Electronic Supporting Information

Composition regulation of Ni-BDC MOF architecture to enhance electrocatalytic urea oxidation in alkaline solution

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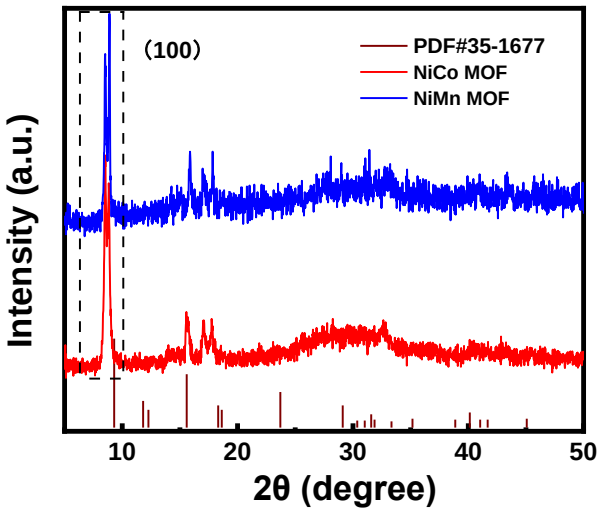

Fig. S1 PXRD patterns of binary NiCo MOF and NiMn MOF.

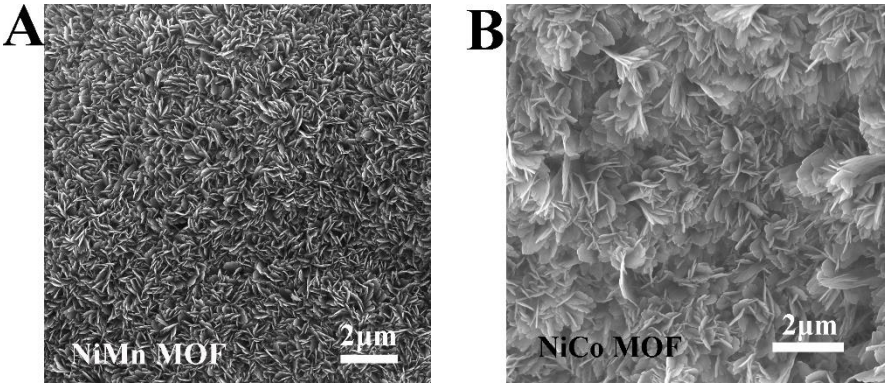

Fig. S2 FE-SEM graphs of NiMn MOF(A) and NiCo MOF (B).

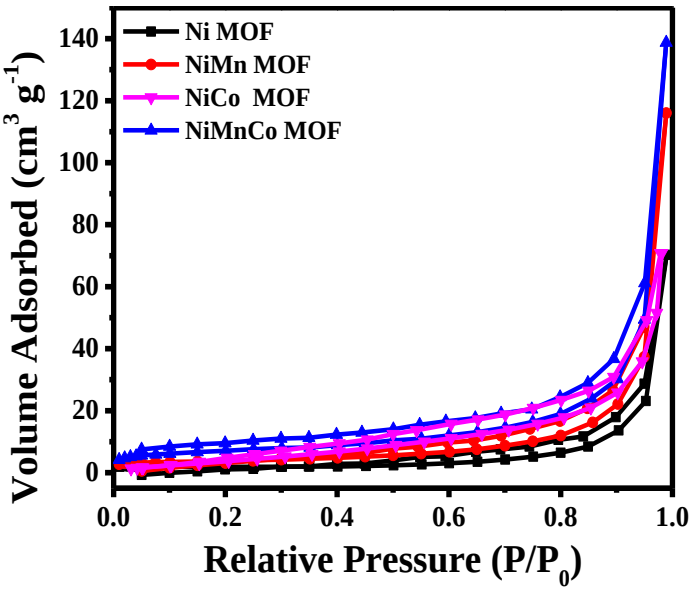

Fig. S3 N_2 adsorption-desorption isotherms of all samples.

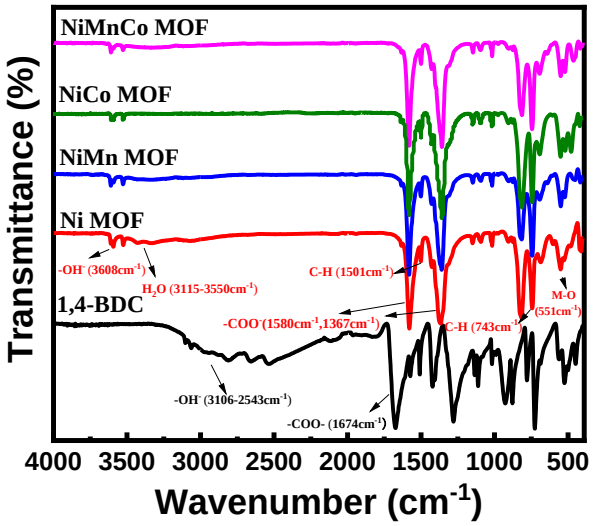

Fig. S4 FT-IR spectra of all samples.

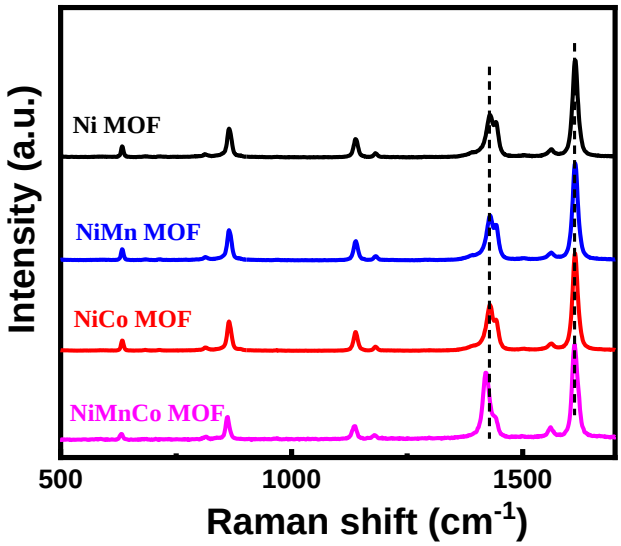

Fig. S5 Raman spectra of all samples.

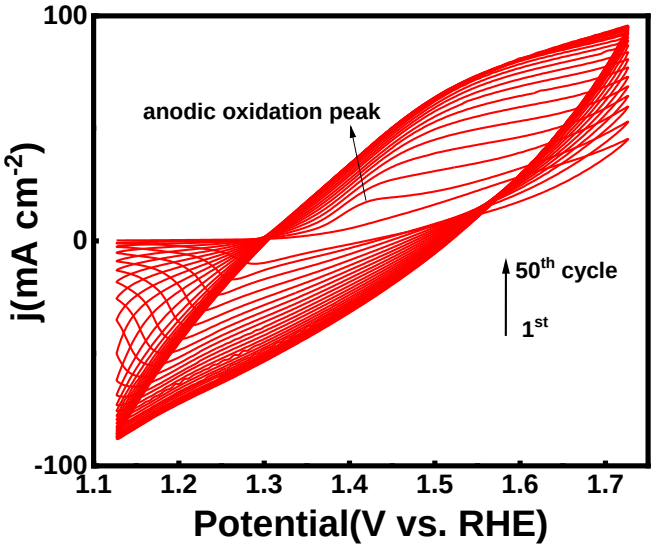

Fig. S6. Electro-chemical activation of NiMnCo MOF electrode.

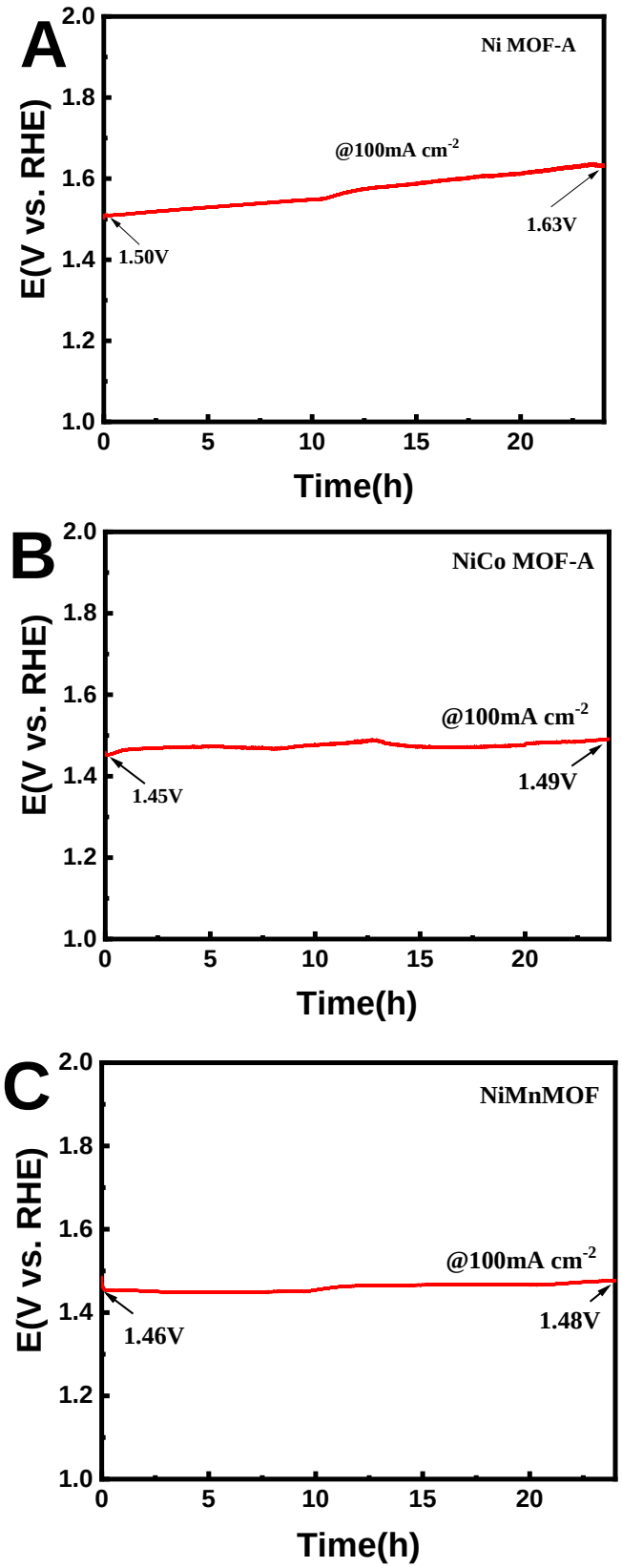

Fig. S7. Chronopotentiometric curves of Ni MOF-A (A), NiCo MOF-A (B) and NiMn MOF-A (C) at constant current density of 100 mA cm^{-2}.

Table S1. Comparison of UOR activity of NiMnCo MOF/NF with other catalysts reported.

Catalyst	Electrolyte	E_j=10(V)	Tafel slope mV dec^{-1}	Ref.
NiMnCo MOF/NF	**1.0 M KOH 0.33 M urea**	**1.29**	**46**	**This work**
$Fe_2P@Ni_xP$/NF	**1 M KOH 0.5 M urea**	**1.26**	**30**	**[1]**
CoFeCr LDH/NF	**1.0 M KOH 0.33 M urea**	**1.31**	**85**	**[2]**
O-NiMoP/NF	**1 M KOH 0.5 M urea**	**1.31**	**35**	**[3]**
Ni_2P/Fe_2P/NF	**1 M KOH 0.5 M urea**	**1.37**	**79**	**[4]**
Ni_3N/NF	**1 M KOH 0.5 M urea**	**1.34**	**41**	**[5]**
Ni-Co_2VO_4/NF	**1 M KOH 0.5 M urea**	**1.28**	**46**	**[6]**
NiO-NiPi	**1 M KOH 0.5 M urea**	**1.35**	**70.6**	**[7]**
P/Cr_{60}-$NiMoO_4$	**1.0 M KOH 0.33 M urea**	**1.33**	**32**	**[8]**
Fe-$Co_{0.85}Se$/FeCo-LDH	**1 M KOH 0.5 M urea**	**1.29**	**40**	**[9]**
Fe-$Ni_{12}P_5/Ni_3P$	**1 M KOH 0.5 M urea**	**1.3**	**82.8**	**[10]**
Ni_4N/Cu_3N/CF	**1 M KOH 0.5 M urea**	**1.34**	**56**	**[11]**

[1] T. Guo, X. Xu, X. Wang, J. Zhou, H. Wang, Z. Shi, M. Huang, Enabling the full exposure of $Fe_2P@Ni_xP$ heterostructures in tree-branch-like nanoarrays for promoted urea electrolysis at high current densities, Chem. Eng. J. 417 (2021) 128067. https://doi.org/10.1016/j.cej.2020.128067.

[2] Z. Wang, W. Liu, Y. Hu, M. Guan, L. Xu, H. Li, J. Bao, H. Li, Cr-doped CoFe layered double hydroxides: highly efficient and robust bifunctional electrocatalyst for the oxidation of water and urea, Appl. Catal. B 272 (2020) 118959. https://doi.org/10.1016/j.apcatb.2020.118959.

[3] H. Jiang, M. Sun, S. Wu, B. Huang, C.S. Lee, W. Zhang, Oxygen-incorporated NiMoP nanotube arrays as efficient bifunctional electrocatalysts for urea-assisted energy-saving hydrogen production in alkaline electrolyte, Adv. Funct. Mater. 31 (2021) 2104951.

https://doi.org/10.1002/adfm.202104951.

[4] L. Yan, Y. Sun, E. Hu, J. Ning, Y. Zhong, Z. Zhang, Y. Hu, Facile in-situ growth of Ni_2P/Fe_2P nanohybrids on Ni foam for highly efficient urea electrolysis, J. Colloid Interface Sci. 541 (2019) 279-286. https://doi.org/10.1016/j.jcis.2019.01.096.

[5] S. Hu, C. Feng, S. Wang, J. Liu, H. Wu, L. Zhang, J. Zhang, Ni_3N/NF as bifunctional catalysts for both hydrogen generation and urea decomposition, ACS Appl. Mater. Interfaces 11 (2019) 13168-13175. https://doi.org/10.1021/acsami.8b19052.

[6] M. Pan, G. Qian, T. Yu, J. Chen, L. Luo, Y. Zou, S. Yin, Ni modified Co_2VO_4 heterojunction with poor/rich-electron structure for overall urea-rich wastewater oxidation, Chem. Eng. J. 435 (2022) 134986. https://doi.org/10.1016/j.cej.2022.134986.

[7] X. Xu, T. Guo, J. Xia, B. Zhao, G. Su, H. Wang, M. Huang, A. Toghan, Modulation of the crystalline/amorphous interface engineering on Ni-P-O-based catalysts for boosting urea electrolysis at large current densities, Chem. Eng. J. 425 (2021) 130514. https://doi.org/10.1016/j.cej.2021.130514.

[8] Y. Li, H. Guo, Y. Zhang, R. Song, Cooperative phosphorus and chromium doping induced electronic and morphological dual modulation in $NiMoO_4$ hydrate for energy-efficient urea-assisted hydrogen production, Appl. Catal. B 341 (2024) 123296. https://doi.org/10.1016/j.apcatb.2023.123296.

[9] H. Yu, S. Zhu, Y. Hao, Y. Chang, L. Li, J. Ma, H. Chen, M. Shao, S. Peng, Modulating local interfacial bonding environment of heterostructures for energy-saving hydrogen production at high current densities, Adv. Funct. Mater. 33 (2023) 2212811. https://doi.org/10.1002/adfm.202212811.

[10] X. Xu, C. Zhang, J. Li, H. Liu, G. Su, Z. Shi, M. Huang, Redistributing interfacial charge density of $Ni_{12}P_5/Ni_3P$ via Fe doping for ultrafast urea oxidation catalysis at large current densities, Chem. Eng. J. 452 (2023) 139362. https://doi.org/10.1016/j.cej.2022.139362.

[11] J. Li, C. Yao, X. Kong, Z. Li, M. Jiang, F. Zhang, X. Lei, Boosting hydrogen production by electrooxidation of urea over 3D hierarchical Ni_4N/Cu_3N nanotube arrays, ACS Sustainable Chem. Eng. 7 (2019) 13278-13285. https://doi.org/10.1021/acssuschemeng.9b02510.

Table S2. Comparison of the electrocatalytic performance of NiMnCo MOF/NF||NiMnCo MOF/NF towards overall urea electrolysis in alkaline media with catalysts reported previously.

Anode//Cathode	Electrolyte	Cell voltage (V) (10 mA cm^{-2})	Ref.
NiMnCo MOF/NF (+/-)	**1 M KOH 0.33 M urea**	**1.38**	**This work**
FeNi-MOF NSs (+/-)	**1 M KOH 0.33 M urea**	**1.43**	**[12]**
NiCoMOF-Fc/NF (+/-)	**1 M KOH 0.33 M urea**	**1.41**	**[13]**
NiCo MOF/NF-EA // NiCoP/NF	**1 M KOH 0.33 M urea**	**1.447**	**[14]**
Ni-MOF-0.5/NF (+/-)	**1 M KOH 0.5 M urea**	**1.52**	**[15]**
MOF-Ni@MOF-Fe-S (+/-)	**1 M KOH 0.5 M urea**	**1.54**	**[16]**
PBA@MOF-Ni/Se (+/-)	**1 M KOH 0.5 M urea**	**1.49**	**[17]**
NiFe-MIL-53-NH_2 (+/-)	**1 M KOH 0.33 M urea**	**1.566**	**[18]**

[12] X. Zhang, X. Fang, K. Zhu, W. Yuan, T. Jiang, H. Xue, J. Tian, Fe-doping induced electronic structure reconstruction in Ni-based metal-organic framework for improved energy-saving hydrogen production via urea degradation, J. Power Sources 520 (2022) 230882. https://doi.org/10.1016/j.jpowsour.2021.230882.

[13] L. Xu, X. Wang, L. Zhang, H. Sun, X. Xie, Y. Zhang, B. Tan, R. Yuan, Carboxyferrocene modulated Ni/Co bimetallic metal-organic framework for highly efficient electrocatalysis of urea oxidation reaction, Electrochim. Acta 428 (2022) 140877. https://doi.org/10.1016/j.electacta.2022.140877.

[14] D. Wei, W. Tang, N. Ma, Y. Wang, NiCo bimetal organic frames derived well-matched electrocatalyst pair for highly efficient overall urea solution electrolysis, J. Alloys Compd. 874 (2021) 159945. https://doi.org/10.1016/j.jallcom.2021.159945.

[15] S. Zheng, Y. Zheng, H. Xue, H. Pang, Ultrathin nickel terephthalate nanosheet three-dimensional aggregates with disordered layers for highly efficient overall urea electrolysis, Chem. Eng. J. 395 (2020) 125166. https://doi.org/10.1016/j.cej.2020.125166.

[16] H. Xu, K. Ye, K. Zhu, J. Yin, J. Yan, G. Wang, D. Cao, Efficient bifunctional catalysts synthesized from three-dimensional Ni/Fe bimetallic organic frameworks for overall urea electrolysis, Dalton Trans. 49 (2020) 5646-5652. https://doi.org/10.1039/d0dt00605j.

[17] H. Xu, K. Ye, K. Zhu, Y. Gao, J. Yin, J. Yan, G. Wang, D. Cao, Hollow bimetallic selenide derived from a hierarchical MOF-based Prussian blue analogue for urea electrolysis, Inorg. Chem. Front. 8 (2021) 2788-2797. https://doi.org/10.1039/d1qi00230a.

[18] Z. Gao, Y. Wang, L. Xu, Q. Tao, X. Wang, Z. Zhou, Y. Luo, J. Yu, Y. Huang, Optimizing local charge distribution of metal nodes in bimetallic metal-organic frameworks for efficient urea oxidation reaction, Chem. Eng. J. 433 (2022) 133515. https://doi.org/10.1016/j.cej.2021.133515.