

Supporting Information:

**Self-supported Bimetallic Ni-Co Compounds Electrodes for
Urea and Neutralization Energy Assisted Electrolysis
Hydrogen Production**

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1. The electrochemical neutralization energy-the Effects of pH gradient (ΔpH) between anode and cathode

As showed in the pourbaix diagram of water (Figure S10), the theoretical applied voltage for water splitting is always 1.23 V as long as the same electrolyte in both anode and cathode chamber. However, bipolar membrane allows the sustainable use of distinct electrolyte compositions with different pH in two separate chambers, and the applied voltage can be tuned by differing pH between the anode chamber and cathode chamber. When HER in 0.5 M H_2SO_4 (pH = 0) as the cathode and OER in 1.0 M KOH (pH = 14) as the anode are assembled in the two chambers forming a pH-gradient concentration cell for water electrolysis, the reactions and its corresponding Nernst equations can be expressed as following:

For water electrolysis in the base-acid electrolyzer:

HER at the cathode:



$$E_{\text{HER}} = E_{\text{H}^+/\text{H}_2}^\theta - 2.303 \frac{RT}{2F} \log \left[\frac{\alpha_{\text{H}_2}}{(\alpha_{\text{H}^+})^2} \right] = 0 \text{ V} - 0.059 * \text{pH}_{\text{cathode}} = 0$$

$$(E_{\text{H}^+/\text{H}_2}^\theta = 0 \text{ V vs. RHE}) \quad (\text{Eq.1})$$

OER at the anode:



$$E_{\text{OER}} = E_{\text{O}_2/\text{OH}^-}^\theta - 2.303 \frac{RT}{4F} \log \left[\frac{(\alpha_{\text{OH}^-})^4}{(\alpha_{\text{H}_2\text{O}})^2(\alpha_{\text{O}_2})} \right] = 1.23 \text{ V} - 0.059 * \text{pH}_{\text{anode}} = 0.404$$

$$(E_{\text{O}_2/\text{OH}^-}^\theta = 1.23 \text{ V vs. RHE}) \quad (\text{Eq.2})$$

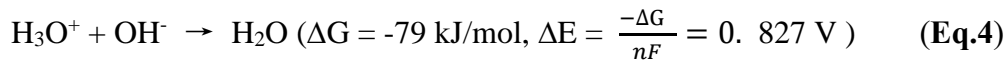
The overall reaction for water splitting:



$$\begin{aligned}
V_{\text{theoretical required}} &= E_{O_2/OH^-}^\theta - E_{H^+/H_2}^\theta - 2.303 \frac{RT}{4F} \log \left[\frac{(\alpha_{H_2O})^2 (\alpha_{O_2}) (\alpha_{H_2})^2}{(\alpha_{H^+})^4 (\alpha_{OH^-})^4} \right] \\
&= 1.23 - 0.059 * (pH_{\text{anode}} - pH_{\text{cathode}}) = \mathbf{0.404}
\end{aligned}$$

(Eq.3)

In these equations, F is the Faraday constant, 96 485 C mol⁻¹, T is the room temperature (commonly 298.15 K), R is the gas constant (8.314 J mol⁻¹ K⁻¹), $pH_{\text{anode}} - pH_{\text{cathode}}$ is the pH difference (ΔpH) of the two chambers, and the $2.303 \frac{RT}{F} * \Delta pH$ is equal to the electrochemical neutralization energy deriving from the reaction of hydroxide ion and proton combining to water, which provides an additional energy or voltage for water splitting as presented in **Equation 4**,



Therefore, assisted by the electrochemical neutralization energy, the theoretical applied voltage is only 0.404 V for electrochemical water electrolysis in an alkaline-acid electrolyzer with $\Delta pH = 14$, which greatly lowered the energy input for hydrogen production. Therefore, when the anode OER was replaced by urea oxidation reaction (UOR), the applied voltage can be further decreased, and the reactions and its corresponding Nernst equations can be expressed as following:

For water electrolysis in the base-acid electrolyzer with UOR replacing OER:

HER at the cathode:

The same as R1

UOR at the anode:



$$E_{UOR} = E_{UOR}^\theta - 2.303 \frac{RT}{6F} \log \left[\frac{(\alpha_{CO(NH_2)_2}) (\alpha_{OH^-})^6}{(\alpha_{N_2}) (\alpha_{H_2O})^5 (\alpha_{CO_2})} \right] = 0.37 \text{ V} - 0.059 * pH = -0.456$$

$$(E_{UOR}^{\theta} = 0.37 \text{ V vs. RHE}) \quad (\text{Eq.5})$$

The overall reaction:



V Theory required or open circuit

$$\begin{aligned} &= E_{UOR}^{\theta} - E_{\frac{\text{H}^+}{\text{H}_2}}^{\theta} \\ &- 2.303 \frac{RT}{6F} \log \left[\frac{(\alpha_{\text{H}_2\text{O}})^5 (\alpha_{\text{N}_2}) (\alpha_{\text{H}_2})^3 (\alpha_{\text{CO}_2})}{(\alpha_{\text{CO(NH}_2)_2}) (\alpha_{\text{H}^+})^6 (\alpha_{\text{OH}^-})^6} \right] \\ &= 0.37 - 0.059 * (\text{pH}_{\text{anode}} - \text{pH}_{\text{cathode}}) = \mathbf{-0.456} \quad (\text{Eq.6}) \end{aligned}$$

According to the **Equation 6**, once the UOR replace the OER, the theoretical applied voltage is -0.456 V, suggesting that the as-proposed alkaline-acid electrolyzer can theoretically supply power with simultaneous hydrogen production. However, the electrolyzer still need applied voltage to drive the electrolysis H₂ production, owing to the overpotentials from the two half reactions, HER and UOR. Even so, coupling UOR with pH-gradient concentration cell, energy input for hydrogen production could largely be reduced compared with traditional water splitting.

2. Calculation of turnover Frequency (TOF)

The TOF was calculated by assuming every metal atom taking part in the UOR:

$$\text{TOF} = \frac{jS}{6nF}$$

Where j (mA cm⁻²) is the measured current density at $\eta_{\text{UOR}} = 1.1$ V, S (1 cm²) is the geometric surface area of the carbon cloth, 6 means the number of electrons transferred per mole of urea, F is the faradaic constant (96485 C mol⁻¹), and n is the moles of the metal atom involved in the electrode which is calculated from the weight of the catalysts supported on the carbon cloth.

3. Production quantification analysis

The produced H₂ in the cathode was collected by drainage method and H₂ was analyzed by the gas chromatograph equipped with a thermal conductivity detector (TCD). The Faradaic Efficiency calculation formula is expressed as below (Eq.7), α denotes the numbers of transferred electrons (*e.g.* $\alpha = 2$ for H₂), n denotes the number of moles of the obtained products, F is the faradaic constant, 96 485 C mol⁻¹, and Q denotes the whole passed charge. H₂ and N₂ was collected by the chronopotentiometry experiment conducted at 20 mA cm⁻² in the homemade cell with gas collection setup (Figure S9) separated by a bipolar membrane with Ni_{0.67}Co_{0.33}(OH)₂/CC as the anode for UOR in 1.0 M KOH and Ni_{0.67}Co_{0.33}S₂/CC as the cathode for HER in 0.5 M H₂SO₄. The time were recorded every produced 0.5 mL H₂ in the cathode at room temperature (25 °C) and the specific data was presented in Table S4.

$$EF = \frac{\alpha n F}{Q} \quad (\text{Eq.7})$$

In these work, the whole passed charge Q could be obtained from the applied current and the maintained time, namely, $Q = I * t$, while n could be obtained by the volume of obtained H₂ (V), *i.e.*, $n = V/24.5$, (24.5 L mol⁻¹ is the gas constant at 25 °C), and the volume can be qualitatively determined by the GC analysis. The actual equation can be expressed as following:

$$EF = \frac{\alpha V F}{I t * 24.5} \quad (\text{Eq. 8})$$

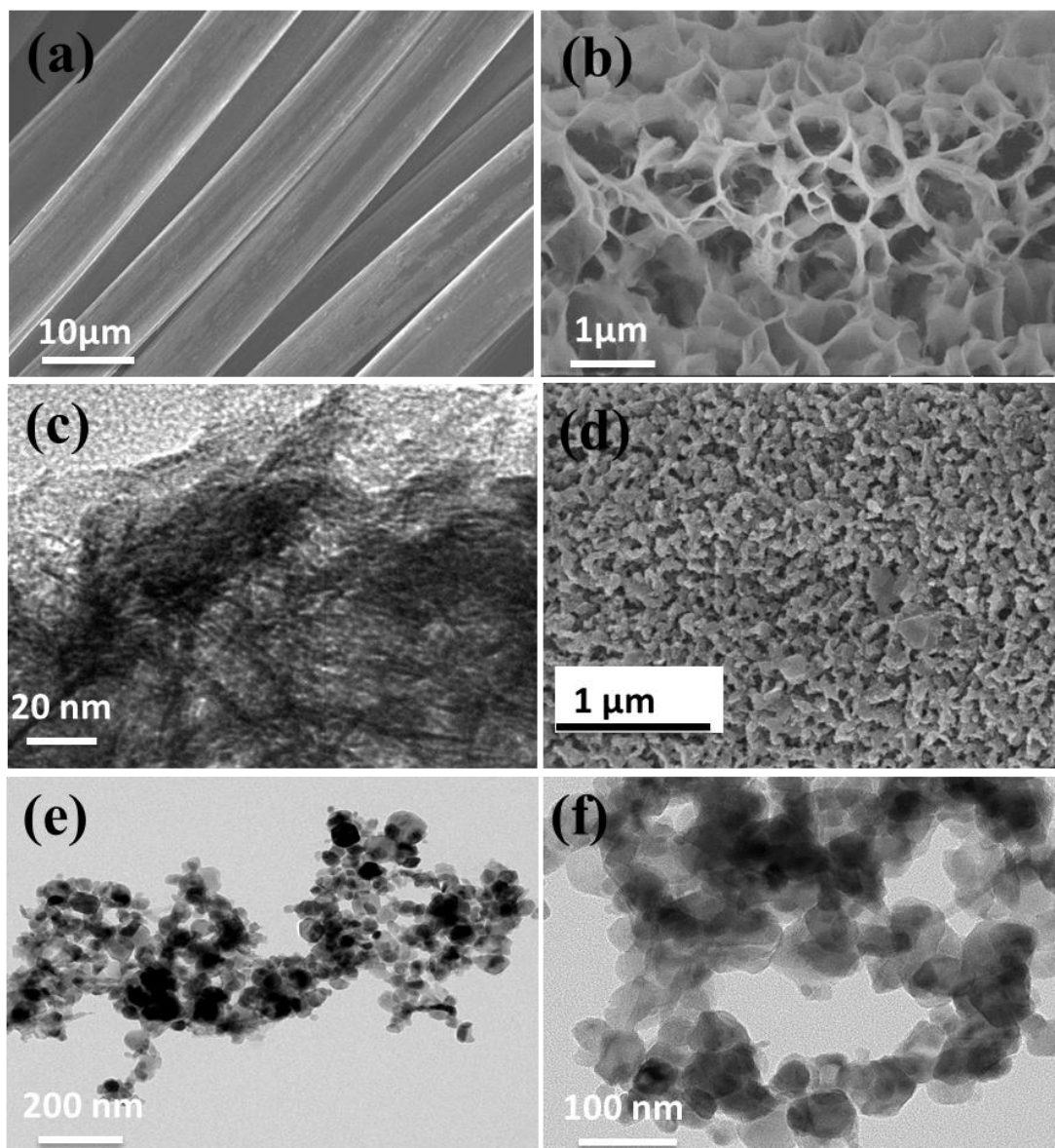


Figure S1. SEM images of carbon cloth (a), Ni_{0.67}Co_{0.33}(OH)₂/CC (b), Ni_{0.67}Co_{0.33}S₂/CC (d), and TEM images for Ni_{0.67}Co_{0.33}(OH)₂/CC (c) and Ni_{0.67}Co_{0.33}S₂/CC (e-f).

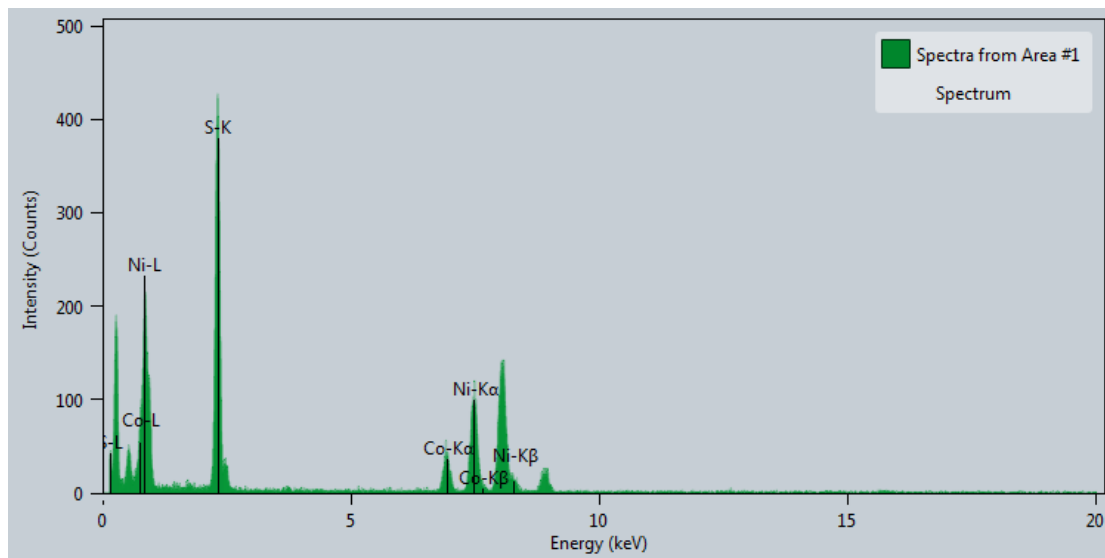


Figure S2. the EDX elemental distribution spectrum of $\text{Ni}_{0.67}\text{Co}_{0.33}\text{S}_2$

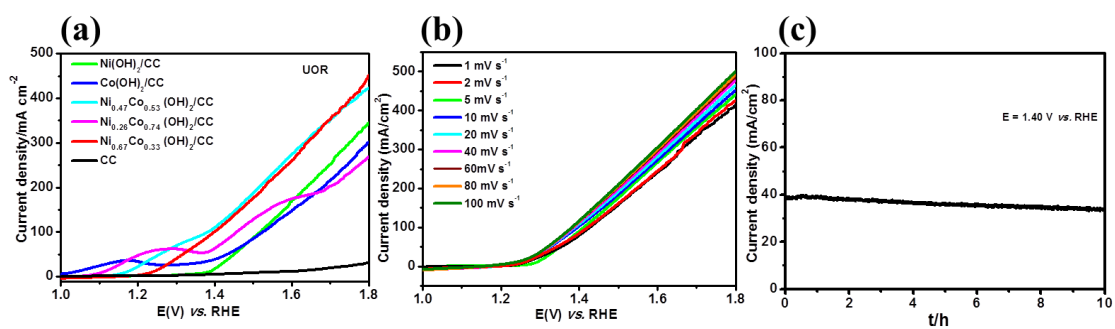


Figure S3. (a) UOR polarization curves of Ni(OH)₂/CC, Co(OH)₂/CC, Ni_{0.47}Co_{0.53}(OH)₂/CC, Ni_{0.26}Co_{0.74}(OH)₂/CC, Ni_{0.67}Co_{0.33}(OH)₂/CC, and CC; (b) LSV curves of Ni_{0.67}Co_{0.33}(OH)₂/CC electrode in 1 M KOH with 0.5 M urea at different scan rate; (c) it curves of Ni_{0.67}Co_{0.33}(OH)₂/CC electrode in 1 M KOH with 0.5 M urea concentration at 1.40 V vs. RHE;

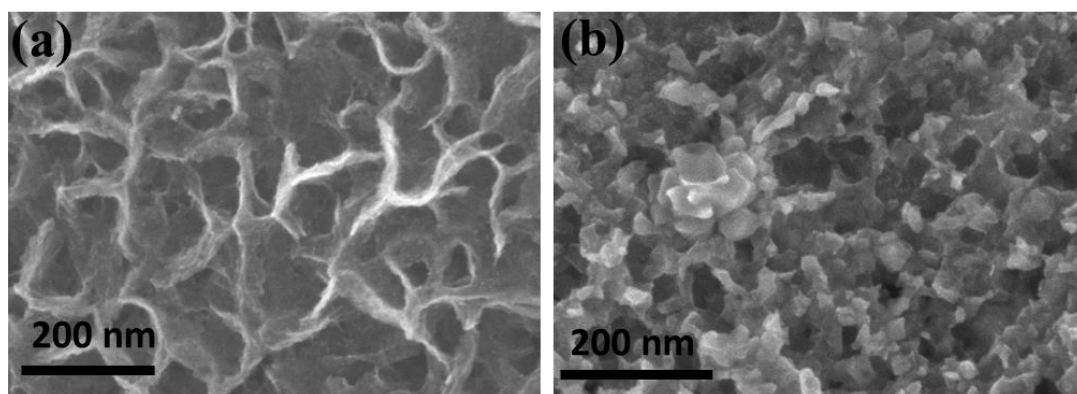


Figure S4. SEM image of $\text{Ni}_{0.67}\text{Co}_{0.33}(\text{OH})_2$ after 10-hours durability measurement at 1.40 V in 1.0 M KOH containing 0.5 M urea (a) and nearly 15 h continuous operation in 0.5 M H_2SO_4 at a current density of 10 mA cm^{-2} .

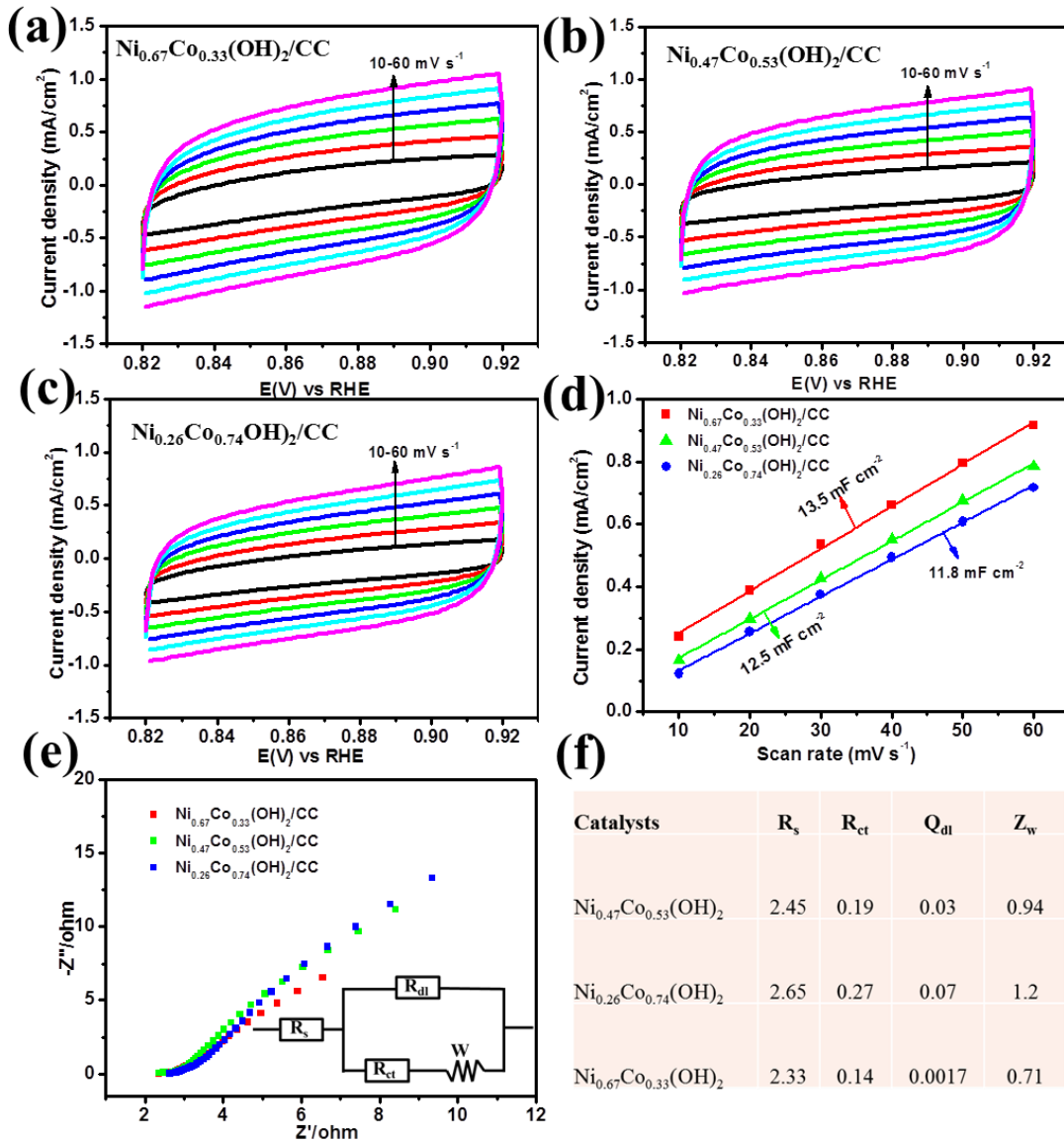


Figure S5. Electrochemical cyclic voltammetry curves of $Ni_{0.67}Co_{0.33}(OH)_2/CC$ (a), $Ni_{0.47}Co_{0.53}(OH)_2/CC$ (b), and $Ni_{0.26}Co_{0.74}(OH)_2/CC$ (c) with scan rates ranging from 10 mV s^{-1} to 60 with a step of 10 mV s^{-1} , the potential is scanned from 0.82 to 0.92 V vs. RHE where no faradic current was detected (d) The extracted double-layer capacitances (C_{dl}) of different Ni/Co ratio electrodes using a cyclic voltammetry method (e) EIS Nyquist plots recorded on different Ni/Co ratio electrodes at 1.36 V vs. RHE . Inset shows the proposed equivalent circuit. (f) the corresponding fitted parameters. R_s and R_{ct} : Ω , Q_{dl} : $\Omega^{-1}\cdot S^n$. Z_w : $\Omega^{-1}\cdot S^{1/2}$.

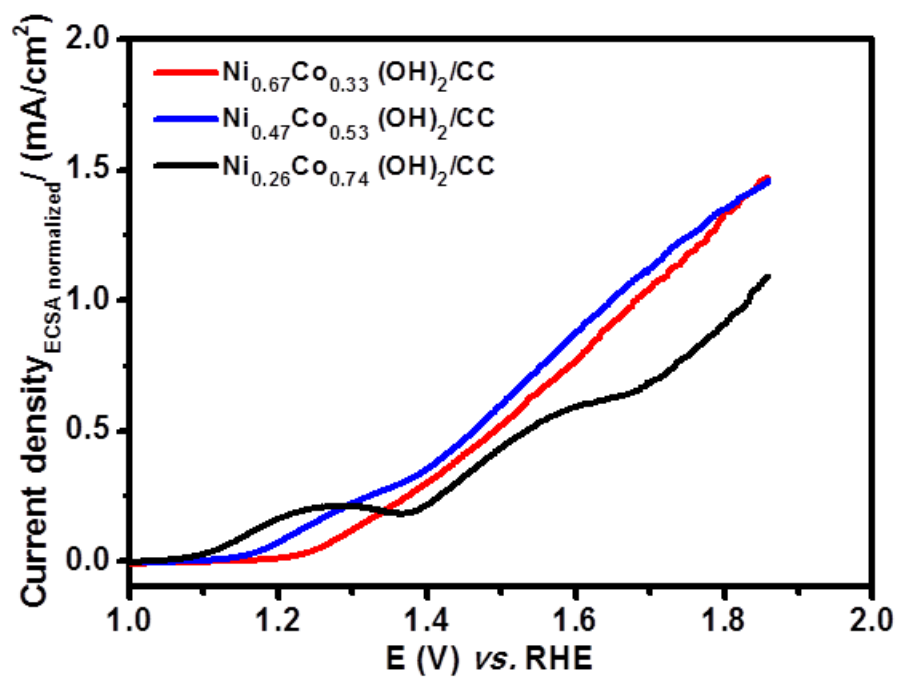


Figure S6. The normalized polarization curves of Ni_{1-x}Co_x(OH)₂/CC by ECSA .

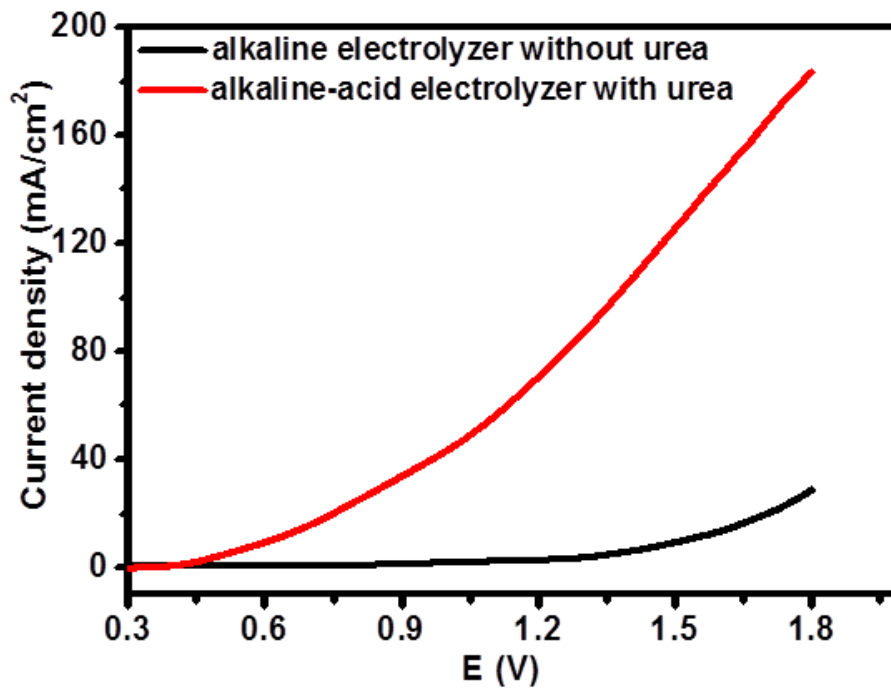


Figure S7. LSV curves for the alkaline (1.0 M KOH)-acid (0.5 M H₂SO₄) electrolyzer with urea oxidation in anode and traditional water electrolysis in 1.0 M KOH

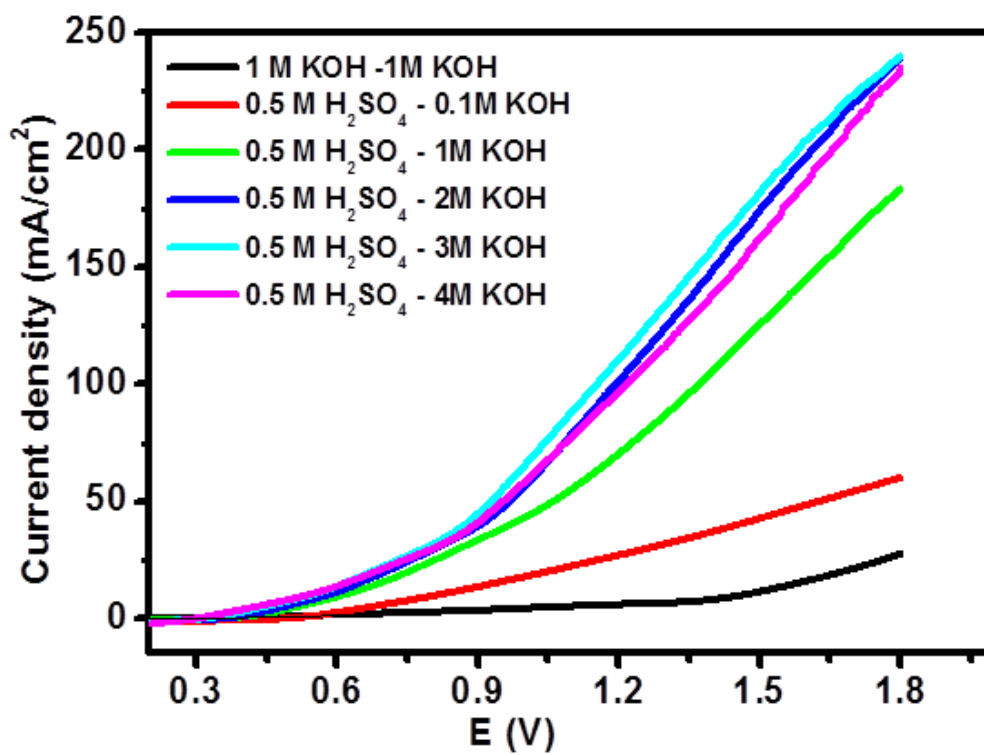


Figure S8. LSV curves for the electrolyzer (HER&UOR) under different pH difference of the anode and cathode chambers

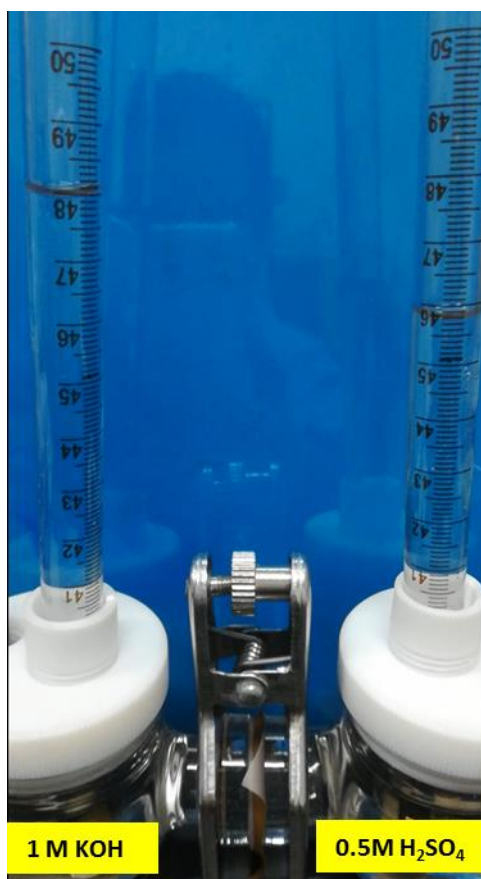


Figure S9. Home-made electrolyzer (HER&UOR) for evaluating Faradaic Efficiency of H₂

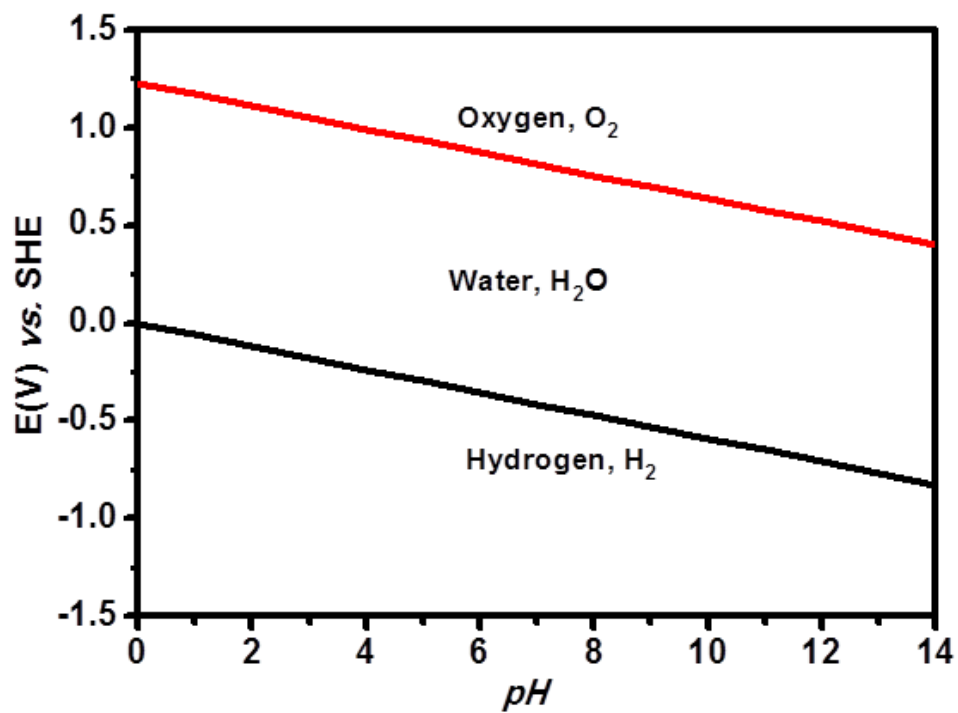


Figure S10. A pourbaix diagram of water with curves obtained by the Nernst equation (Equations 1 and 2)

Table S1. List of catalysts' performance for urea oxidation in recent reports

Catalysts	Urea concentration	Electrolytes	Applied voltage at 10 mA cm ⁻² /(V)	Refs
Ni-MOF	0.33 M	1.0 M KOH	1.36	1
Ni ₂ P/CC	0.5 M	1.0 M KOH	1.38	2
Ni ₃ N/CC	0.5 M	1.0 M KOH	1.35	3
Carbon/Ni-Fe/NF	0.33 M	1.0 M KOH	1.39	4
Metallic Ni(OH) ₂	0.33 M	1.0 M KOH	1.39	5
MnO ₂ /MnCo ₂ O ₄	0.5 M	1.0 M KOH	1.33	6
S-MnO ₂	0.5 M	1.0 M KOH	1.33	7
NF/NiMoO-Ar	0.5 M	1.0 M KOH	1.37	8
Ni _{0.67} Co _{0.33} (OH) ₂ /CC	0.5 M	1.0 M KOH	1.23	This work

Table S2. Elemental compositions of the products obtained by ICP^a

Ni/Co feed ratio	Ni/Co ratio in	Composition of Ni _{1-x} Co _x (OH) ₂
1/1	0.887	Ni _{0.47} Co _{0.53} (OH) ₂
1/2	0.351	Ni _{0.26} Co _{0.74} (OH) ₂
2/1	2.030	Ni _{0.67} Co _{0.33} (OH) ₂
2/1	2.08 (after sulfidizing)	Ni _{0.67} Co _{0.33} S ₂

^a The error in the ICP measurement was 5%

Table S3. Comparison of the reported double-cell with biomass oxidation and single-cell with urea oxidation in recent two years

Catalysts	Anodic oxidation	Electrolytes	Applied voltage at 10 mA cm ⁻² /(V)	Refs
Ni ₃ S ₂ /NF ^d	10 mM HMF	1.0 M KOH	1.46	9
Ni ₂ P NPA/NF ^d	10 mM HMF	1.0 M KOH	1.44	10
Co-P/CF ^d	10 mM HMF	1.0 M KOH	1.39 ^m	11
hp-Ni ^d	Benzyl alcohol	1.0 M KOH	1.50	12
Ni ₂ P/Ni/NF ^d	30 mM furfural	1.0 M KOH	1.48	13
3D PdCu alloy NSs ^d	1.0 M Ethanol	1.0 M KOH	NG	14
Ultrathin Co ₃ O ₄ NSs ^d	1.0 M Ethanol	1.0 M KOH	NG	15
Zn _{0.08} Co _{0.92} P ^s	0.5 M urea	1.0 M KOH	1.38	16
Ni ₂ P NF/CC ^s	0.5 M urea	1.0 M KOH	1.0 ^m	2
MnO ₂ /MnCo ₂ O ₄ /Ni ^s	0.5 M urea	1.0 M KOH	1.58	6
Small-sized MnO ₂ ^s	0.5 M urea	1.0 M KOH	1.41	7
CoS ₂ NA/Ti ^s	0.3 M urea	1.0 M KOH	1.59	17
Ni-Mo-O nanorod	0.3 M urea	1.0 M KOH	1.38	8
Ni ₃ N nanosheet/CC	0.33 M urea	1.0 M KOH	1.44	3
CuCl/rGO	0.5 M urea	2.0 M KOH and 0.5 M H ₂ SO ₄	0.83 V	18
Ni _{0.67} Co _{0.33} (OH) ₂ /CC ^d	0.5 M urea	1.0 M KOH and 0.5 M H ₂ SO ₄	0.61	this work
	0.5 M urea	3.0 M KOH and 0.5 M H ₂ SO ₄	0.54	this work

HMF: 5-hydroxymethylfurfural,

CC: Carbon cloth

d: double-cell

s: single-cell

m: evaluated in its figures

NG: not given

Table S4. The recorded data for Faradaic Efficiency of H₂ at current density of 20 mA cm⁻²

t/s	V/mL	n/mol	Evolution rate of H ₂ (μmol h ⁻¹)	EF
415	0.5	4.08163E-5	354.06934	0.94896
618	1	6.12245E-5	356.64751	0.95586
830	1.5	8.16327E-5	354.06934	0.94896
1050	2	1.02041E-4	349.85423	0.93766
1218	2.5	1.22449E-4	361.91817	0.96999
1416	3	1.42857E-4	363.19613	0.97342
1608	3.5	1.63265E-4	365.51934	0.97964
1810	4	1.83673E-4	365.3174	0.9791
2000	4.5	2.04082E-4	367.34694	0.98454
2190	5	2.2449E-4	369.02432	0.98904
2376	5.5	2.44898E-4	371.05751	0.99449
2569	6	2.65306E-4	371.7797	0.99642
2782	6.5	2.85714E-4	369.72373	0.99091
2973	7	3.06122E-4	370.68309	0.99348
3156	7.5	3.26531E-4	372.46838	0.99827
3360	8	3.46939E-4	371.72012	0.99626
3657	8.5	3.67347E-4	361.62127	0.9692
3826	9	3.87755E-4	364.85059	0.97785

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