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Supporting Information

Trimetallic NiCoMo/graphene multifunctional electrocatalysts with moderate structural/electronic effects for highly efficient alkaline urea oxidation reaction

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Experimental Section

1. Synthesis of NiCoMo/graphene (NCM/G) catalysts

All of the chemicals used in this experiment were analytical level (A.R.) without further purification. NCM/G catalysts with various Ni/Co/Mo ratios were synthesized by a facile co-precipitation method. Here, we take the fabrication of the NCM/G 811（the original feeding atom ratio for Ni/Co/Mo is 80:10:10） as an example, other samples with diverse Ni/Co/Mo ratios were synthesized in the same way but adjusted the amount of $NiCl_2•6H_2O$, $CoCl_2•6H_2O$ and $Na_2MoO_4•2H_2O$. In a typical procedure, 1.6 mmol $NiCl_2•6H_2O$, 0.2 mmol $CoCl_2•6H_2O$, 0.2 mmol $Na_2MoO_4•2H_2O$ and 1.7 mmol tri-sodium citrate dehydrate ($Na_3C_6H_5O_7•2H_2O$) were dissolved into 50.0 mL H_2O under vigorous stirring. Then 10.0 mL graphene oxide (GO: 5.0 mg mL^{-1}) aqueous solutions were added into the above solution and the resulted mixture were ultrasonicated for at least 30 min in order to obtain dispersed well suspension. At last, 30.0 mL freshly prepared $NaBH_4$ solution (1.0 M) was added into the suspension drop by drop and kept magnetic stirring for another 1 hour. After the reaction finished completely, the black precipitates were collected and washed by water and ethanol for several times and dried at 60 °C for 24 h.

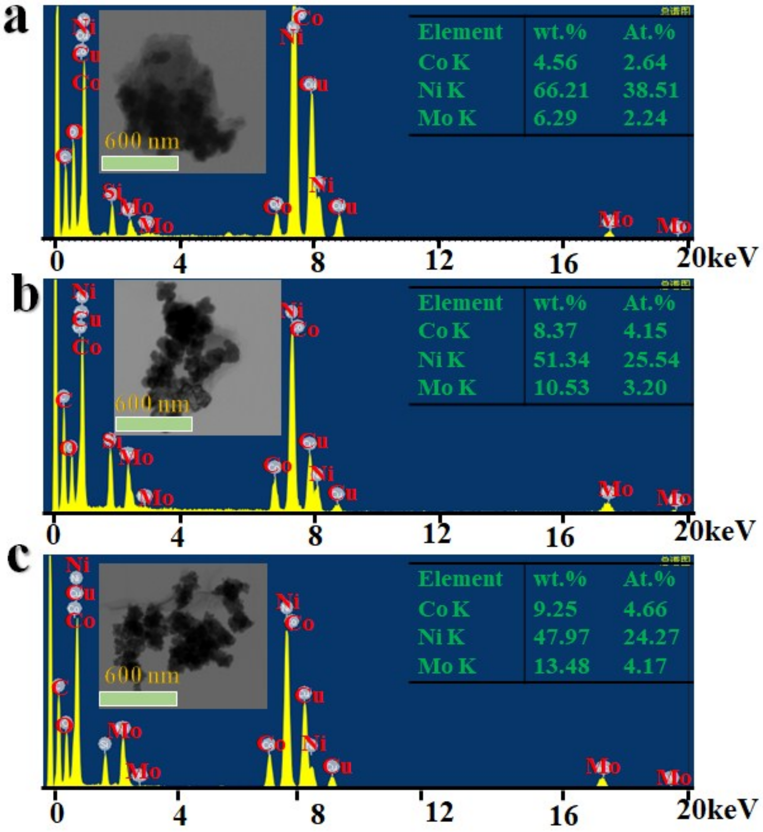
2. Physicochemical characterizations.

X-ray diffraction (XRD) was conducted to investigate the phase composition. X-ray photoelectron spectra (XPS) was performed to study the surface chemical composition and electronic structure. Scanning/transmission electron microscopy (SEM/TEM) were used to examine the particle morphology and size. The element composition and distribution are measured by X-Ray energy dispersive spectra (EDS) and mapping. The specific surface area, pore volume and size distribution are examined by nitrogen isothermal sorptions with Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods.

3. Electrochemical measurements.

All of the electrochemical measurements are conducted on CHI 660E (CH Instruments Ins, Shanghai, China) with traditional three-electrode system. In our experiments, glassy carbon electrode (diameter: 3.0 mm) was used as working electrode (WE) and polished with alumina oxide before loading catalysts, Pt plate was served as counter electrode (CE) and Ag/AgCl with saturated KCl was used as reference electrode (RE). The catalyst ink was fabricated by mixing 5.0 mg catalyst with 950.0 μL ethanol and 50.0 μL Nafion solution and sonicated for 30 min. Then 7.0 μL of the ink was dropped onto the working electrode and dried naturally. The mass loading of the catalysts was about 0.495 mg cm^{-2}. The electrocatalytic performances for urea oxidation reaction (UOR) on the active materials investigated by Cyclic voltammetry (CV), Linear sweeping voltammetry (LSV) and Chronoamperometry (CA) in 1.0 M KOH with or without 0.33 M urea. The potential range for CV and LSV was -0.1-0.6 V and the CA was tested at a constant potential of 0.5 V. The scan rate for CV was 10 mV s^{-1} and for LSV was 1 mV s^{-1}. The direct urea-hydrogen peroxide fuel cells (DUHPFCs) were assembled with the Ni-Mo/G, Pd/C (10 wt.%) and Nafion 115 cation exchange membrane as anode catalysts, cathode catalysts and solid polymer electrolyte (SPE) respectively. The fuel cell was operated with 1.0 M KOH+0.33 M urea anolytes and 0.5 M H_2SO_4+0.5 M H_2O_2 catholytes at room temperature. Multi-step chronopotentiometric analysis (ISTEP) was executed by applying a staircase current density from 0 up to 10 mA cm^{-2}.

Supplemental figures



Element	wt.%	At.%
Co K	4.56	2.64
Ni K	66.21	38.51
Mo K	6.29	2.24

Element	wt.%	At.%
Co K	8.37	4.15
Ni K	51.34	25.54
Mo K	10.53	3.20

Element	wt.%	At.%
Co K	9.25	4.66
Ni K	47.97	24.27
Mo K	13.48	4.17

Fig. S1 EDS element content of NCM/G 90505 (a), 811(b) and 71515 (c) catalysts.

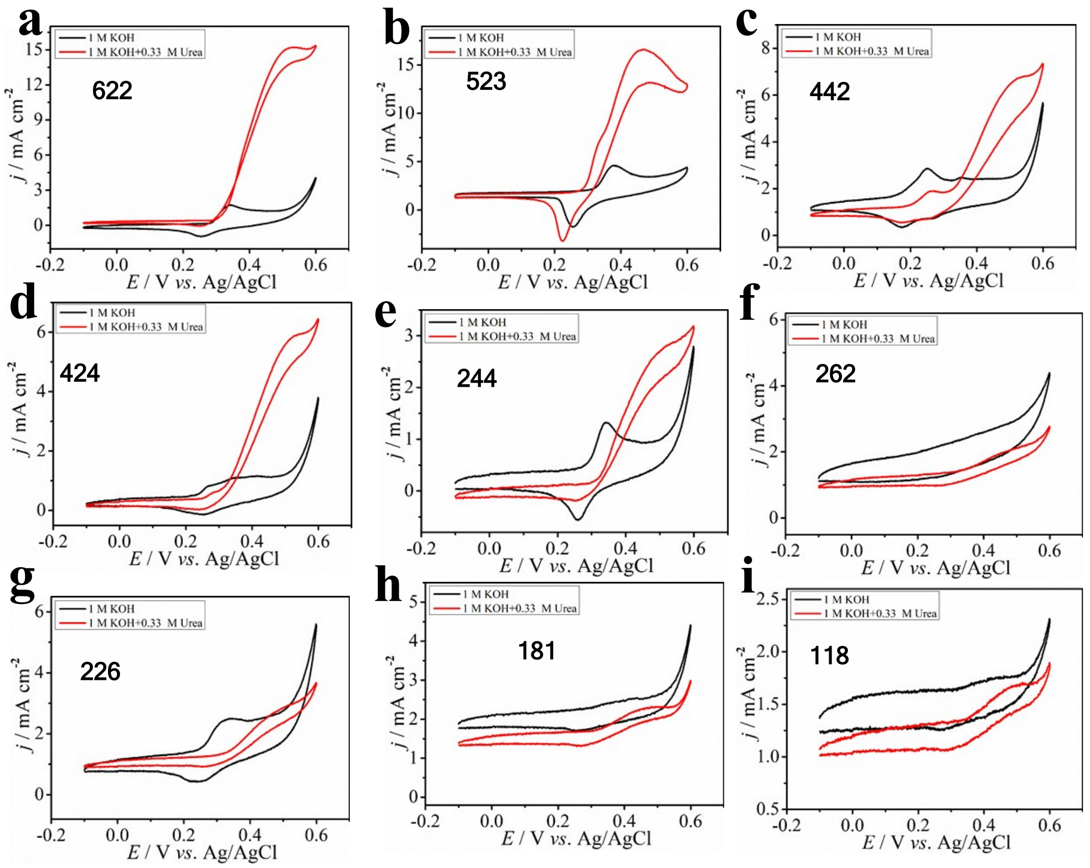


Fig. S2 CV curves of NCM/G catalysts with Ni/Co/Mo original feeding ratios from 622 to 118 tested in 1.0 M KOH with or without 0.33 M urea. Scan rate: 10 mV s^{-1}.

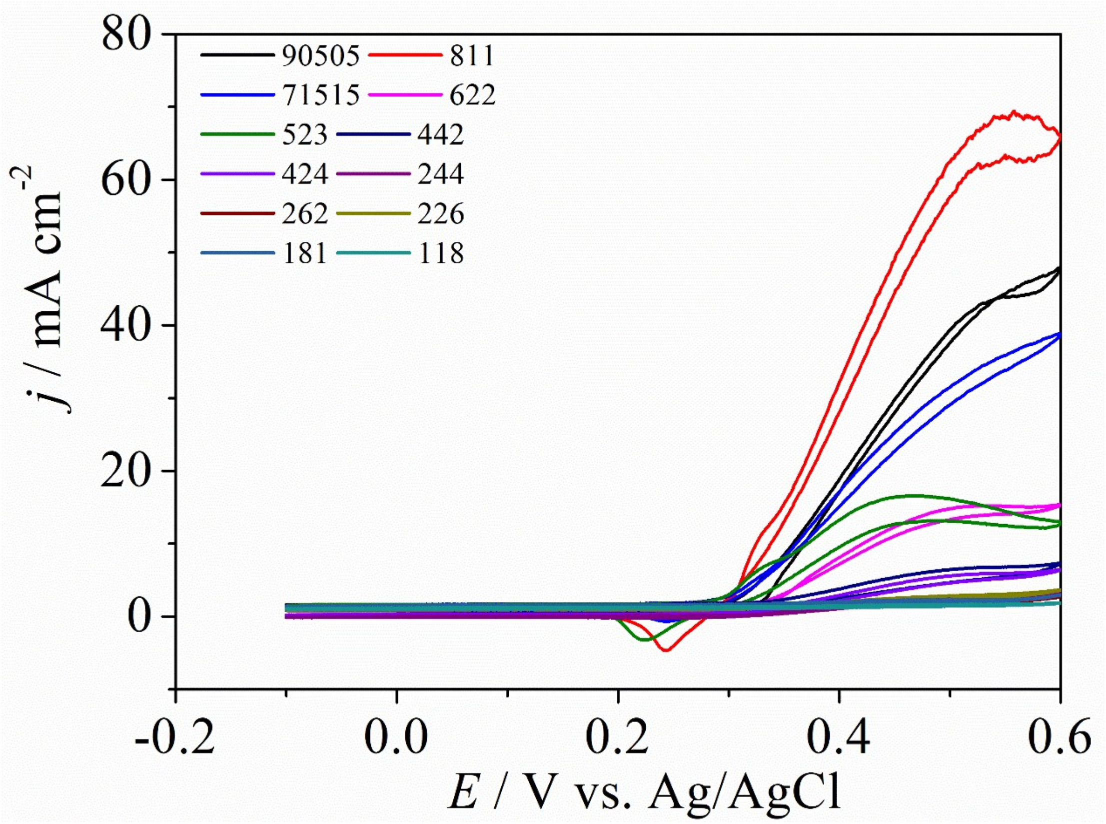


Fig. S3 The comparison of CVs for UOR on NCM/G catalysts. Electrolyte: 1.0 M KOH+0.33 M urea; scan rate: 10 mV s^{-1}.

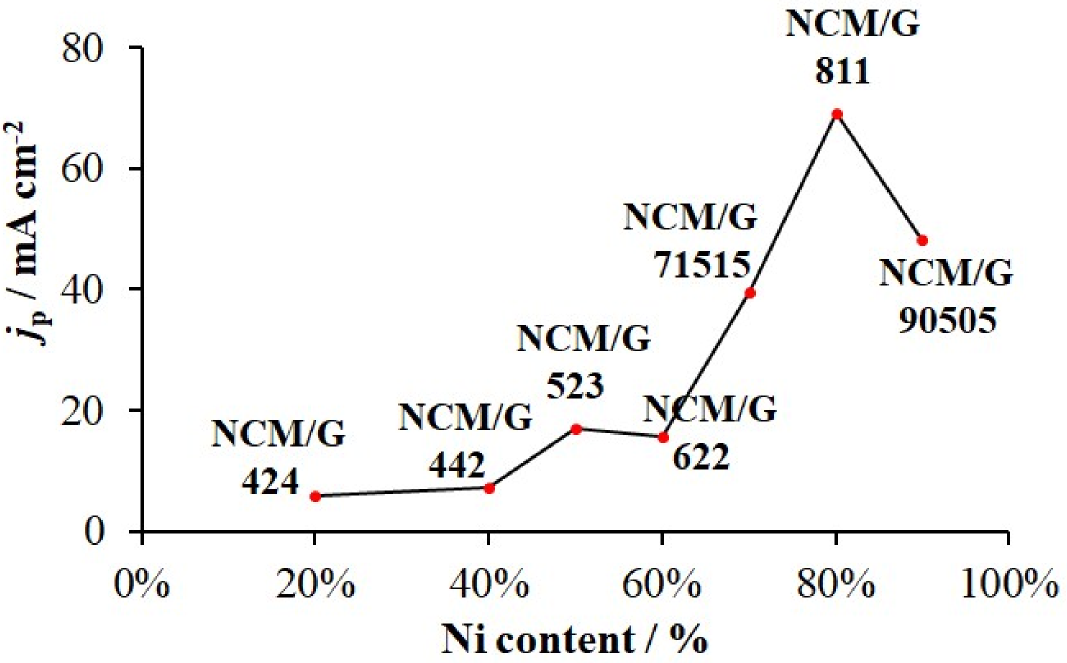


Fig. S4 The relationship of peak current density (j_p) and original feeding Ni content.

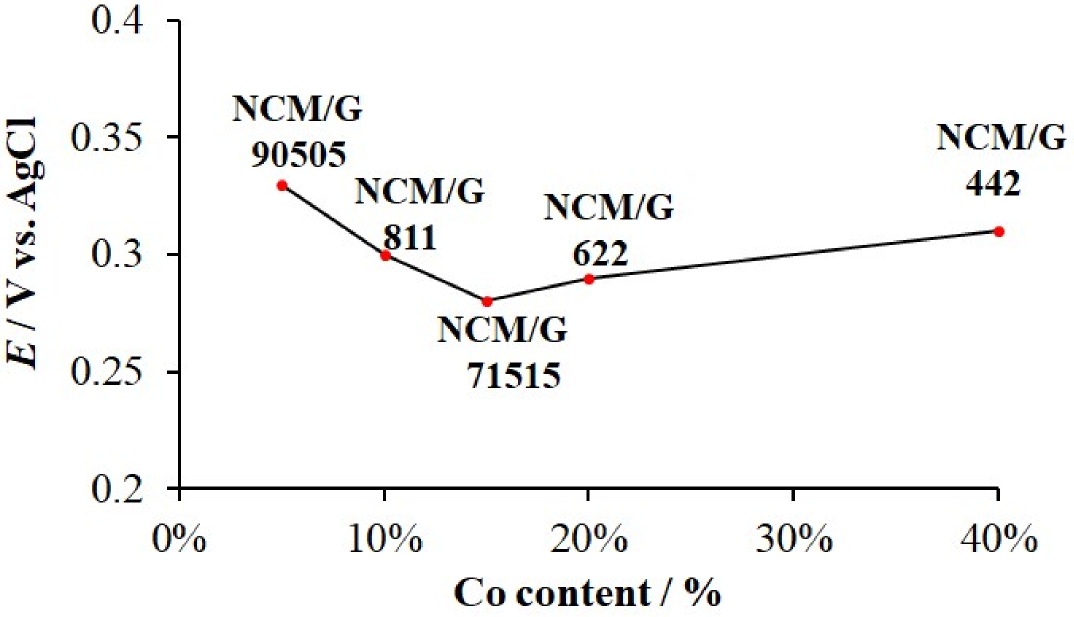


Fig. S5 The relationship of onset potential (E_{onset}) for UOR and original feeding Co content.

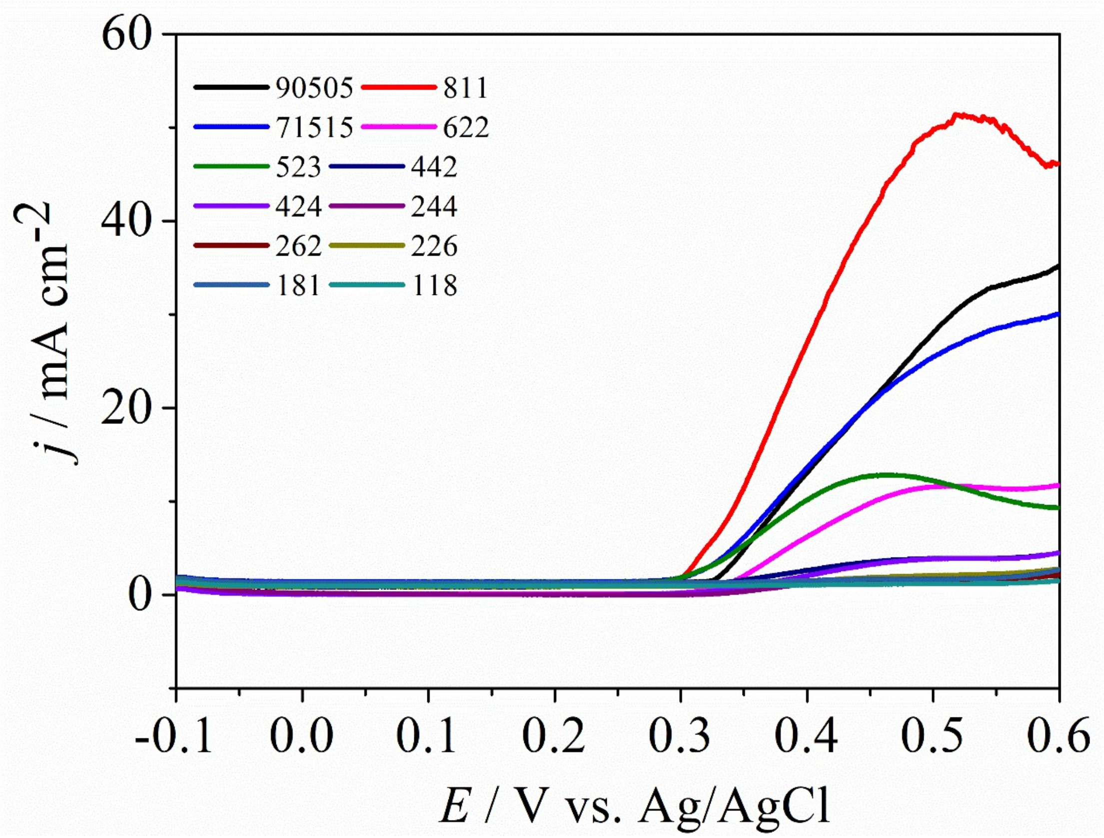


Fig. S6 LSV plots for the NCM/G catalysts in 1.0 M KOH with 0.33 M urea. Scan rate: 1 mV s^{-1}.

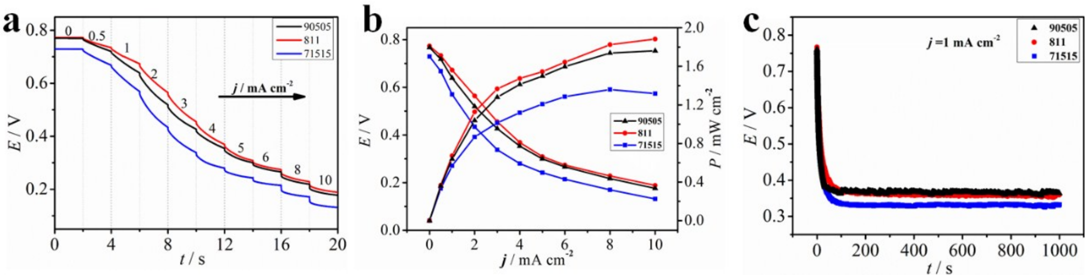


Fig. S7 Performances of the DUHPFCs with NCM/G anode catalysts: Multi-step chronopotentiometric analysis (ISTEP) (a), Voltage (*E*)~Current density (*j*) and Power density (*P*)~Current density (*j*) relationship (b) and ISTEP plots at constant current density of 1 mA cm^{-2} (c).

The H-type DUHPFCs fabricated by NCM/G anode catalysts and commercial Pd/C (10 wt%) are operated under room temperature. Fig. S7(a) exhibits the ISTEP analysis of the DUHPFCs, NCM/G 811 and 90505 bears higher open voltage than that of NCM/G 71515. With the increment of current densities from 0 to 10 mA cm^{-2}, the potentials of NCM/G 811, 90505 and 71515 decreased step-by-step while NCM/G 811 possess the highest potential value. The correlation of power density and cell voltage with the increasing of current density are also displayed in Fig. S7(b). The maximum power density and voltage of the DUHPFC with NCM/G 811 anode are about 1.85 mW cm^{-2} and 0.79 V, respectively, higher than that of NCM/G 90505 (1.79 mW cm^{-2}/0.79 V) and NCM/G 71515 (1.39 mW cm^{-2}/0.74 V) anodic materials under room temperature. Fig. S7(c) shows the operation stability of the DUHPFCs, demonstrating DUHPFC with NCM/G 811 anode exhibits superior voltage retention after 1000 s functioning at current density of 1 mA cm^{-2}. The excellent DUHPFC performance of NCM/G 811 catalysts confirm its outstanding UOR electrocatalytic capability.

Table S1 List of recently reported UOR performance on Ni-based catalysts tested on glassy carbon electrode (potentials have been converted to RHE for convenient comparison).

Catalyst	j_{peak} / mA cm^{-2}	E_{peak} / V vs.RHE	Catalyst loading /mg	Mass activity /mA mg$_{\text{cat}}^{-1}$	v / mV s^{-1}	Ref.
20% Pt/C	5	1.6	0.05	98.0	10	1
Ni-MOF	41	1.6	0.05	160.72	10	1
graphene–nickel nanocomposites	35	1.62	/	/	10	2
Ni-Co bimetallic nanoparticles	20	1.52	0.03	47.1	10	3
Metallic $Ni(OH)_2$	36	1.62	0.04	67.3	50	4
Ni_2P/C	70	1.5	0.026	188.5	10	5
$Ni_{1.5}Mn_{1.5}O_4$	7	1.5	/	/	10	6
$Ni(OH)_2$/PPy/GO	2	1.72	0.005	28.26	10	7
β-Ni $(OH)_2$ nanosheets	24.8	1.6	0.02	86.8	10	8
NCM/G 811	**69.8**	**1.55**	**0.035**	**140.9**	**10**	**This work**

The conversion is based on the equations: $E_{RHE} = E_{Hg/HgO} + E^0_{Hg/HgO} + 0.059\ pH$ [9]$= E_{Hg/HgO} + 0.098 + 0.059\ pH$, $E_{RHE} = E_{SCE} + E^0_{SCE} + 0.059\ pH$ [10] $= E_{SCE} + 0.24 + 0.059\ pH$ and $E_{RHE} = E_{Ag/AgCl} + E^0_{Ag/AgCl} + 0.059\ pH$ [11] $= E_{Ag/AgCl} + 0.205 + 0.059\ pH$, where pH is the pH value of the electrolyte.

Ref.

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Table S2 List of UOR performance on recently developed advanced catalysts to attain current density of 10 mA cm^{-2}.

Catalyst	Urea concentration /M	Potential/ V vs. RHE	Ref.
20% Pt/C	0.33	1.64	1
Ni-MOF	0.33	1.36	1
graphene–nickel nanocomposites	0.33	1.43	2
Ni-Co bimetallic nanoparticles	0.33	1.42	3
Metallic $Ni(OH)_2$	0.33	1.45	4
Ni_2P/C	0.33	1.33	5
β-Ni $(OH)_2$ nanosheets	0.33	1.55	8
L-MnO_2	0.5	1.37	12
Ni nanowire	0.33	1.48	13
NiCo sheet array	0.33	1.37	14
NCM/G 811	**0.33**	**1.32**	**This work**

Ref.

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Table S3 Comparison of UOR performance on NCM/G catalysts with different Ni/Co/No feeding atom ratios.

Catalysts	E_{onset} / V	j_{peak} / mA cm^{-2}	Tafel slope /mV dec^{-1}	Current retention /%
90505	0.33	48.3	48	71.8
811	0.30	69.8	41	74.3
71515	0.28	39.6	92	82.4
622	0.29	15.6	/	/
523	0.29	16.9	/	/
442	0.31	7.3	/	/
424	/	6.0	/	/
244	/	3.1	/	/
262	/	/	/	/
226	/	/	/	/
181	/	/	/	/
118	/	/	/	/

Table S4 Comparison of peak positions of Ni 2P, Co 2p and Mo 3d for NCM/G 90505, 811 and 71515 in XPS spectra.

Catalysts	**Ni 2p $_{3/2}$ (eV)**	**Ni 2p $_{1/2}$ (eV)**	**Co 2p $_{3/2}$ (eV)**	**Co 2p $_{1/2}$ (eV)**	**Mo 3d $_{5/2}$ (eV)**	**Mo 3d $_{3/2}$ (eV)**
90505	856.3	873.9	781.9	797.0	232.2	235.5
811	856.4	874.0	782.0	797.1	232.4	235.7
71515	856.5	874.1	782.2	797.2	232.6	235.9