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## **Supplementary Information**

## Balancing Dynamic Evolution of Active Sites for Urea Oxidation in Practical Scenarios

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**Supplementary Fig. 1.** (a) XRD patterns of  $Ni(OH)_2$  and  $Ru_1$ - $Ni(OH)_2$  catalysts with diverse feed amounts of Ru, including 5, 10, and 15 mg RuCl<sub>3</sub> H<sub>2</sub>O. (b) the loading mass of Ru species quantified by MP-AES.



**Supplementary Fig. 2.** Morphologies of Ni(OH)<sub>2</sub> and Ru<sub>1</sub>-Ni(OH)<sub>2</sub> with different feed amounts of Ru source, including 5, 10, and 15 mg RuCl<sub>3</sub> H<sub>2</sub>O, labeled as Ru-5, Ru-10 and Ru-15, respectively.



Supplementary Fig. 3. EDS mapping of the Ru<sub>1</sub>-Ni(OH)<sub>2</sub> catalyst, including elements of Ni, O, and Ru.



**Supplementary Fig. 4.** Ru K-edge and Ni-K EXAFS fitting results of Ru<sub>1</sub>-Ni(OH)<sub>2</sub>: (a)  $k^2$ -weighted k-space EXAFS. (b)  $k^2$ -weighted R-space (magnitude) EXAFS. The experimental data is plotted in black circle scatters, while the fitted spectrum is plotted in red curve. Ni-K EXAFS fitting results of Ru<sub>1</sub>-Ni(OH)<sub>2</sub>: (c)  $k^2$ -weighted k-space EXAFS. (d)  $k^2$ -weighted R-space (magnitude) EXAFS. The experimental data is plotted in black circle scatters, while the fitted spectrum is plotted in red curve.



**Supplementary Fig. 5.** *In-situ* EIS for OER and UOR in different potentials. (a) bode plots and (b) Nyquist plots of Ni(OH)<sub>2</sub>-CP for OER. (c) bode plots and (d) Nyquist plots of Ru<sub>1</sub>-Ni(OH)<sub>2</sub>-CP for OER. (e) bode plots and (f) Nyquist plots of Ni(OH)<sub>2</sub>-CP for UOR. (g) bode plots and (h) Nyquist plots of Ru<sub>1</sub>-Ni(OH)<sub>2</sub>-CP for UOR.



High frequency interface: surface oxidation

Low frequency interface: OER



High frequency interface - - - - -



**Supplementary Fig. 6.** The schematic illustrations of the relationship among surface species, interfaces, and reactions during the OER (a), and UOR (b) as reported by Wang's group<sup>1</sup>.



Supplementary Fig. 7. The adsorption energy of  $OH^-$  on  $Ni(OH)_2$  and  $Ru_1$ -Ni(OH)\_2 model.



**Supplementary Fig. 8.** (a) Tafel slopes. (b) LSV curves of  $Ru_1$ -Ni(OH)<sub>2</sub> catalysts during UOR and OER. (c) LSV curves of  $Ru_1$ -Ni(OH)<sub>2</sub> with different feed amounts of Ru source. (d) The ratios between current and loading mass of different feed amounts of Ru source.



**Supplementary Fig. 9.** The investigation of the dynamic Ni<sup>3+</sup> active site generation ability. (a-b) integrated Ni<sup>2+</sup> to Ni<sup>3+</sup> oxidation peak of Ru<sub>1</sub>-Ni(OH)<sub>2</sub>-NF and Ni(OH)<sub>2</sub>-NF, respectively. Q is the faradaic charge transfer of Ni<sup>2+</sup> to Ni<sup>3+</sup> and the value can be calculated by the equation: Q=S/v, where S represents the integrated mathematical area (yellow shadow), v is the scan rate (5 mV/s). (c) CV curve of Ru<sub>1</sub>-Ni(OH)<sub>2</sub> and Ni(OH)<sub>2</sub> catalysts on nickel foam in the electrolyte of 1M KOH +0.33M urea. (d-e) CV scanning curves at different scan rates in the non-Faradaic potential region. (f) Capacity current density at 0.07 V vs. Ag/AgCl as functional of scan rate (data obtained from d and e).



Supplementary Fig. 10. LSV curves and chronopotentiometry test of (a)-(b) MOR and (c)-(d) EOR.



**Supplementary Fig. 11.** (a) Schematic illustration of *In-situ* attenuated total reflection surface-enhanced IR absorption spectroscopy (ATR-SEIRAS) measurement. (b) FTIR spectra during one-hour urea electrolysis at 1.37 V vs. RHE.



**Supplementary Fig. 12.** (a) Schematic illustration of *In-situ* Raman spectra measurement. (b)-(d) Raman spectra of Ru<sub>1</sub>-Ni(OH)<sub>2</sub>, Ni(OH)<sub>2</sub>, and pristine nickel foam during the UOR at different applied potentials.



**Supplementary Fig. 13.** (a) Raman spectra during the OER. (b) Raman spectra during the half-hour urea electrolysis at 1.37 V *vs* RHE.



Supplementary Fig. 14. (a) Raman spectra during the UOR with a high concentration of urea (2M). (b) Raman spectra

of intermittent UOR test.



Supplementary Fig. 15. Raman spectra of MOR and EOR in different concentrations.



**Supplementary Fig. 16.** (a) LSV curves during the UOR in low and high urea concentrations. (b) CV curve of  $Ru_1$ -Ni(OH)<sub>2</sub> and Ni(OH)<sub>2</sub> catalysts on nickel foam in the electrolyte of 1M KOH + 2M urea.



**Supplementary Fig. 17.** The investigation of the Ru sites after reaction. (a) CV curves after 20 cycles. (b) XPS spectra of Ru 3p3/2.



Supplementary Fig. 18. The morphology after 20 cycles of CV test during (a) OER and (b) UOR.



 $\label{eq:supplementary Fig.19.} Bader charges and charge density difference for Ru_1-Ni(OH)_2 from DFT calculations.$ 



Supplementary Fig. 20. Charging curves of the Zn-battery, Zn-urea-air battery before and after 100 h test.



Supplementary Fig. 21. (a) The XRD pattern of as-synthesized heterogeneous Ni phosphides. (b) HR-TEM image.



Supplementary Fig. 22. HER performance of the heterogeneous catalysts of Ni phosphides catalysts. (a) LSV curves.
(b) LSV curves after 2000<sup>th</sup> cycling. (c) Stability test over 45 hours.



**Supplementary Fig. 23.** (a) Polarization curves of two-electrode for HER-UOR and HER-OER. (b) Polarization curves of two-electrode for comparison with the benchmark. (c) Stability test under 0.2 A cm<sup>-2</sup> over 100 h (adding fresh electrolyte every 20 h).



Supplementary Fig. 24. LSV curves of alkaline urine electrolysis.



Supplementary Fig. 25. LSV curves in the MEA system

Sample	Absorption Edge	Scattering Path	C.N.	$\sigma^2(\dot{A}^2)$	R(Å)	$\Delta E_0 (eV)$	
Ru <sub>1</sub> -Ni(OH) <sub>2</sub>	Ni K-edge -	Ni-O	6.0±0.3	$0.0060 \pm 0.0005$	2.05±0.01	4.8±0.5	
		Ni-Ni	6.0±0.3	0.0072±0.0004	3.10±0.01		
	Ru K-edge -	Ru-O	4.1±0.3	0.0024±0.0009	2.05±0.01	– 1.7±1.2	
		Ru-Ni	3.0±0.5	0.0120±0.0006	2.70±0.02		

Supplementary Table 1. Fitting results of Ni and Ru K-edge EXAFS for Ru<sub>1</sub>-Ni(OH)<sub>2</sub>.

 $C.N. = coordination number; R = interatomic distance; R_{ref} = interatomic distances of reference materials; \sigma^2 = Debye-Waller factor. \Delta E_0 = energy shift refers to the E_0 position in the EXAFS fitting model.$ 

Catalyst	Potential at 100	Electrolyte	Reference
	mA cm <sup>-2</sup> (V vs.		
	RHE)		
Ru <sub>1</sub> -Ni(OH) <sub>2</sub>	1.37	0.33M urea	This work
FeCoSe/FeCo LDH	1.38	0.5M urea	Adv. Funct. Mater. 2023 2212811
W-Ni(OH) <sub>2</sub>	1.381	0.33M urea	Chem. Eng. J. 2022 134497
Ni-Mo-S	1.385	0.33M urea	J. Alloys Compd. 2022 163346
Ni-MnO <sub>2</sub>	1.39	0.33M urea	Inorg. Chem. <b>2023</b> 5023-5031
V-Ni <sub>3</sub> N	1.395	0.33M urea	J. Mater. Chem. A, 2021 4159
Cu <sub>3</sub> P@CuO <sub>x</sub>	1.40	0.33M urea	Appl. Surf. Sci. 2023 156925
Cu-Ni(OH) <sub>2</sub>	1.405	0.33M urea	J. Mater. Chem. A 2019 13577
NiMoP	1.41	0.5 M urea	Small 2022 2205547
Hcp-CoNi-N/C	1.42	0.33M urea	Chem. Eng. J. 2023 142570
Fc-NiCo-BDC	1.44	0.33M urea	Chem. Eng. J. 2022 132733
Mn-Co LDH	1.45	0.33M urea	Chem. Eur. J. <b>2020</b> 9382 – 9388
$VS_2$	1.46	0.33M urea	Int J Energy Res. 2022 1–11
Ov-V-Ni(OH)2	1.47	0.33M urea	Adv. Funct. Mater. 2022 2209698
CoNiOP/NF	1.48	0.33M urea	J. Colloid Interface Sci. 2022 546-555
CoMoO@Co/GF	1.51	0.5M urea	J. Colloid Interface Sci. 2022 413-423
Ni <sub>1.5</sub> Co <sub>1.5</sub> -O/CC	1.52	0.33M urea	J. Alloys Compd. 2021 161790
Ni MOF	1.53	0.33M urea	Chem. Commun. 2017 10906
Co, V-NiS <sub>2</sub>	1.54	0.33M urea	ACS Catal. 2022 569-579
NiFeCoSx@FeNi <sub>3</sub>	1.56	0.33M urea	J. Mater. Chem. A 2022 5442
NiF <sub>3</sub> /Ni <sub>2</sub> P@CC	1.57	0.33M urea	Chem. Eur. J. 2022 130865
F-P-Co <sub>3</sub> O <sub>4</sub> /NF	1.62	0.5M urea	Dalton Trans. 2022 4909-4918

**Supplementary Table 2**. Comparison of UOR, MOR, and EOR performance for recently reported electrocatalysts in alkaline media.

$Co_3S_4$	1.67	0.33M urea	Mater. Sci. Eng. B. 2022 115654	
Ru <sub>1</sub> -Ni(OH) <sub>2</sub>	1.43	0.5M methanol	This work	
h-NiSe/CNTs	1.43	1M methanol	Adv. Funct. Mater. 2021, 2008812	
Cu <sub>2</sub> Se/Co <sub>3</sub> Se <sub>4</sub>	1.46	1M methanol	Appl. Catal. B. 2021, 119800	
Mo-Co <sub>4</sub> N	1.49	3M methanol	J. Mater. Chem. A <b>2021</b> 21094	
Ru&Fe-WOx	1.5	3M methanol	Appl. Catal. B. 2021, 120359	
Ni <sub>1</sub> - <sub>x</sub> Fe <sub>x</sub> Se <sub>2</sub>	1.58	1M methanol	Small <b>2021</b> , 2006623	
Ru <sub>1</sub> -Ni(OH) <sub>2</sub>	1.38	0.5M ethanol	This work	
Co(OH)2@Ni(OH)2	1.39	1M ethanol	Energy Environ. Sci., <b>2022</b> , 5300	
Ni-Fe-P	1.4	1M ethanol	Appl. Surf. Sci. 2021 150080	
CuCo <sub>2</sub> S <sub>4</sub> /CC	1.49	1M ethanol	J. Colloid Interface Sci. 2022 325-333	
CO-S-P	1.53	1M ethanol	Inorg. Chem. Front., <b>2020</b> 4498	
Co <sub>3</sub> S <sub>4</sub>	1.72	0.5M ethanol	J. Mater. Chem. A <b>2020</b> 16902	

## **Reference for the Support information**

1. Chen W, *et al.* Activity Origins and Design Principles of Nickel-Based Catalysts for Nucleophile Electrooxidation. *Chem* **6**, 2974-2993(2020).