pH + E^o_{(SCE)} \tag{15}$$
$$(E^o_{(SCE)} = 0.244 \text{ V vs. RHE})$$

1.2.2 Anode

The potential of the Hg/HgO reference electrode was converted to vs. RHE by the Nernst formula:

$$E_{RHE} = E_{Hg/HgO} + 0.059 \times pH + E^o_{(Hg/HgO)} \tag{16}$$
$$(E^o_{(Hg/HgO)} = 0.098 \text{ V vs. RHE})$$

1.3 The calculation formulas of ECSA and Tafel slope

$$\text{ECSA}=\frac{C_{dl}}{C_s} \tag{17}$$
$$(C_s = 40 \text{ } \mu F \cdot cm^{-2})$$

Cyclic voltammetry (CV) tests for ECSA evaluation were performed in 1.0 M KOH electrolyte with as-prepared material as working electrode and Pt as the counter electrode. In this way, the final Δj ($\Delta j = j_{anodic} - j_{cathodic}$) obtained is plotted against CV scan rate. The slope of the line fitted to these points is equivalent to the C_{dl} of the sample [1]. C_s means the specific capacitance of the flat surface for nickel-based materials [2,3].

II：Figures
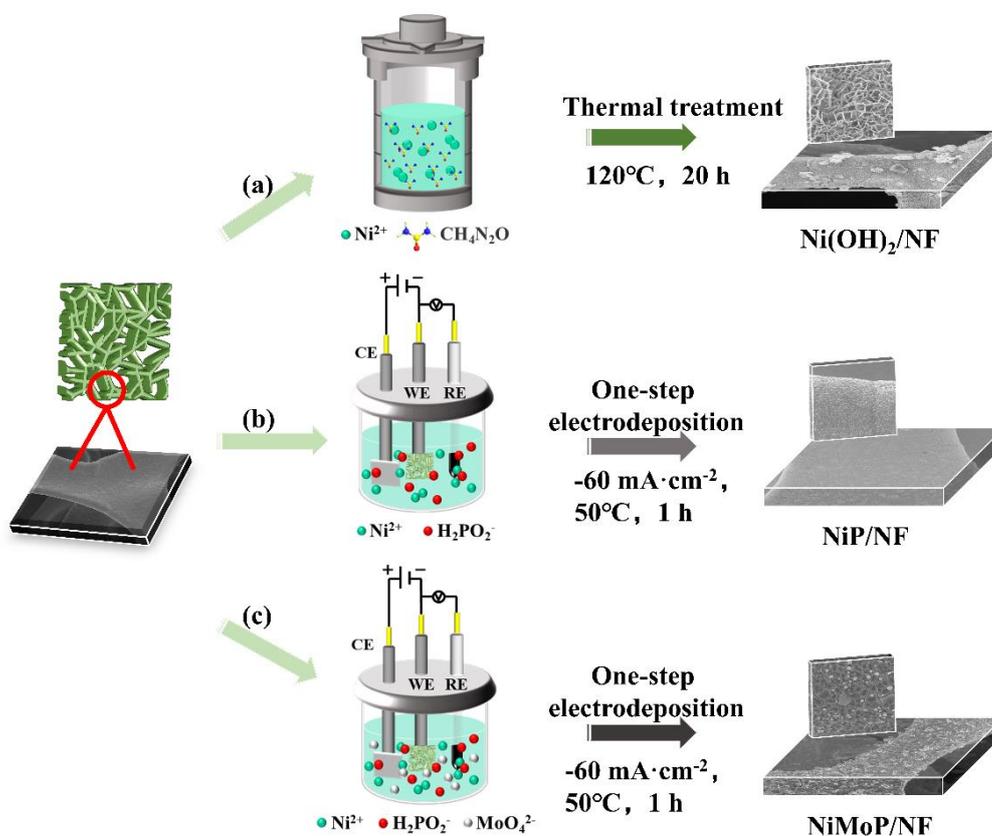
Figure S1. Schematic illustration of the synthesis process for (a) Ni(OH)$_2$/NF, (b) NiP/NF and (c) NiMoP/NF.
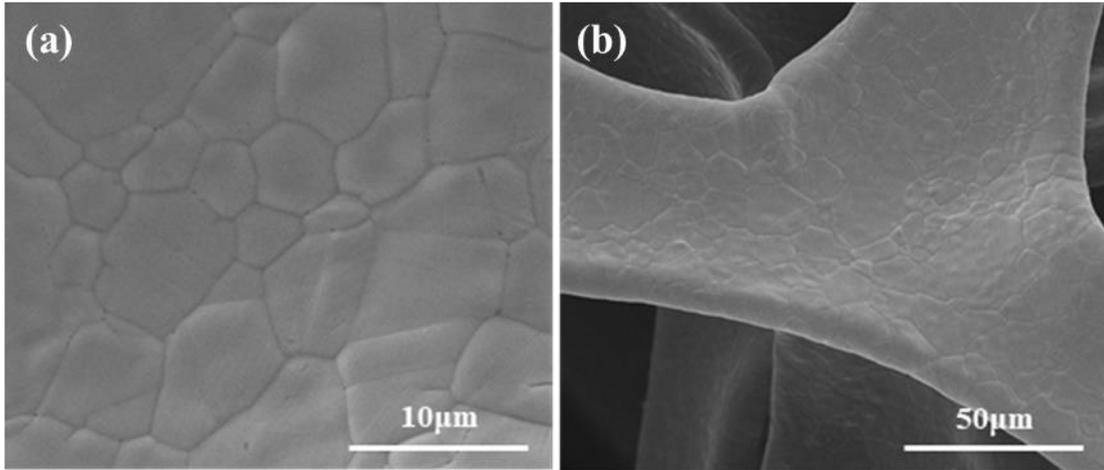
Figure S2. The scanning electron microscopy (SEM) figures of cleaned nickel foam (NF) surface.
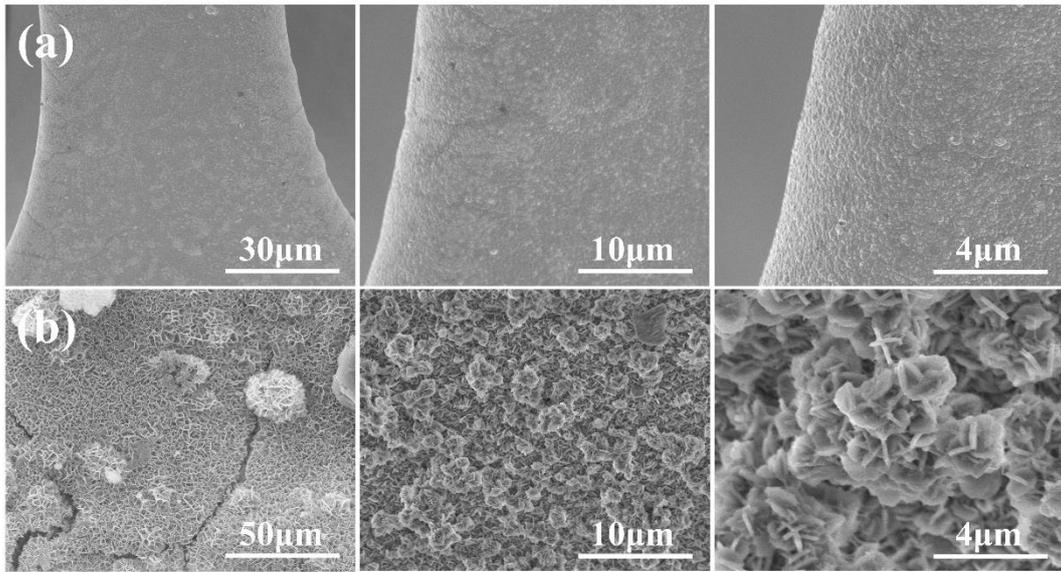
**Figure S3.** SEM images of (a) NiP/NF, (b) Ni(OH)$_2$/NF.
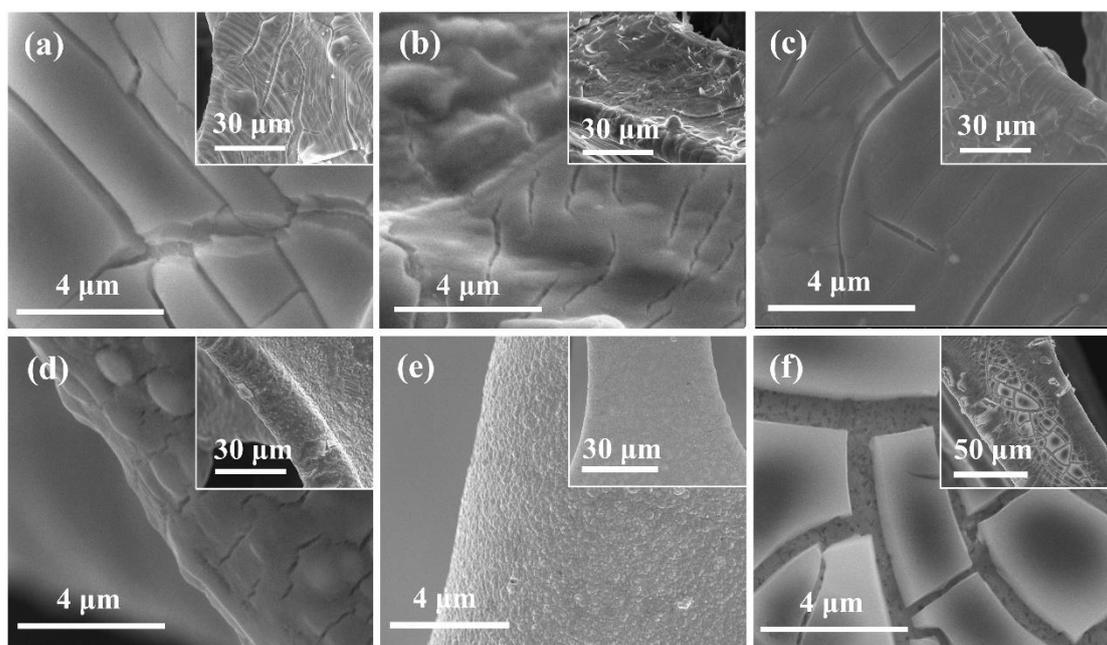
Figure S4. The SEM images of NiMoP/NF catalysts with different Ni/Mo ratios : (a) Ni_1Mo_1P/NF (b) Ni_2Mo_1P/NF (c) Ni_4Mo_1P/NF (d) Ni_5Mo_1P/NF (e) NiP/NF (f) NiMo/NF.
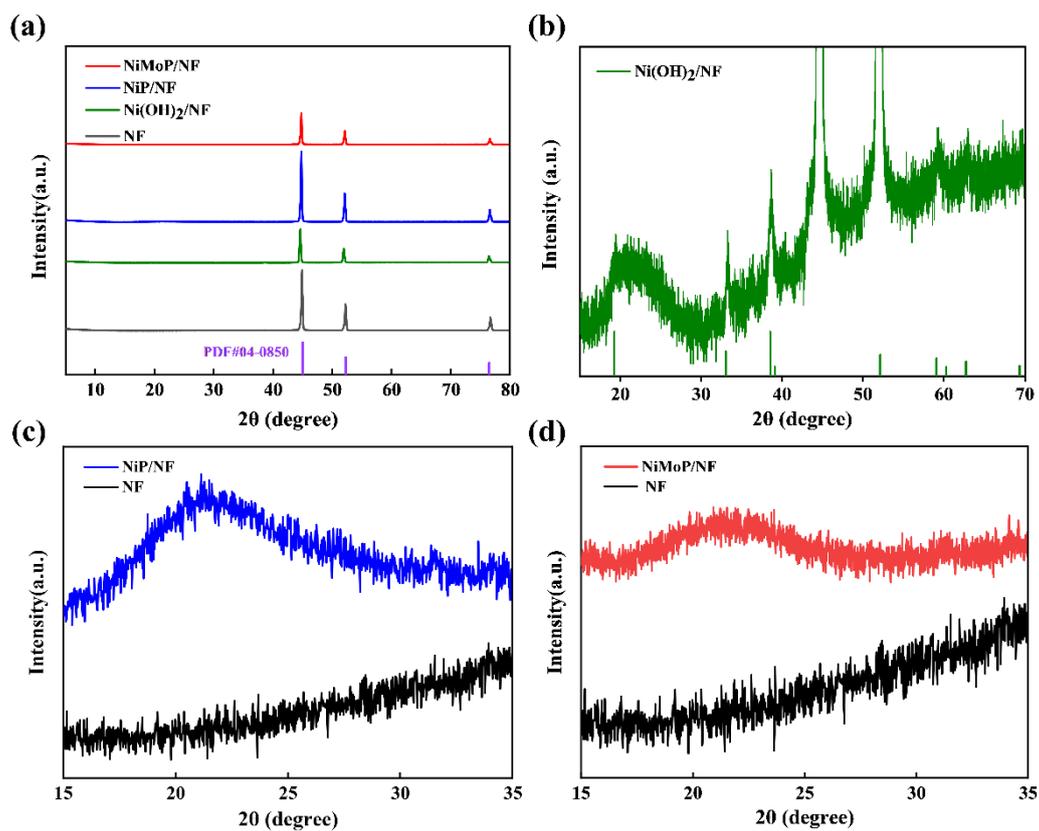
Figure S5. (a) XRD patterns of NF, Ni(OH)$_2$/NF, NiP/NF and NiMoP/NF; XRD fine patterns of (b) Ni(OH)$_2$/NF, (c) NiP/NF and (d) NiMoP/NF local areas, respectively.
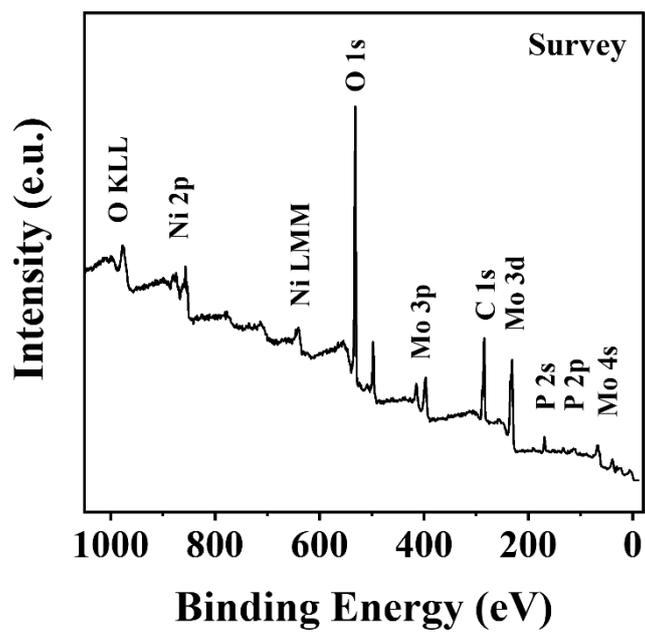
Figure S6. XPS spectra survey of NiMoP/NF.
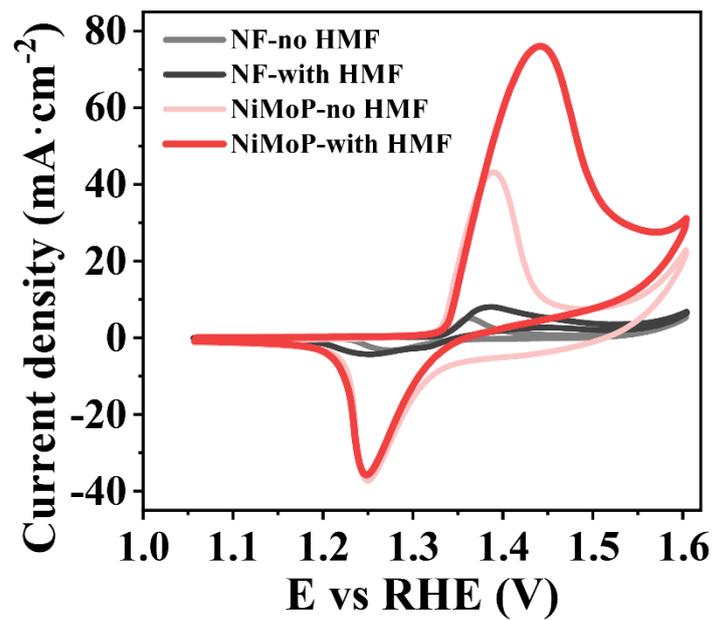
Figure S7. Cyclic voltammogram (CV) curves of NiMoP/NF and NF electrodes measured at a scan rate of 10 mV·s^{-1} in 1.0 M KOH with and without 10 mM HMF.
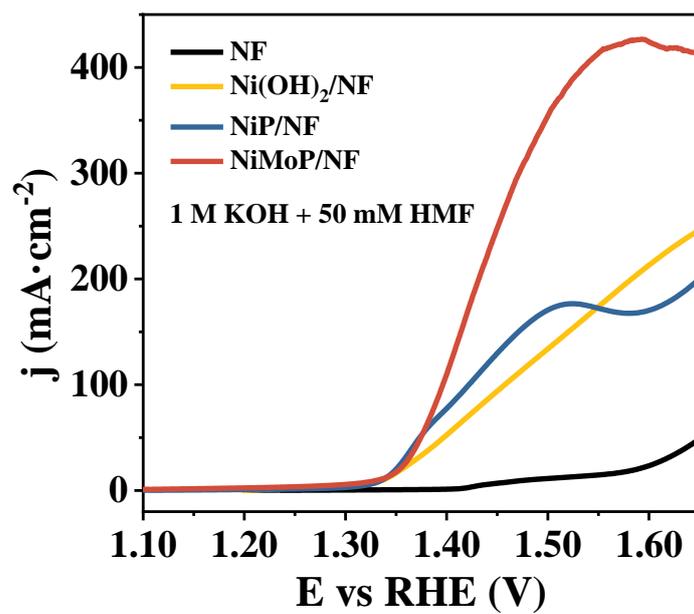
Figure S8. LSV curves at 10 mV·s⁻¹ scan rate with NF, Ni(OH)₂/NF, NiP/NF and NiMoP/NF as working electrodes in 1.0 M KOH & 50 mM HMF electrolyte.
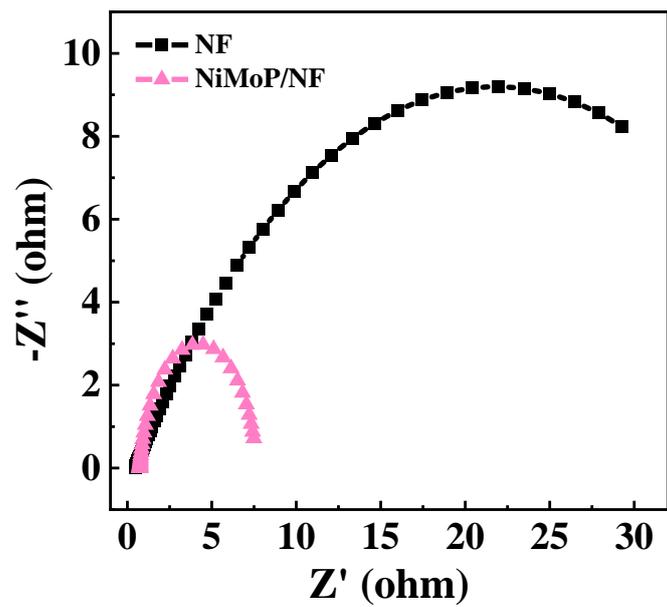
Figure S9. Nyquist plots obtained with $Ni(OH)_2/NF$ as working electrode in 1.0 M KOH & 50 mM HMF solution.
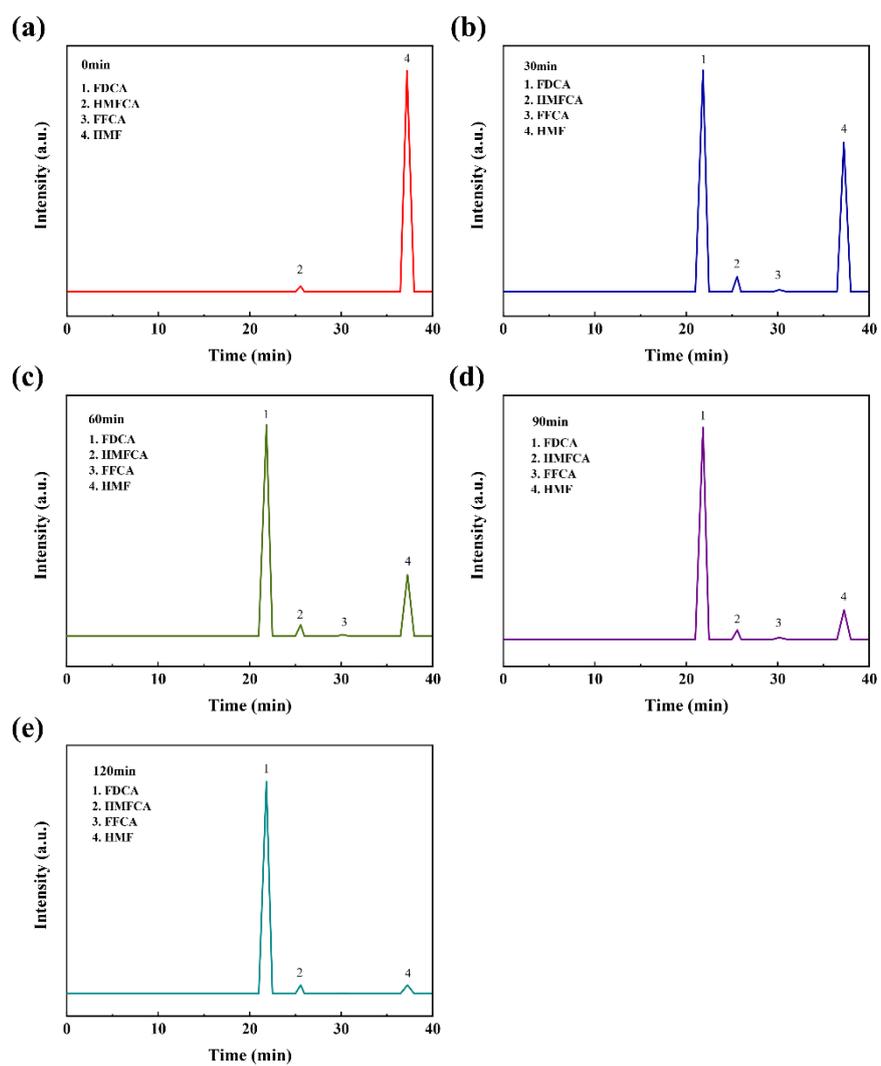
Figure S10. High-performance liquid chromatography (HPLC) results (peak height trends) at various electrolysis times.
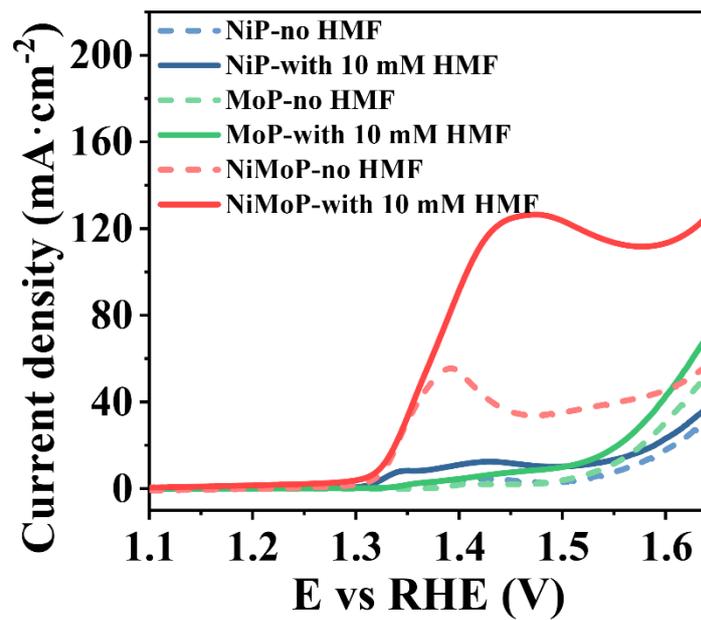
**Figure S11.** The LSV of NiMoP/NF and NF for HMFOR and OER.
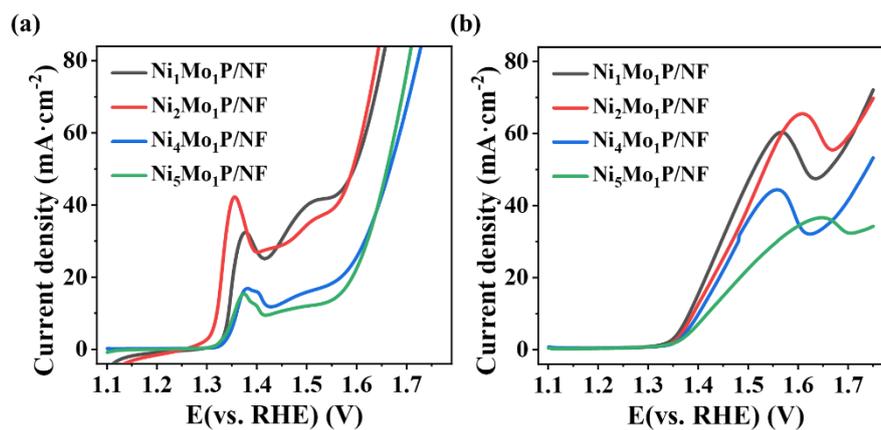
Figure S12. LSV curves of NiMoP/NF with different Ni/Mo ratio for (a) OER and (b) HMFOR (10 mM HMF) in 1.0 M KOH.
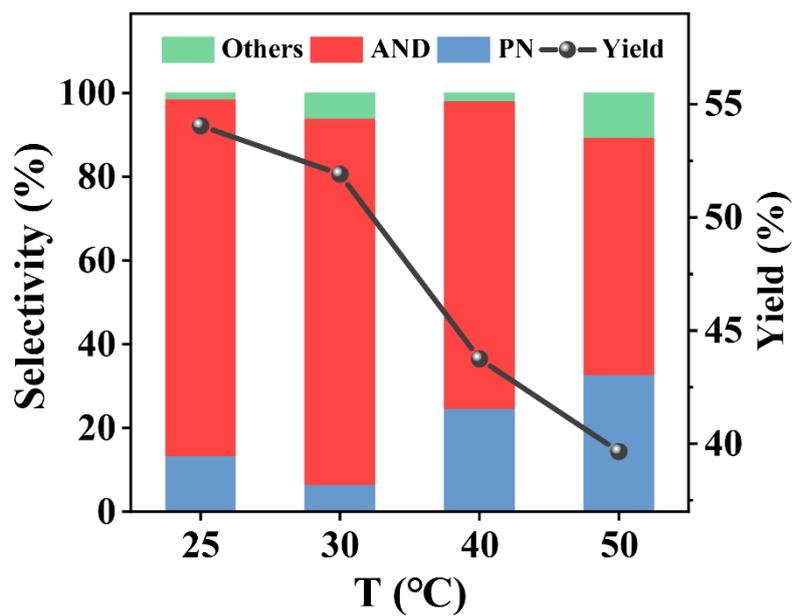
Figure S13. The selectivity and yield for electrohydrodimerization of AN under different temperatures, conditions: 1.32 M initial AN concentration, 1.56 M DMF, 0.20 M TAA, -62.5 mA·cm^{-2}).
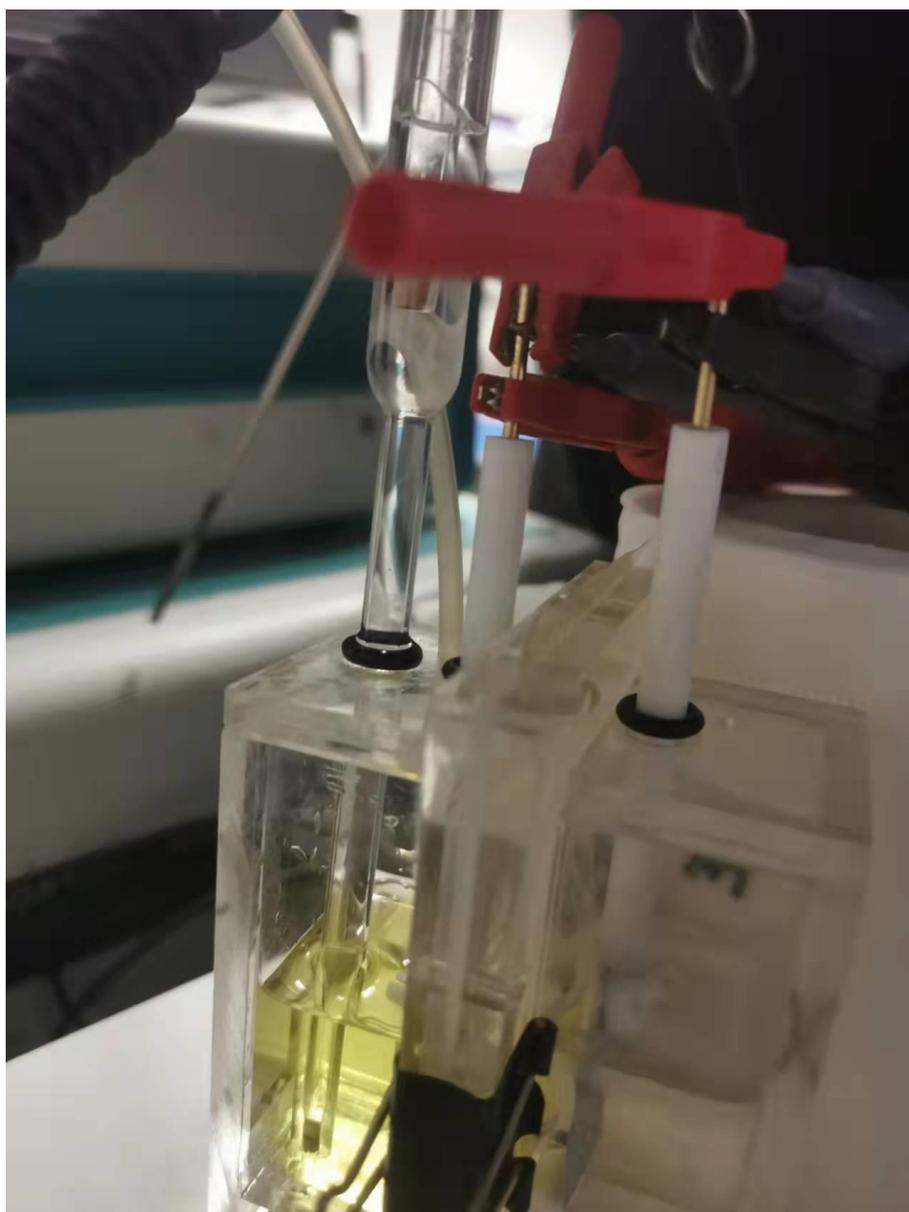
Figure S14. Experimental device of paired system: HMFOR (left) and EHD of AN (right).
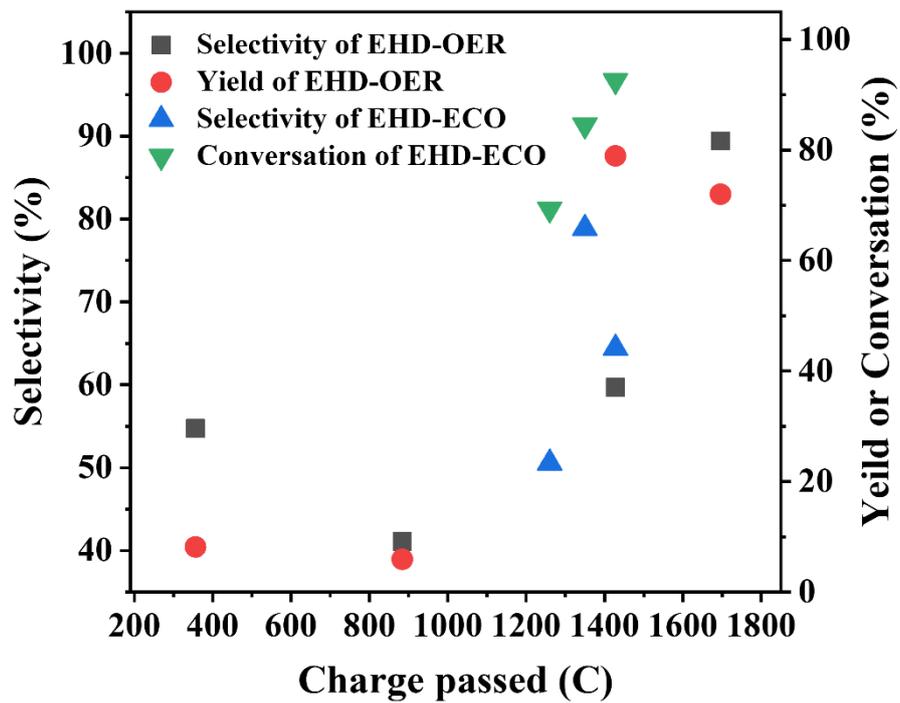
**Figure S15.** Selectivity, yield and conversion for ECO of HMF in two system.
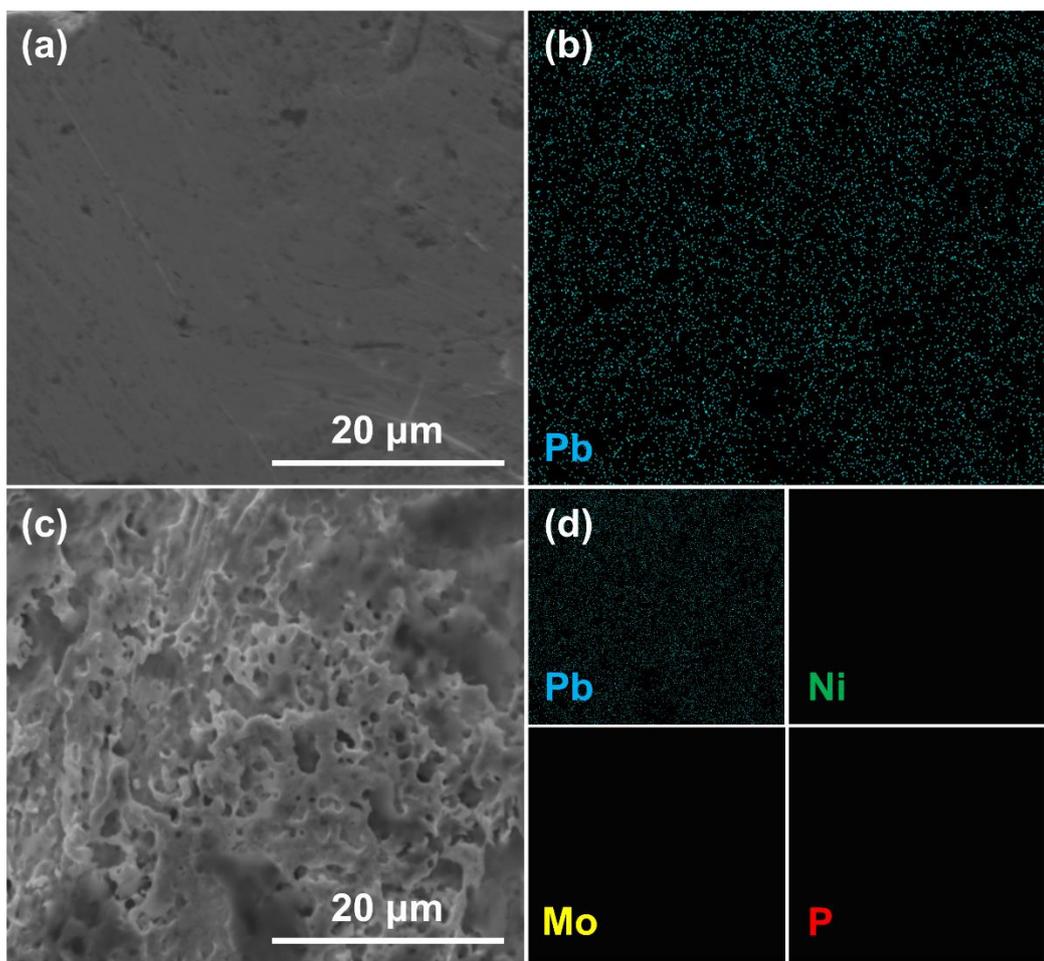
Figure S16. SEM image and corresponding element mapping for Pb cathode (a-b) before and (c-d) after paired electrolysis.
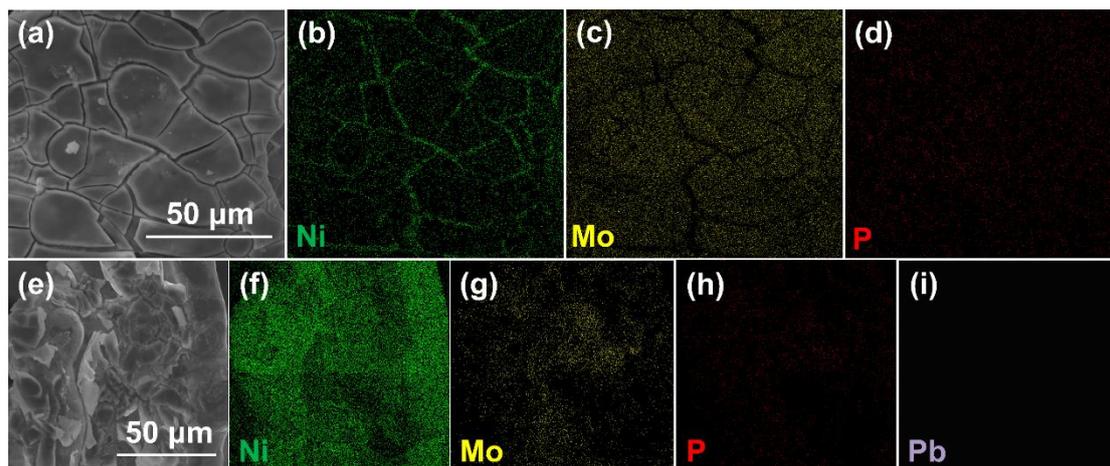
Figure S17. SEM image and corresponding element mapping for NiMoP/NF anode (a-d) before and (e-i) after paired electrolysis.
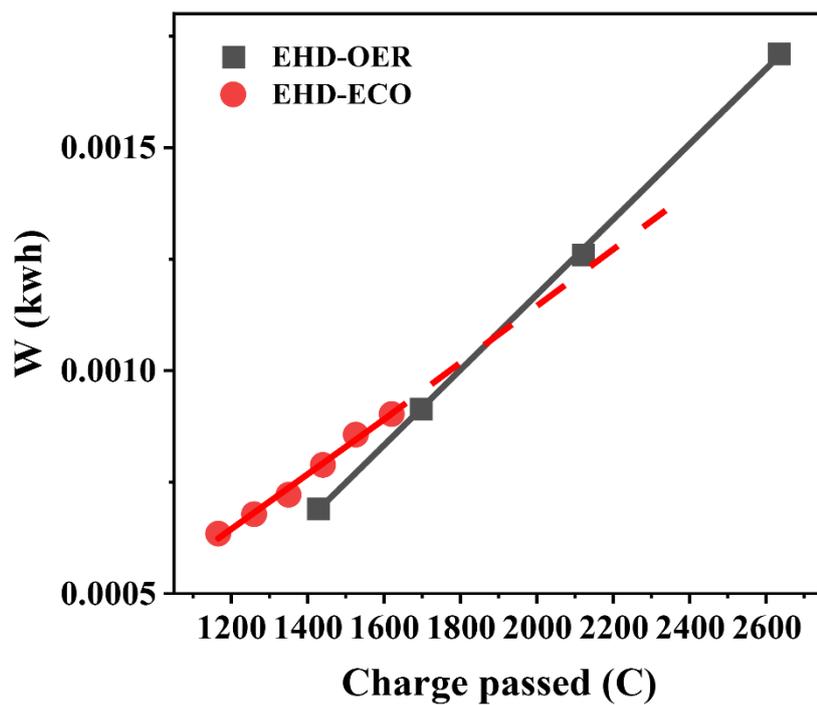
Figure S18. The energy consumption＆trend in ANEHD-HMFOR and ANEHD-OER system.
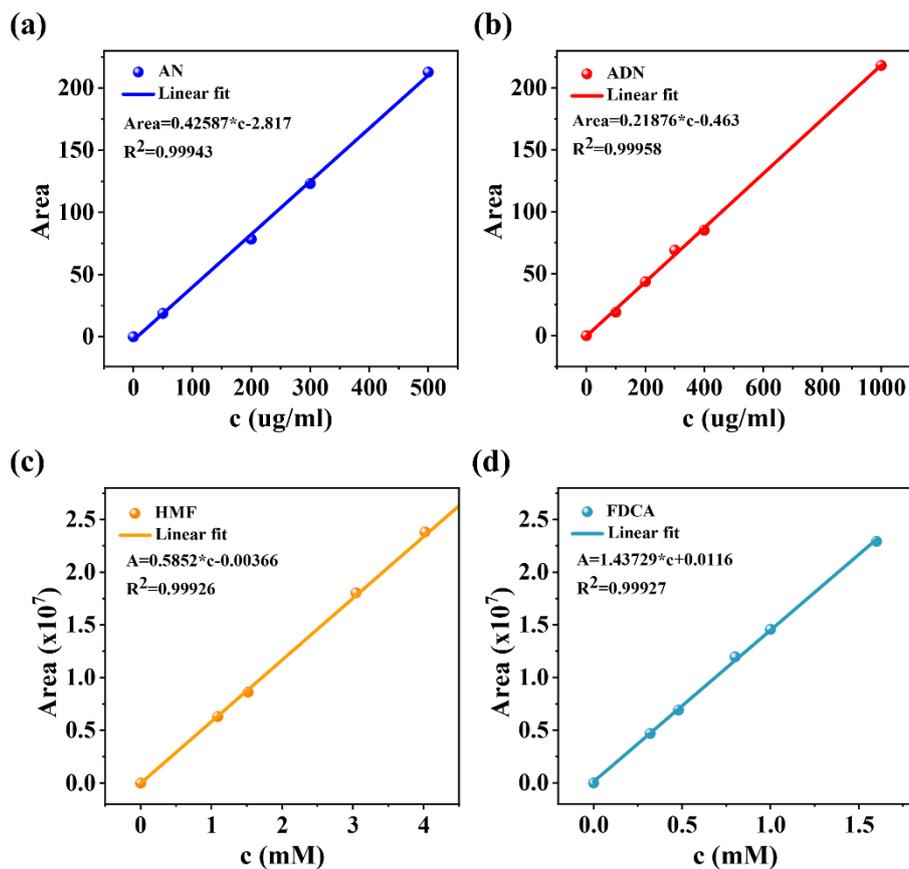
Figure S19. GC standard curves of (a) AN, (b) ADN; HPLC standard curves of (c) HMF, (d) FDCA.

References

1. Anantharaj, S.; Ede, S.; Karthick, K.; Sankar, S.S.; Sangeetha, K.; Karthik, P.; Kundu, S. Precision and correctness in the evaluation of electrocatalytic water splitting: revisiting activity parameters with a critical assessment. Energy Environ. Sci. 2018, 11, 744-771.

2. Zhou, Y.; Li, T.; Xi, S.; He, C.; Yang, X.; Wu, H. One-step Synthesis of Self-standing Ni3S2/Ni2P Heteronanorods on Nickel Foam for Efficient Electrocatalytic Hydrogen Evolution over a Wide pH Range. ChemCatChem 2018, 10, 5487-5495, doi:https://doi.org/10.1002/cctc.201801373.

3. Zhang, W.; Zheng, J.; Gu, X.; Tang, B.; Li, J.; Wang, X. Facile synthesis, characterization and DFT studies of a nanostructured nickel–molybdenum–phosphorous planar electrode as an active electrocatalyst for the hydrogen evolution reaction. Nanoscale 2019, 11, 9353-9361.