

Supporting Information

Hierarchical NiCo pearl strings as efficient electrocatalysts for urea electrooxidation

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Experimental Section

1. Materials

All reagents in this study were of analytical grade and were used without further purification and displayed in **Table S1**.

2. Synthesis of hierarchical Nickel-Cobalt alloy pear string (NCPS)

Hierarchical NiCo alloy pear strings were prepared using hydrazine ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$) as a reducing agent and cetyltrimethylammonium bromide (CTAB) as a surfactant. Take the Ni₄Co₁ as paradigm. 0.010g Co (AC)₂·4H₂O, 0.040g Ni (AC)₂·4H₂O were dissolved in 8.0 mL deionized water. Then, 8.0 mL $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ (80 wt.%) was introduced into the above solution drop by drop with violent stirring for 30 min, and then, 0.1g CTAB was added and kept for magnetic agitation another 3 h. The mixture was transferred into a Teflon-lined stainless-steel autoclave and kept at 160°C for 24 h. After the autoclave cooled down to room temperature, the resultant black precipitate was filtered, and then rinsed with distilled water and absolute ethanol alternatively for several times. The final product was dried in an oven at 50°C for 4 h. The Ni-Co catalysts with other Ni/Co molar ratios (1:0, 2:1, 3:2, 1:1 and 0:1) were also prepared as described above.

3. Characterizations

X-ray diffraction (XRD) was used to identify the phase composition and crystalline structure. Scan electron microscopy (SEM) and Transmission electron microscopy (TEM) were used to observe the surface morphology and particle size. High resolution TEM (HRTEM) and selected area electron diffraction (SAED) were conducted to confirm the crystalline microstructures. Energy dispersive spectrometer mapping was used to observe the elements dispersion and inductively coupled plasma-optical emission spectrometer (ICP-OES) was used to confirm the real Ni and Co content. The surface chemical compositions and electronic structures are checked by X-ray photoelectron spectra (XPS). The specific surface area, pore volume and size

distribution are examined by nitrogen adsorption-desorption isotherms with Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods.

4. Electrochemical measurement

The electrocatalytic performance toward urea oxidation (UOR) of hierarchical NiCo alloy pear strings were carried out by using a three-electrode system connected to CH Instruments electrochemical workstation (600E, CH Instruments, Shanghai, China). The working electrode was prepared by depositing 10.0 μL of the catalyst ink onto glassy carbon electrode (GCE) (diameter: 4.0 mm). The catalysts ink were fabricated by dispersing 5.0 mg catalyst powder and 5 mg superconducting carbon in 950.0 μL of ethanol and 50.0 μL Nafion solution (5 wt.% aqueous solution). The suspension was immersed in an ultrasonic bath for 2 h to prepare a homogeneous ink. Ag/AgCl (saturated KCl as the filling electrolyte solution) and platinum net were used as reference and counter electrodes, respectively. All of the electrochemical tests were conducted at room temperature. The electrocatalytic performances were examined by cyclic voltammetry (CV), linear sweep voltammetry (LSV), Tafel and Electrochemical Impedance Spectroscopy (EIS) methods. Before CV or LSV test, the electrode was first activated using CV method with a scan rate of 200 mV s^{-1} for 20 cycles in 1.0 M KOH aqueous solution in order to active the electrode. The scan rate for CV is 10 mV s^{-1} and for LSV is 5 mV s^{-1} . The potential range for CV and LSV was -0.2-0.6 V and the CA was tested at a constant potential of 0.45 V. CV measurement was used for ECSA test in 1.0 M KOH. Scan potential was from -0.195 V to -0.175 V vs. Ag/AgCl and scan rates were 10, 20, 30, 40, and 50 mV s^{-1} , respectively. Based on CV curves, $|j_a-j_c|$ value (j_a and j_c are anodic and cathodic current density at -0.185 V, respectively) divides corresponding scan rate to plot a straight line, which slope is the C_{dl} value. The direct urea-hydrogen peroxide fuel cell (DUHPFC) was carried out in a standard two-electrode setup. The fuel cell was composed of the NiCo alloy catalysts (anode), Pd/C (10 wt.%, cathode) and Nafion 115 cation exchange membrane as anode catalysts, cathode catalysts and solid polymer electrolyte (SPE) respectively. The fuel cell was operated with 4.0 M KOH + 0.33 M urea anolyte and 2.0 M H_2SO_4 + 2.0 M H_2O_2

catholyte at room temperature. Multi-Current Steps (ISTEP) was executed by applying a staircase current density from 0 up to 15 mA cm⁻².

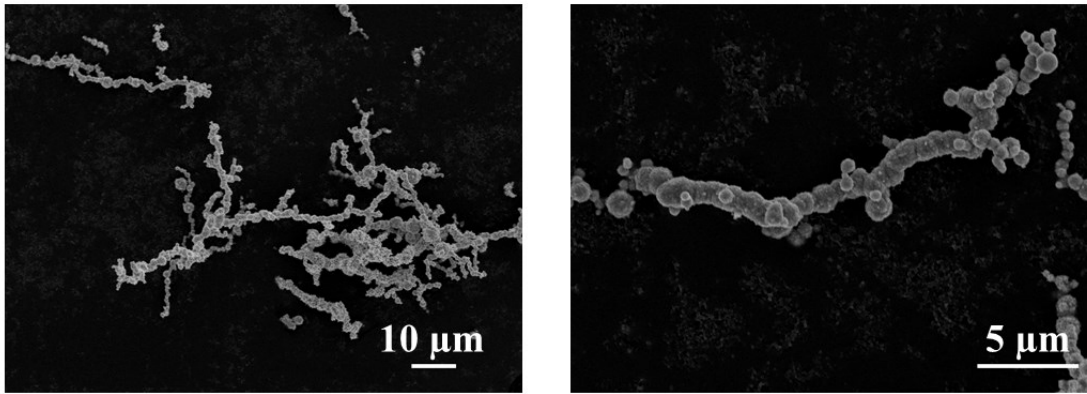


Fig. S1. SEM images of NCPS Ni.

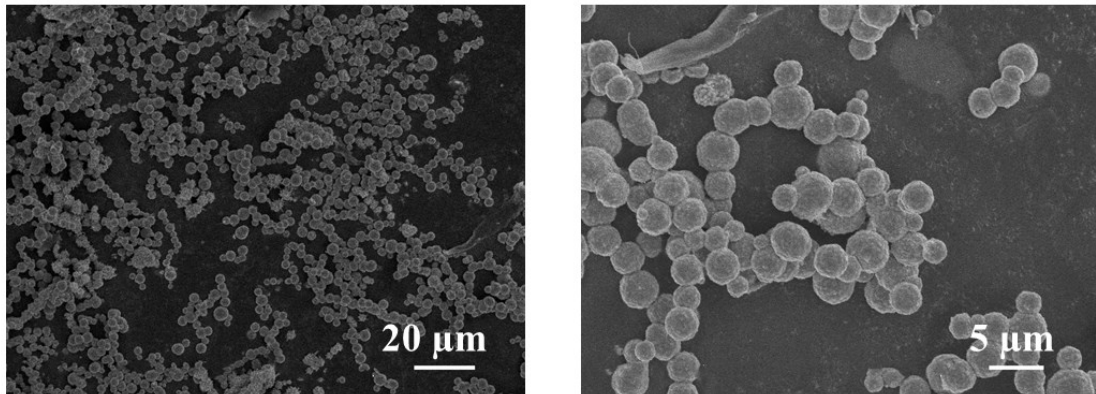


Fig. S2. SEM images of NCPS Ni₂Co₁.

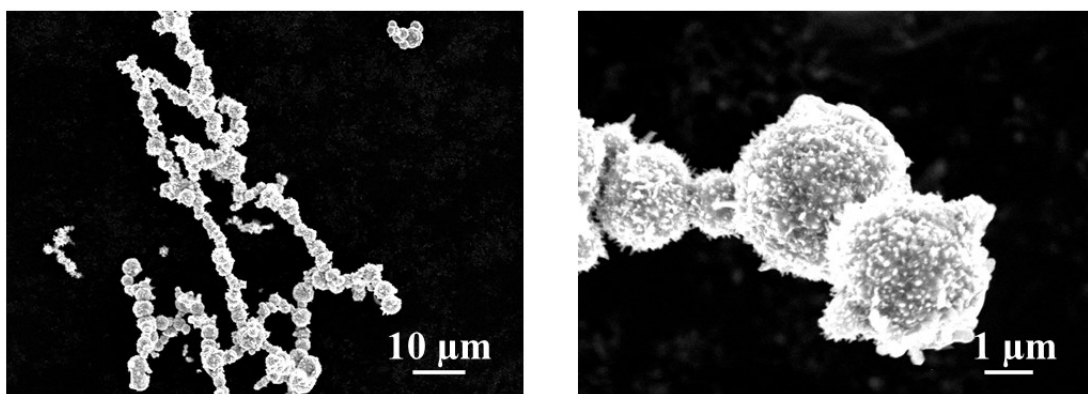


Fig. S3. SEM images of NCPS Ni₃Co₂.

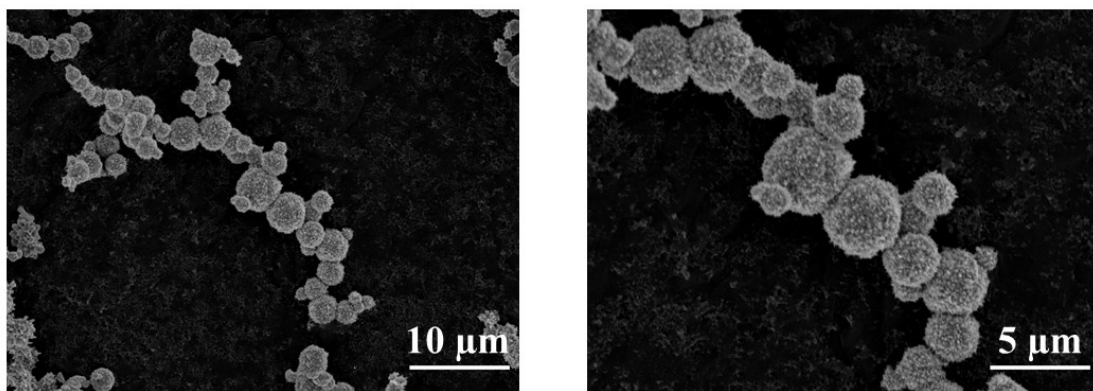


Fig. S4. SEM images of NCPS Ni1Co1.

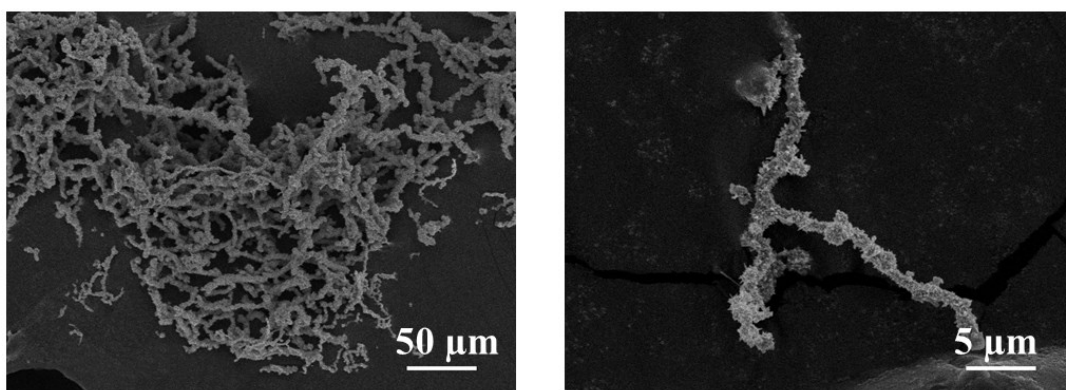


Fig. S5. SEM images of Co pear strings.

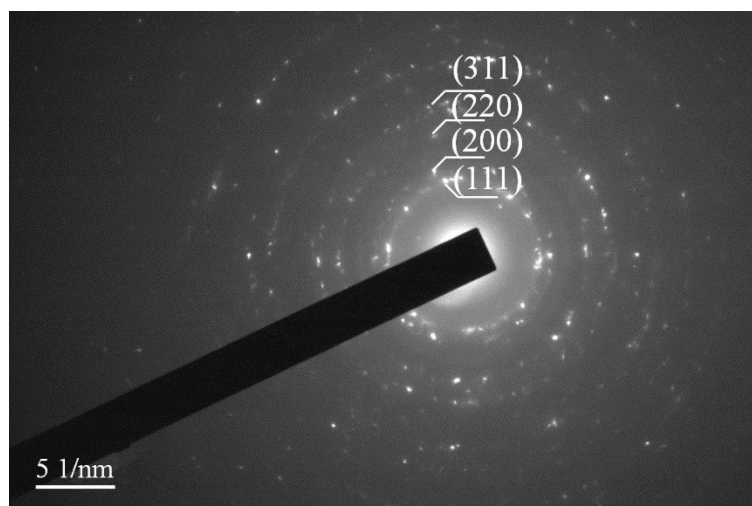


Fig. S6. SAED image of NCPS Ni₄Co₁ electrocatalysts.

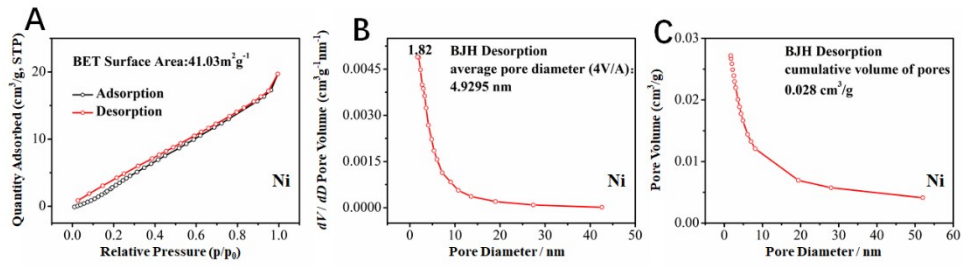


Fig. S7. N_2 adsorption-desorption behaviors that used to examine the surface area and pore feature of Ni.

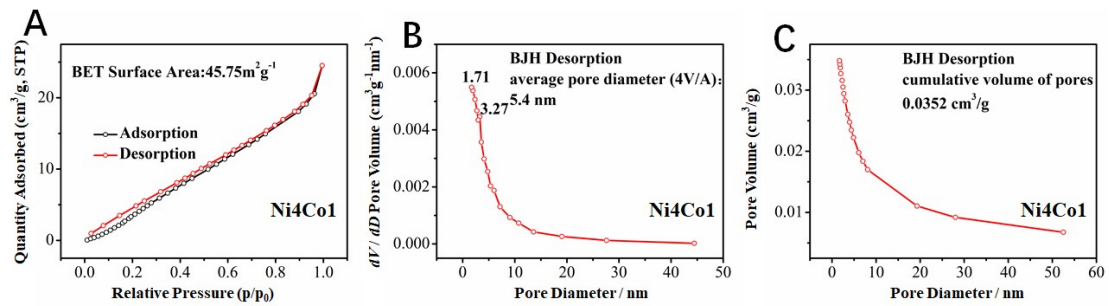


Fig. S8. N_2 adsorption-desorption behaviors that used to examine the surface area and pore feature of NCPS Ni4Co1.

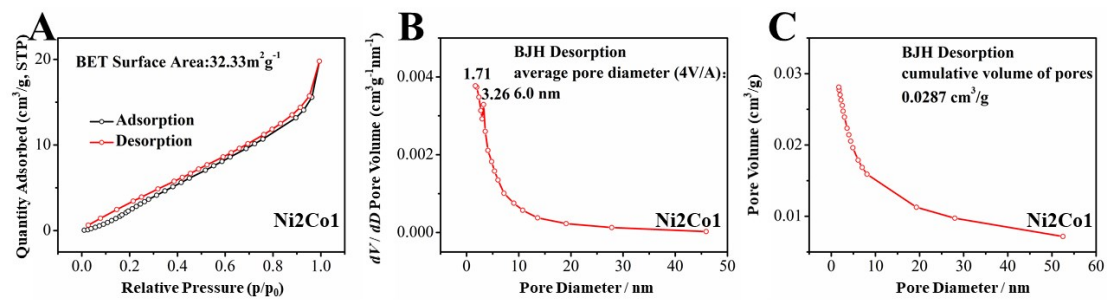


Fig. S9. N₂ adsorption-desorption behaviors that used to examine the surface area and pore feature of NCPS Ni₂Co₁.

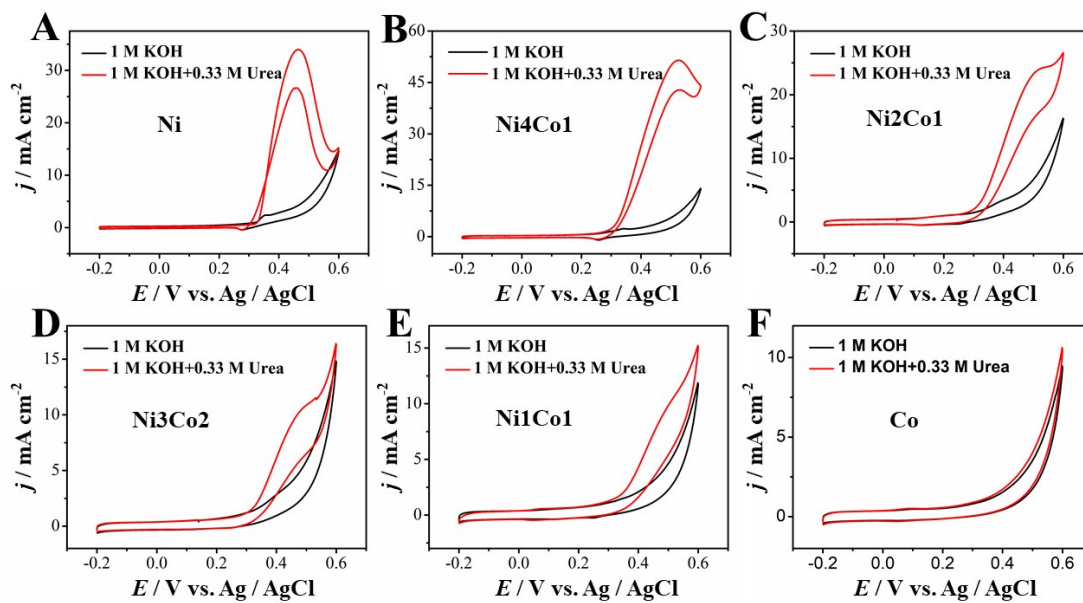


Fig. S10. CV curves of Ni, NiCo alloy and Co electrocatalysts measured in 1.0 M KOH and 1.0 M KOH with 0.33 M urea. Scan rate: 10 mV s⁻¹.

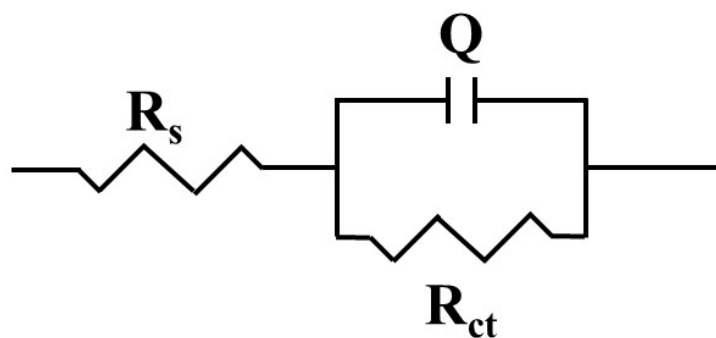


Fig. S11. The equivalent circuit of Electrochemical impedance spectroscopy of NiCo alloy.

The R_s means the intrinsic resistances of electrolytes and materials and contact resistances. The R_{ct} associates with the kinetic resistance of electron transfer at the interfaces of electrode/electrolytes. The CPE (Q) replaces the double-layer capacitance (C_{dl}) because of the deviation from an ideal capacitor.

Ref.

1. L. Sha, K. Ye, G. Wang, J. Shao, K. Zhu, K. Cheng, J. Yan, G. Wang and D. Cao, *Chem. Eng. J.*, 2019, **359**, 1652-1658.
2. Z. J. Ji, J. Liu, Y. Deng, S. T. Zhang, Z. Zhang, P. Y. Du, Y. L. Zhao, *J. Mater. Chem. A*, 2020, **8**, 14680-14689.

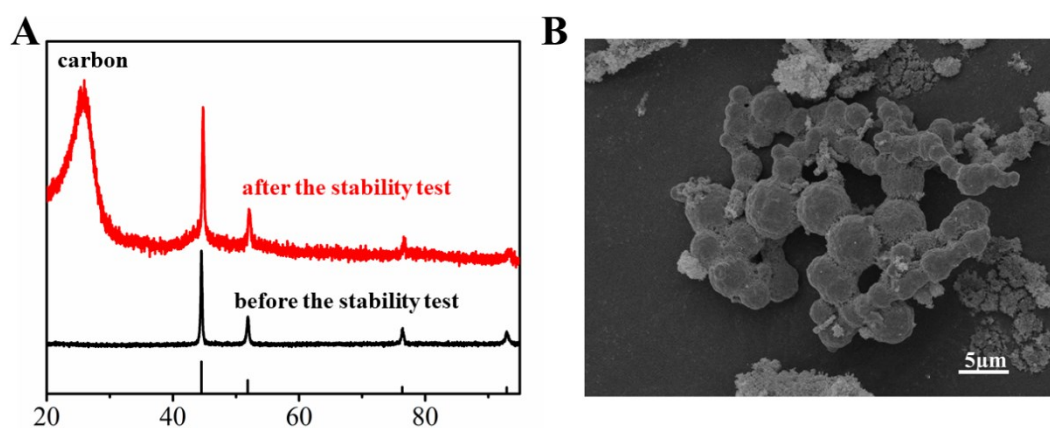


Fig. S12 XRD pattern (A) and SEM image (B) of Ni₄Co₁ catalyst after the stability test.

After the stability test, the structure of Ni₄Co₁ catalysts was explored. Fig. 11a shows the XRD pattern of Ni₄Co₁ before and after *i-t* test. All of the diffraction peaks matched well with each other, no new phase was detected, indicating its strong stability. Besides, the morphology of Ni₄Co₁ also kept the same as the original one.

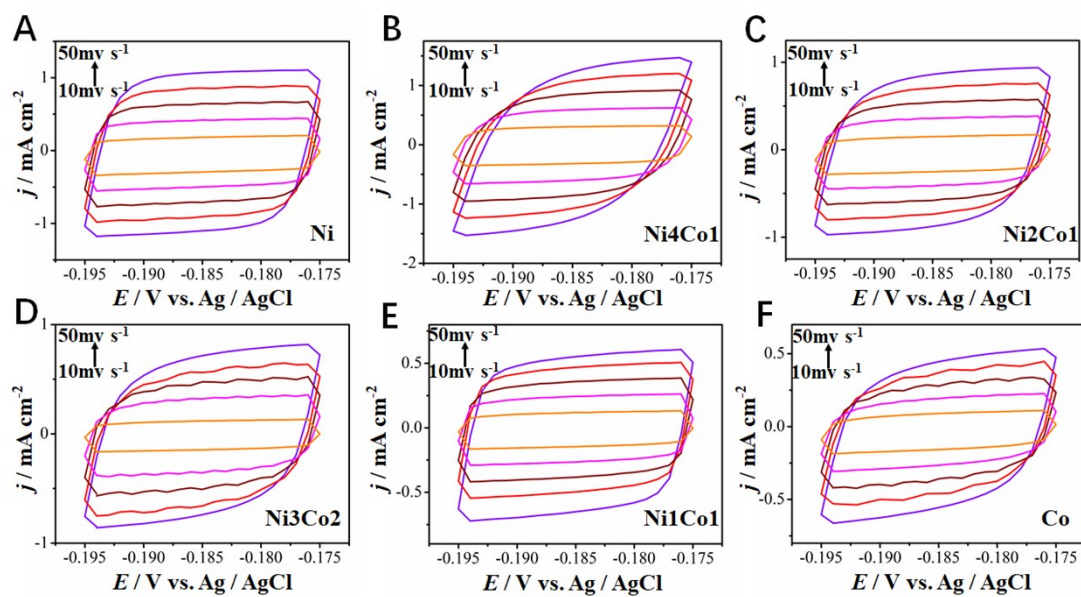


Fig. S13. Cyclic voltammograms of Ni, NiCo alloys and Co electrodes in narrow potential range of -0.195V to -0.175 V in 1.0 mol L⁻¹ KOH at different scan rates.

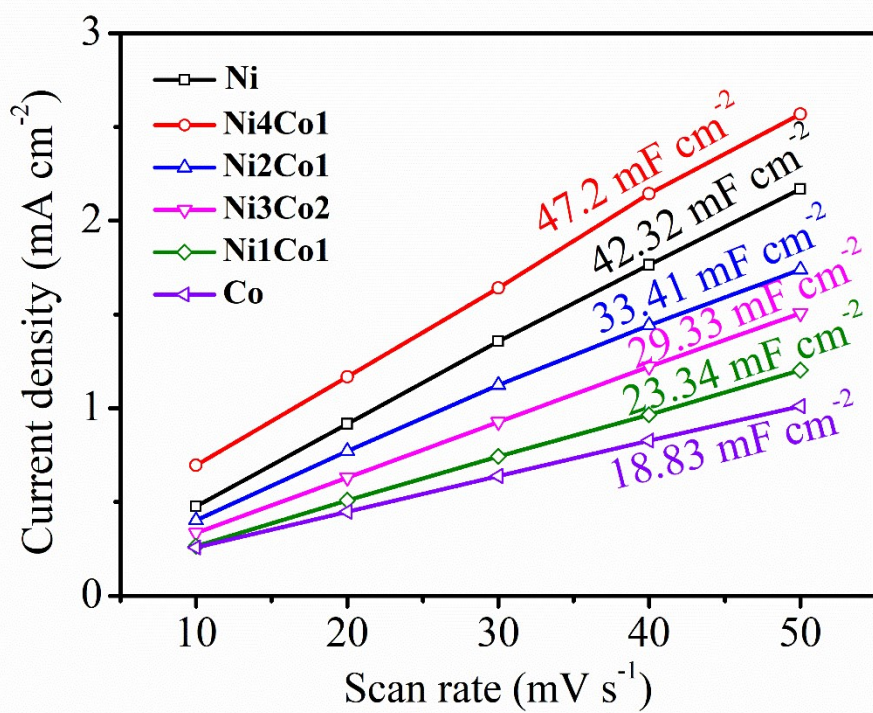


Fig. S14. Corresponding capacity current density as a function of scan rate in the range of -0.195 to -0.175 V vs. Ag/AgCl in 1.0 M KOH of NCPS Ni, Ni₄Co₁, Ni₂Co₁, Ni₃Co₂, Ni₁Co₁ and Co.

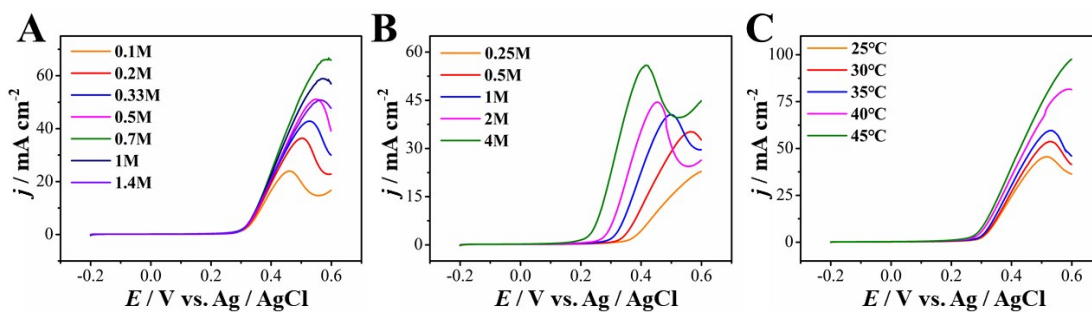


Fig. S15. Influence of KOH concentration, urea concentration and working temperature for UOR.

As can be seen, the UOR performance shows a positive relation with KOH content/testing temperature. This is because high OH^- concentration or temperature are propitious to mass transfer.¹ The content of urea is another prerequisite for UOR, the current density showed a volcano-shape correlation with urea content, the suitable urea content for UOR in 1.0 M KOH solution at room temperature is about 0.7 M. Here, 0.33 M for urea is adapted in order to keep the same as real urine.²

Ref.

1. W. Shi, R. Ding, X. Li, Q. Xu and E. Liu, *Electrochim. Acta*, 2017, **242**, 247-259.
2. G. Wang, Y. Ling, X. Lu, H. Wang, F. Qian, Y. Tong and Y. Li, *Energy Environ. Sci.*, 2012, **5**, 8215-8219.

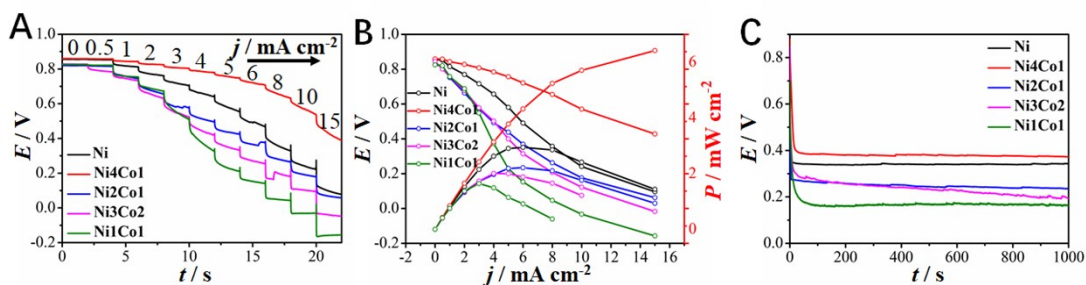


Fig. S16 Performance of the DUHPFCs with NiCo alloy pearl strings anode catalysts (Ni, Ni₄Co₁, Ni₂Co₁, Ni₃Co₂ and Ni₁Co₁): ISTEP plots at different current densities (A), voltage (E) and maximum power density (P_m) as a function of current density (j) (B), ISTEP plots at constant current density of 2 mA cm^{-2} (C). Anolyte: $4.0 \text{ M KOH} + 0.33 \text{ M urea}$; catholyte: $2.0 \text{ M H}_2\text{SO}_4 + 2 \text{ M H}_2\text{O}_2$; T: $25 \text{ }^\circ\text{C}$)

The direct urea hydrogen-peroxide fuel cells (DUHPFCs) that assembled with NiCo alloy electrocatalysts as anode and commercial Pd/C as cathode are test by multi-current steps method. The fuel cell are opened with $4.0 \text{ M KOH} + 0.33 \text{ M urea}$ analytes and $2.0 \text{ M H}_2\text{SO}_4 + 2.0 \text{ M H}_2\text{O}_2$ catholytes at room temperature. As can be seen, in the current density rang of 0 to 15 mA cm^{-2} , NCPS Ni₄Co₁ exhibit voltage of 0.86 - 0.38 V , much higher than that of Ni and other NiCo alloy catalysts (Fig.S16A. The correlation between working voltage (E)/maximum power density (P_m) and current density (j) shown in Fig.S16B demonstrated that the DUHPFC with Ni₄Co₁ anode has highest open voltage of 0.86 V and highest power density of 6.41 mW cm^{-2} , much better than Ni ($2.94 \text{ mW cm}^{-2}/0.85 \text{ V}$), Ni₂Co₁ ($2.21 \text{ mW cm}^{-2}/0.82 \text{ V}$), Ni₃Co₂ ($2.0 \text{ mW cm}^{-2}/0.84 \text{ V}$) and Ni₁Co₁ ($1.65 \text{ mW cm}^{-2}/0.82 \text{ V}$). The ISTEP plots at 2 mA cm^{-2} for 1000 s displayed in Fig. S16C demonstrated that DUHPFC with Ni₄Co₁ anode catalyst possess the superior voltage retention compared with Ni and other NiCo alloy catalysts. The excellent DUHPFC performance of Ni₄Co₁ catalyst proves its superior UOR catalytic performance.

The DUHPFC performance with different anode catalysts in reported literature are compared in Table S5. The synthesized Ni₄Co₁ alloy catalyst exhibited a comparable or higher performance when comparing with those reported works, revealing that Ni₄Co₁ is a promising anode to be applied in DUHPFC.

Table S1. Materials, chemicals and reagents used in this work.

Materials, chemicals and reagents	Type	Company	Characteristics
Ni (CH ₃ COO) ₂ ·4H ₂ O	A.R.	Sinopharm Chemical Reagent Co.,Ltd	Purity≥98%
Co (CH ₃ COO) ₂ ·4H ₂ O	A.R.	Sinopharm Chemical Reagent Co.,Ltd	Purity≥99%
C ₁₉ H ₄₂ BrN	A.R.	Sinopharm Chemical Reagent Co.,Ltd	Purity≥99%
KOH	A.R.	Sinopharm Chemical Reagent Co.,Ltd	Purity≥85%
CH ₄ N ₂ O	A.R.	Sinopharm Chemical Reagent Co.,Ltd	Purity≥99%
KCl	A.R.	Sinopharm Chemical Reagent Co.,Ltd	Purity≥99%
H ₂ O ₂	A.R.	ShanTou GuangHua	Purity≥30%
H ₂ SO ₄	A.R.	ChenDou KeLong	Purity≥98%
N ₂ H ₄ ·H ₂ O	A.R.	HuNan HuiHong	Purity≥80%
CH ₃ CH ₂ OH	A.R.	HuNan HuiHong	Purity≥99%
Super-conductive carbon	#	#	#
Nafion	5% solution	Sigma-Aldrich	#
Working electrode (Glassy carbon)	Diameter: 4mm	TianJing AiDa HengSheng	#
Reference electrode	Ag/AgCl	ShangHai SanShe	#

Table S2. ICP results of the hierarchical Nickel-Cobalt (NiCo) alloy pear strings

	Ni	Ni ₄ Co ₁	Ni ₂ Co ₁	Ni ₃ Co ₂	Ni ₁ Co ₁
Ni / ppm	12	9.274	8.579	7.678	5.841
Co / ppm	0	2.101	4.091	4.091	5.325

Table S3. List of recently reported UOR performance on Ni-based catalysts

Catalysts	$j_{\text{peak}} /$ mA cm ⁻²	$E_{\text{peak}} /$ V vs. RHE	$E_{\text{onset}} /$ V vs. RHE	Electrolytes	Scan rate (mV s ⁻¹)	Ref.
graphene–nickel nanocomposites	35	1.62	1.36	0.33M urea +1.M KOH	10	1
Ni-Co bimetallic nanoparticles	20	1.52	1.28	0.33M urea +1.M KOH	50	2
Ni _{1.5} Mn _{1.5} O ₄	7	1.5	1.29	0.33M urea + 1M KOH	10	3
β -Ni(OH) ₂	7	1.44	1.35	0.33M urea + 5M KOH	10	4
Ni–Zn–Co	24	1.4	1.25	0.33M urea + 5M KOH	10	5
Ni (OH) ₂ /PPy/GO	2	1.6	1.35	0.5M urea + 1M KOH	10	6
Ni (OH) ₂ nanosheet	24.8	1.6	1.4	0.33M urea + 5M KOH	20	7
Ni (OH) ₂ nanoflake	142.4	1.6	1.4	0.33M urea + 5M KOH	20	7
Ni ₂ P/C	70	1.5	1.37	0.33M urea + 1M KOH	10	8
20% Pt/C	5	1.6	1.76	0.33M urea +1M KOH	10	9
S-Ni(OH) ₂ nanosheet	35	1.52	1.34	0.33M urea + 1M KOH	50	10
Co ₃ O ₄ @NiO/CC	34	1.4	1.17	0.05M urea + 0.1M KOH	20	11
Ni ₅₃ Co ₄₇ (OH) ₂	47	1.5	1.15	0.33M urea + 5M KOH	10	12
Ni-Co alloy	51.5	1.5	1.23	0.33M urea + 1M KOH	10	This work

Ref.

1. D. Wang, W. Yan, S. H. Vijapur and G. G. Botte, *Electrochim. Acta*, 2013, **89**, 732-736.
2. W. Xu, H. Zhang, G. Li and Z. Wu, *Sci. Rep.*, 2014, **4**, 5863.
3. S. Periyasamy, P. Subramanian, E. Levi, D. Aurbach, A. Gedanken and A. Schechter, *ACS Appl. Mater. Interfaces*, 2016, **8**, 12176-12185.
4. D. Wang, W. Yan, S. H. Vijapur and G. G. Botte, *J. Power Sources*, 2012, **217**, 498-502.
5. W. Yan, D. Wang and G. G. Botte, *Appl. Catal. B: Environ.*, 2012, **127**, 221-226.
6. Z. Cao, H. Mao, X. Guo, D. Sun, Z. Sun, B. Wang, Y. Zhang and X.-M. Song, *ACS Sustain. Chem. Eng.*, 2018, **6**, 15570-15581.
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8. D. Yang, Y. Gu, X. Yu, Z. Lin, H. Xue and L. Feng, *ChemElectroChem*, 2018, **5**, 659-664.
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11. N. Senthilkumar, G. Gnana kumar and A. Manthiram, *Adv. Energy Mater.*, 2017, 1702207
12. W. Yan, D. Wang and G. G. Botte, *Electrochim. Acta*, 2012, **61**, 25-30.

Table S4. The fitting values of EIS parameters of NiCo catalysts for urea electrooxidation in 1.0 M KOH and 0.33 M urea.

Catalysts	$R_s(\Omega)$	$Q (S \cdot \text{sec}^n)$	n	$R_{ct}(\Omega)$
1-0	6.546	0.002989	0.7162	53.19
4-1	7.174	0.004571	0.8214	25.5
2-1	7.953	0.003399	0.8317	91.8
3-2	7.404	0.004767	0.8381	157
1-1	7.828	0.003696	0.7477	178.9

Table S4 lists the fitting values of EIS parameters (R_s , Q , n , R_{ct}). According to the table, one can see that the R_{ct} value (25.5 Ω) relating with urea electrooxidation of the Ni₄Co₁ catalysts is smaller than those of Ni (53.19 Ω), Ni₂Co₁ (91.8 Ω), Ni₃Co₂ (157 Ω), and Ni₁Co₁ (178.9 Ω), which indicates the fast reaction process for Ni₄Co₁, these results are in accordance with the dynamic analyzed by Tafel plots (Fig. 3B).”

Table S5. Comparison of DUHPFCs performance in recently reports

Anode	Cathode	Anolyte	Catholyte	T/°C	$P_m / mW\ cm^{-2}$	Ref.
Ni-Co/NWAs	Pd/CFC	5.0 M KOH + 0.33M urea	2.0 M H ₂ SO ₄ + 2 M H ₂ O ₂	25	5.03	1
CoNi@Ni foam	Pd/CFC	5.0 M KOH + 0.33M urea	2.0 M H ₂ SO ₄ + 0.9 M H ₂ O ₂	20	8.5	2
Ni (OH) ₂ /Ni foam	Pd/C@TiC	5.0 M KOH + 0.6 M urea	2.0 M H ₂ SO ₄ + 2.0 M H ₂ O ₂	20	6.57	3
NiCo precursor@CS	Pd/Ti	5.0 M KOH + 0.2 M urea	2.0 M H ₂ SO ₄ + 1.0 M H ₂ O ₂	25	5.72	4
Ni ₂ Mo ₁ /G	Pd/C	4.0 M KOH + 0.33 M urea	2.0 M H ₂ SO ₄ + 2.0 M H ₂ O ₂	25	9	5
NCPS Ni₄Co₁	Pd/C	4.0 M KOH + 0.33 M urea	2.0 M H₂SO₄ + 2.0 M H₂O₂	25	6.41	This Work

Ref.

1. F. Guo, K. Cheng, K. Ye, G. Wang and D. Cao, *Electrochim. Acta*, 2016, **199**, 290-296.
2. B. Li, C. Song, J. Yin, J. Yan, K. Ye, K. Cheng, K. Zhu, D. Cao and G. Wang, *Int. J. Hydrog. Energy*, 2020, **45**, 10569-10579.
3. K. Ye, H. Zhang, L. Zhao, X. Huang, K. Cheng, G. Wang and D. Cao, *New J. Chem.*, 2016, **40**, 8673-8680.
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5. W. Shi, R. Ding, X. Li, Q. Xu and E. Liu, *Electrochim. Acta*, 2017, **242**, 247-259.