Supporting Information

Integrating electrodeposition with electrolysis for closing loop resource utilization of battery industrial wastewater

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Figure S1. Flowsheet of resource utilization of battery industrial wastewater. First, recycling and synthesis of NiCoMn LTHs electrocatalysts from the industrial wastewater via electrodeposition. Second, reutilization of PE wastewater for hydrogen production via electrolysis. PE: post-electrodeposition.



Figure S2. SEM images of S-3.



Figure S3. TEM image of S-3.



Figure S4. (a-f) SEM images and the schematic illustration of catalysts morphology evolution during the deposition process. (g) Amount of catalysts deposited on CP substrate, and (h) element weight ratio of catalysts with different deposition times.

Since the nanostructure is crucial to the electrochemical performance of catalysts¹, the formation dynamic would be of great interest. The nanostructure, mass loading, and the elemental composition of electrodes obtained at different deposition time intervals and the schematic illustration are shown in **Figures S4**. At the beginning of the electrodeposition, the pretreated CP shows a clean and smooth surface (**Figure S4a**). After 5 min, rich nanoclusters with an average diameter of 100-200 nm (2.7 mg cm⁻²) are formed on the surface of CP (**Figure S4b**). Extending deposition time to 10 min, nanoclusters are evolved into nanospheres with many nanoplates formed on the surface (**Figure S4c**), and the catalyst mass loading climbs to 4.1 mg cm⁻² (**Figure S4g**). The nanospheres are continually growing and agglomerating into nanoflowers after

depositing 20 min, which almost entirely covers the electrode's surface (8.3 mg cm⁻²) (Figure S4d). Further extending the deposition time results in even more catalyst deposition of 10.9 and 13.6 mg cm⁻² on the CP substrate after 30 and 40 min deposition, respectively. Nevertheless, the 3D nanoflowers are gradually destroyed, and some nanoplates are generated on the CP substrate, as evidenced by SEM (Figures S4e, f). This structure evolution would consequently lead to the reduction of the active sites on the electrode. Apart from nanostructure and mass loading evolution, the elemental composition of as-deposited samples was also investigated. According to Figure S4h, the chemical compositions of electrodeposits were calculated as follows: $Ni_{0.76}Co_{0.49}Mn_{0.28}(OH)_2$ (S-1), $Ni_{0.82}Co_{0.57}Mn_{0.31}(OH)_2$ (S-2), $Ni_{1.15}Co_{0.85}Mn_{0.41}(OH)_2$ (S-3), Ni_{0.86}Co_{0.61}Mn_{0.41}(OH)₂ (S-4), Ni_{0.74}Co_{0.54}Mn_{0.49}(OH)₂ (S-5). In can be seen that the contents of both Ni and Co increase first and then decrease from S-1 to S-5, but the ratio of Mn continuously increased. For S-3, the concentration of metals is higher than its counterparts, which reaches 67.33%. Compared to other samples, S-3 with a hierarchical nanoflower structure and rich metal contents may possess higher electrocatalytic activity. In addition, such a nanostructure evolution process makes it possible to tune the morphology via regulating the experimental protocols, like electrodeposition time. This method may pave the way to recycle the metal ions and synthesize hierarchical nanostructures from industrial wastewater.



Figure S5. (a) Wide XPS survey spectrum of S-3. XPS spectra of (b) Ni 2p, (c) Mn 2p, (d) Co 2p, and (e) O 1s in S-3.

The survey spectrum of S-3 reveals the co-presence of Mn, Ni, Co, and O elements (**Figure S5a**). In **Figure S5b**, the Ni 2p peak can be deconvoluted into six peaks, ascribing four spin-orbit doublets and two shakeup satellite peaks. Two binding energies locate at 855.6 and 872.9 eV can be indexed to Ni²⁺ $2p_{3/2}$ and Ni²⁺ $2p_{1/2}$ with two satellite peaks at 862.2 and 880.3 eV, respectively. Additionally, the two peaks with higher binding energies of 856.8 and 874.1 eV can be ascribed to Ni³⁺ $2p_{3/2}$ and Ni³⁺ $2p_{1/2}^2$, separately, inferring high-valence Ni in S-3. In **Figure S5c**, six peaks can be found in the Mn 2p spectrum. The peaks at 640.9 eV and 651.9 could be attributed to Mn²⁺ $2p_{3/2}$ and Mn²⁺ $2p_{1/2}$, respectively. The peaks at 641.6 and 653.1 eV are from Mn³⁺, and another two peaks with higher binding energies of 643.6 and 654.9 eV are indexed to Mn⁴⁺ $2p_{3/2}$ and Mn⁴⁺ $2p_{1/2}$, correspondingly³. For the Co 2p core-line spectrum, both Co²⁺ and Co³⁺ are observed (**Figure S5d**). The binding energies at 781.5

and 796.9 eV can be assigned to $Co^{2+} 2p_{3/2}$ and $Co^{2+} 2p_{1/2}$, and the $Co^{3+} 2p_{3/2}$ and $Co^{3+} 2p_{1/2}$ peaks are located at 779.8 and 795.1 eV, respectively⁴. In addition, the O 1s spectrum can be fitted according to the contributions of three oxygen species in **Figure S5e**. Three peaks at 532.6, 531.6 and 530.2 eV are ascribed to the absorption of moisture water, the oxygen in hydroxyl groups and the typical metal-oxygen bonds, respectively².



Figure S6. Onset potentials and overpotentials at a HER current density of 10 mA cm⁻² of the electrodeposited catalyst and Pt.



Figure S7. CV curves of (a) S-1, (b) S-2, (c) S-3, (d) S-4, and (e) S-5 at different rates, in the region of $0 \sim 0.1$ V vs. RHE. (f) C_{dl} values of the electrodeposited catalysts.

In this study, to understand the effects of nanoflower structure in S-3, the C_{dl} is calculated based on CV measurements at various scan rates, in 0 ~ 0.1 V vs. RHE (**Figure S7**). The calculated C_{dl} of S-3 (69.37 mF cm⁻²) is obviously larger than S-1 (40.45 mF cm⁻²), S-2 (48.15 mF cm⁻²), S-5 (50.11 mF cm⁻²), and S-4 (63.78 mF cm⁻²).



Figure S8. Nyquist plots of the electrodeposited catalysts at -0.1 V vs. RHE.

Apart from the number of electrocatalytic active sites, the charge transfer characteristics during catalysis were further explored by conducting EIS measurements at -0.1 V vs. RHE. The Nyquist plots in **Figure S8** are analyzed and fitted with an equivalent circuit model (**Figure S9**). It can be found that all samples show similar solution resistances (R_s) values in the high-frequency region. In the low-frequency region, S-3 shows the smallest R_{ct} of 67.48 Ω among all the investigated catalysts (**Table S4**), suggesting faster charge transportation during HER for S-3.



Figure S9. Equivalent circuit model for EIS data fitting.



Figure S10. TEM and HRTEM images of S-3 after the HER test.



Figure S11. High-resolution XPS scans of S-3 in (b) Ni 2p, (c) Co 2p, and (d) O 1s regions before and

after the HER and OER tests.



Figure S12. Nyquist plots of the electrodeposited catalysts at 1.5 V vs. RHE.



Figure S13. CV curves of (a) S-1, (b) S-2, (c) S-3, (d) S-4, and (e) S-5 at different rates, in the region

of 1.1 \sim 1.2 V vs. RHE. (f) C_{dl} values of the electrodeposited catalysts.



Figure S14. TEM (left) and HRTEM (right) images of S-3 after the OER test.



Figure S15. Photograph of the PE wastewater with addition of KOH.



Figure S16. Chronoamperometry curve of the S-3||S-3 under 1.6 V vs. RHE in deionized water with 1

M KOH.



Figure S17. Experimental setup for the measurement of produced H_2 from PE wastewater splitting.

Figure S18. Gas chromatogram for H_2 product purity determination.

Ions	Li ⁺	K^+	Na ⁺	Co ²⁺	Ni ²⁺	Mn^{2+}	Cu^{2+}
Concentration (mg L ⁻¹)	1.07	0.23	146.4	134.71	328.43	180.21	0.02
Ions	Al ³⁺	PO ₄ ³⁻	SO4 ²⁻	Cl-	NO ₃ -	TOC*	
Concentration (mg L ⁻¹)	1.63	2.05	0.36	1632.84	-	0.55	

Table S1. The ion concentrations of industrial wastewater.

*TOC: Total organic carbon.

Ions	Li ⁺	K^+	Na ⁺	Co ²⁺	Ni ²⁺	Mn^{2+}	Cu^{2+}
Concentration (mg L ⁻¹)	0.03	0.04	720.5	1.08	2.03	1.54	-
Ions	Al ³⁺	PO ₄ ³⁻	SO4 ²⁻	Cl-	NO ₃ -	TOC*	
Concentration (mg L ⁻¹)	-	0.01	0.04	1156.35	-	0.51	

 Table S2. The ion concentrations of PE wastewater.

Catalyst	Electrolyte	$\eta_{10}(mV)$	Reference
S-3	1.0 M KOH	96	This study
S-1	1.0 M KOH	217	This study
S-2	1.0 M KOH	184	This study
S-4	1.0 M KOH	140	This study
S-5	1.0 M KOH	165	This study
$SrCo_{0.85}Fe_{0.1}P_{0.05}O_{3\text{-}\delta}\text{ nanofilm}$	1.0 M KOH	110	Adv. Mater., 30 (2018) 1804333.
Mn ₃ (PO ₄) ₂	1.0 M KOH	104	Appl. Catal. B., 292 (2021) 120202.
Reduced NiCo ₂ O ₄	1.0 M KOH	135	J. Am. Chem. Soc., 140 (2018) 13644–13653.
Fe-doped CoWO ₄	1.0 M KOH	118	J. Mater. Chem. A, 9 (2021) 9753-9760
o-CoSe ₂ P	1.0 M KOH	104	Nat. Commun., 9 (2018) 2533.
Fe-doped MOF CuCoSe@HCNF	1.0 M KOH	181	Appl. Catal. B., 293 (2021) 120209.
N-doped Ni ₃ S ₂ /NF	1.0 M KOH	155	Adv. Energy Mater., 8 (2018) 1703538.

Table S3. A summary of the HER properties of S-3 and a group of recently documented catalysts.

Mn-CoP nanowire@Mn-CoOOH nanosheet	1.0 M KOH	110	Appl. Catal. B., 292 (2021) 120172.
Ni NP Ni–N–C/EG	1.0 M KOH	147	Energy Environ. Sci., 12 (2019) 149-156.
N-NiMoO ₄ /NiS ₂	1.0 M KOH	99	Adv. Funct. Mater., 29 (2019) 1805298.
1T-Fe/P-WS ₂ @CC	1.0 M KOH	116	Appl. Catal. B., 286 (2021) 119897.
Cu NDs/Ni ₃ S ₂ NTs-CFs	1.0 M KOH	128	J. Am. Chem. Soc., 140 (2018) 610–617.
c-CoSe ₂	1.0 M KOH	190	Adv. Mater., 28 (2016) 7527–7532.
Ni ₃ S ₂ /VG@NiCo LDHs	1.0 M KOH	120	Chem. Eng. J. 415 (2021) 129048.
Mo ₂ N–Mo ₂ C/HGr-3	1.0 M KOH	154	Adv. Mater., 30 (2018) 1704156.
MoS ₂ /Co ₉ S ₈ /Ni ₃ S ₂ /Ni	1.0 M KOH	113	J. Am. Chem. Soc. 141 (2019) 10417-10430.

Table S4. Calculated charge transfer resistance (R_{ct}) and solution resistance (R_s) (in Ohm, Ω) of the materials deposited on NF obtained from the Nyquist plot during the EIS experiments at -0.1 V vs.

Catalyst	R _s	R _{ct}
S-1	2.24	98.76
S-2	2.43	89.01
S-3	2.42	67.48
S-4	2.41	69.01
S-5	2.72	76.77

RHE.

Catalyst	R _s	R _{ct}
S-1	3.64	210.23
S-2	2.89	184.74
S-3	2.61	71.32
S-4	2.60	98.75
S-5	2.94	157.11

Table S5. Calculated charge transfer resistance (R_{ct}) and solution resistance (R_s) (in Ohm, Ω) of the materials deposited on NF obtained from the Nyquist plot during the EIS experiments at 1.5 V vs. RHE.

Catalyst	Potential/V (1 M KOH)	Reference
<u>8-3</u>	1.58	This study
N-NiMoO ₄ /NiS ₂	1.60	Adv. Funct. Mater., 1 (2019) 1805298.
NiFe-LDH/Ni(OH) ₂	1.60	Chem. Eng. J. 419 (2021) 129608.
NiCo ₂ O ₄ /Cu _x O/Cu	1.61	J. Mater. Chem. A, 9 (2021) 14466-14476.
Ni _{0.75} Fe _{0.125} V _{0.125} -LDHs/NF	1.591	Small 14 (2018) 1703257.
CoS _x @Cu ₂ MoS ₄ -MoS ₂ /NSG	1.60	Adv. Energy Mater., 10 (2020) 1903289.
Fe-CoP/Ti	1.60	Adv. Mater., 29 (2017) 1602441.
5%-BCNONF mats	1.79	Nano Energy, 88 (2021) 106246.
Ni@NC	1.60	Adv. Mater., 29 (2017) 1605957.
Co/Ni-CW	1.64	Adv. Funct. Mater., (2021) 2010951.
graphene/Ni ₃ Se ₂ /Co ₉ S ₈	1.62	Nano Lett., 17 (2017) 4202-4209.
CoFeZr oxides	1.63	Adv. Mater., 31 (2019) 1901439.
NiMoO ₄ (V _o)	1.59	J. Mater. Chem. A, 9 (2021) 11691-11704.
NiSe	1.63	Angew. Chem. Int. Ed., 54 (2015) 9351-9355.
Cu _{0.3} Co _{2.7} P/NC	1.64	Adv. Energy Mater., 7 (2017) 1601555.
CoP/NCNHP	1.64	J. Am. Chem. Soc., 140 (2018) 2610-2618.
$(Co_{1-x}Ni_x)(S_{1-y}P_y)_2/G$	1.65	Adv. Energy Mater., 11 (2018) 1802319.
SA-Ir@GS	1.65	Adv. Funct. Mater., 31 (2021) 2010916.

Table S6. A summary of the overall water splitting performance of S-3 and the recently documented

 bifunctional catalysts.

NiFe/NiCo ₂ O ₄ /NF	1.67	Adv. Funct. Mater., 26 (2016) 3515-3523.
Co/CoP-HNC	1.68	Mater. Horiz., 5 (2018) 108-115.
S:CoP NPs	1.72	Nano Energy, 53 (2018) 286-295.
Fe-Ni ₂ P	1.62	Nano Energy, 84 (2021) 105861.
Co/CoP-5	1.74	Adv. Energy Mater., 7 (2017) 1602355.
CoP/PCPTF films	1.92	Adv. Mater., 27 (2015) 3175-3180.
Ni-Mo ₂ C/NC@NF	1.59	Appl. Catal. B., 292 (2021) 120168.

Catalysts/Materials	Suppliers	Prices (US\$)	Price per 1 m ² catalyst on CP (US\$)
20% Pt/C	Macklin	77.93 g ⁻¹	1407
RuO ₂	Aladdin	156.17 g ⁻¹	799
Carbon paper (CP)	Taobao	8.61 (21*10 cm ²)	-
Wastewater	A factory in China	0	-
S-3	Home made	0.005 (1*1 cm ²)	229

Table S7. A comparison of the prices of employed materials in this work.

References

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