

## 1 **Supporting Information**

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3 Dual cation-modified hierarchical nickel hydroxide nanosheets arrays as  
4 efficient and robust electrocatalysts for urea oxidation reaction

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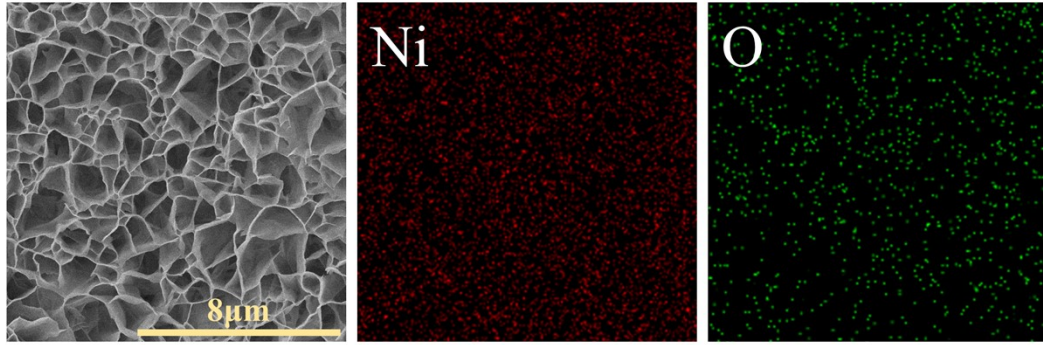
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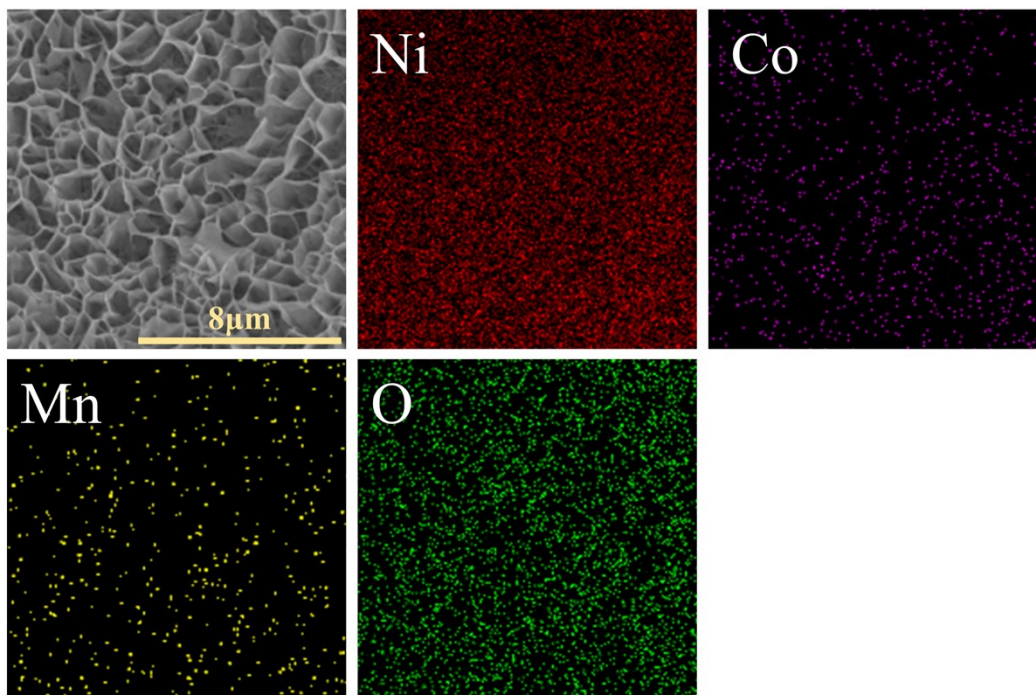


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22 Fig. S1. SEM image and EDS mapping spectrum of Ni(OH)<sub>2</sub>.

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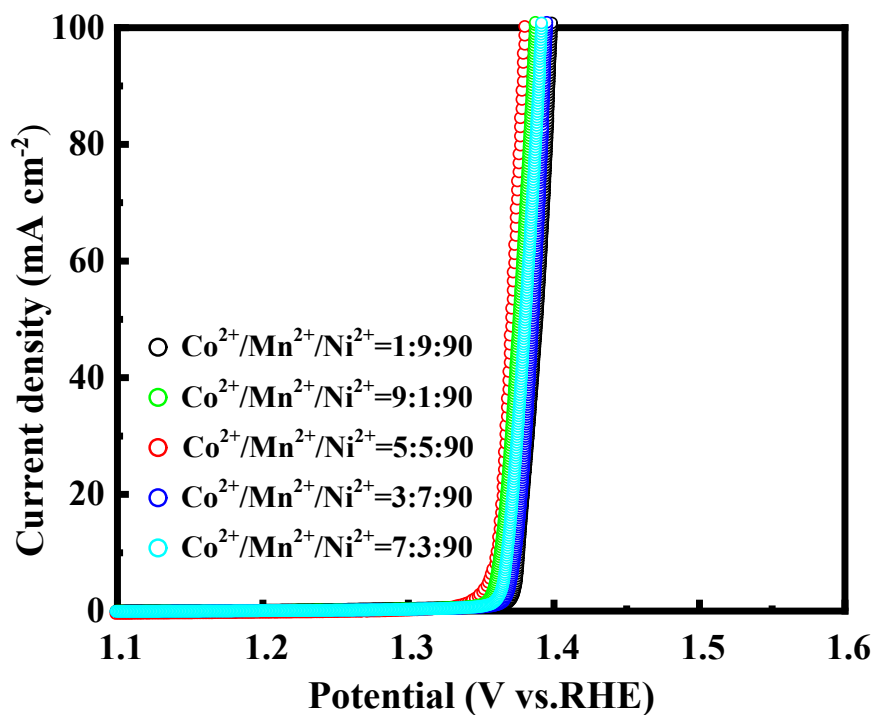
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26 Fig. S2. SEM image and EDS mapping spectrum of Co/Mn-Ni(OH)<sub>2</sub>.

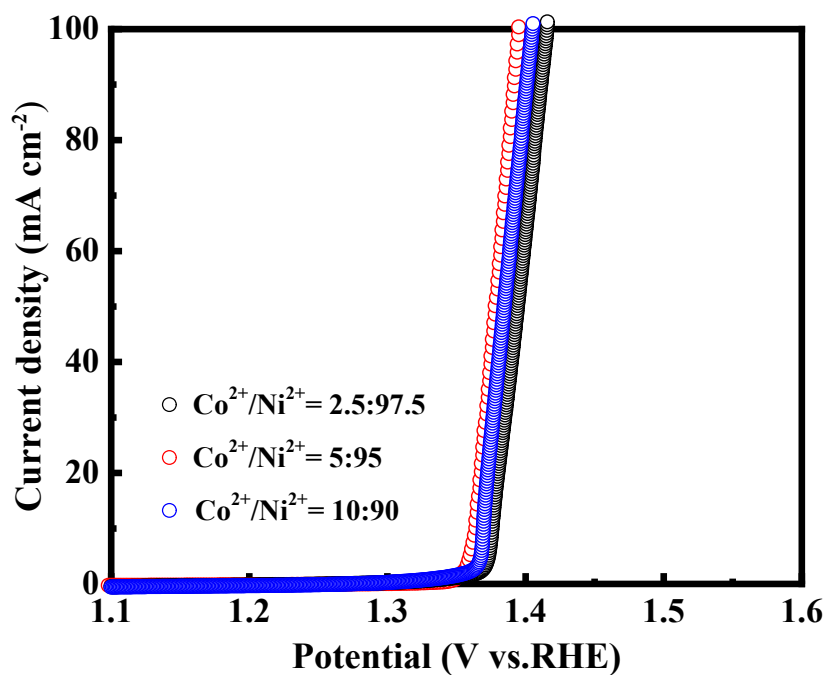
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30 Fig. S3. LSV curves of Co/Mn-Ni(OH)<sub>2</sub> catalysts prepared with different ratios of the  
 31 Co<sup>2+</sup>:Mn<sup>2+</sup>:Ni<sup>2+</sup> in the solution. The Co/Mn-Ni (OH)<sub>2</sub> catalysts prepared with the Co<sup>2+</sup>:  
 32 Mn<sup>2+</sup>: Ni<sup>2+</sup> ratios of 1:9:90, 9:1:90, 5:5:90, 3:7:90 and 7:3:90 in the solution require the  
 33 potential of 1.398 V, 1.387 V, 1.380 V 1.395 V and 1.391 V to achieve the current  
 34 density of 100 mA cm<sup>-2</sup>, respectively.

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37 Fig. S4. LSV curves of Co/Mn-Ni(OH)<sub>2</sub> catalysts prepared with different ratios of the  
 38 Co<sup>2+</sup>:Ni<sup>2+</sup> in the solution. The Co-Ni (OH)<sub>2</sub> catalysts prepared with the Co<sup>2+</sup>: Mn<sup>2+</sup>: Ni<sup>2+</sup>  
 39 ratios of 2.5:97.5, 5:95, 10:90 in the solution require the potential of 1.415 V, 1.395 V  
 40 and 1.405 V to achieve the current density of 100 mA cm<sup>-2</sup>, respectively.

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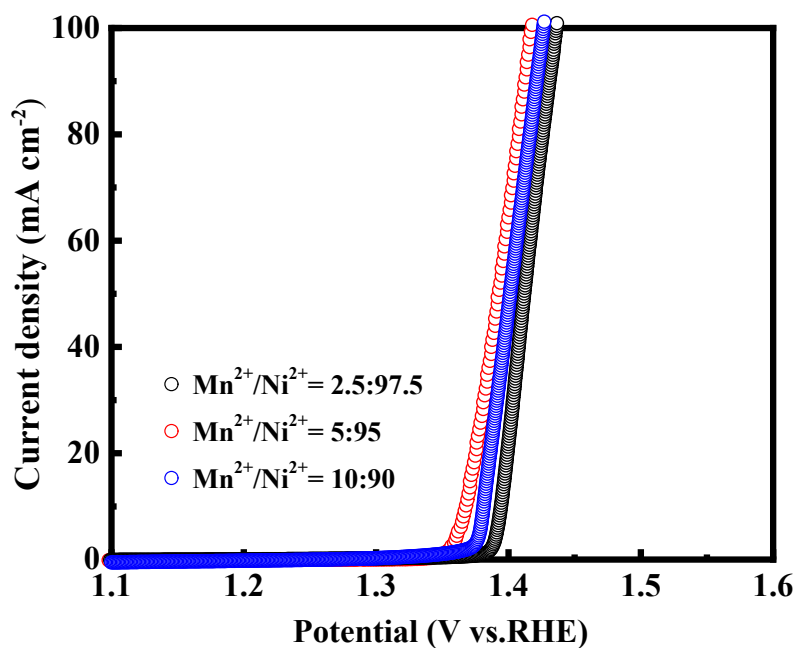
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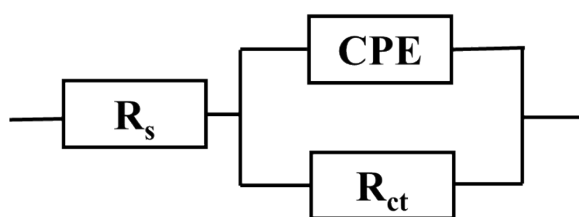
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49 Fig. S5. LSV curves of Mn-Ni(OH)<sub>2</sub> catalysts prepared with different ratios of the  
 50 Mn<sup>2+</sup>:Ni<sup>2+</sup> in the solution. The Mn-Ni (OH)<sub>2</sub> catalysts prepared with the Mn<sup>2+</sup>: Ni<sup>2+</sup>  
 51 ratios of 2.5:97.5, 5:95, 10:90 in the solution require the potential of 1.436 V, 1.418 V  
 52 and 1.427 V to achieve the current density of 100 mA cm<sup>-2</sup>, respectively.

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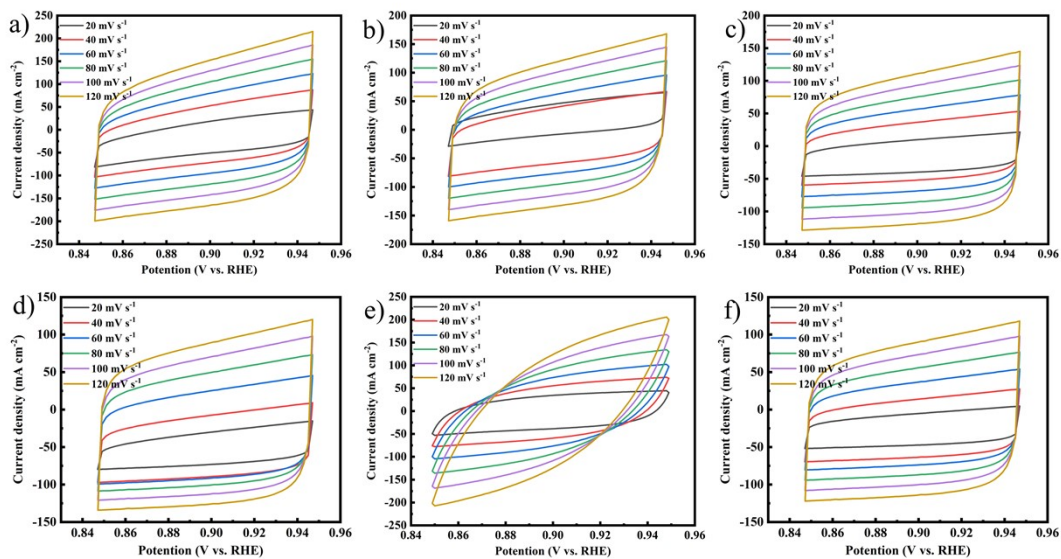
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57 Fig. S6. The equivalent circuit mode. R<sub>s</sub> represents the electrolyte resistance. CPE is  
 58 constant phase element (CPE). R<sub>ct</sub> is the charge transfer resistance at the interface  
 59 between the solid-liquid interfaces and is related to the kinetics of the catalytic reaction.



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61 Fig. S7. CV curves of different catalysts at different sweep speeds are as follows: a)

62 Co/Mn-Ni(OH)<sub>2</sub>, b) Co-Ni(OH)<sub>2</sub>, c) Mn-Ni(OH)<sub>2</sub>, d) Ni(OH)<sub>2</sub>, e) RuO<sub>2</sub>, f) NF.

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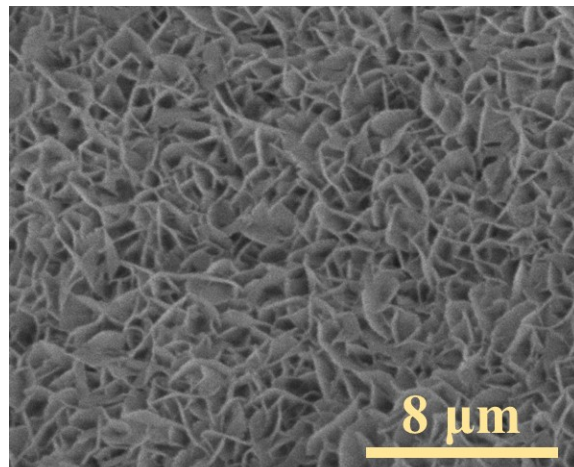
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Fig. S8. SEM image of the Co/Mn-Ni(OH)<sub>2</sub> after stability test.

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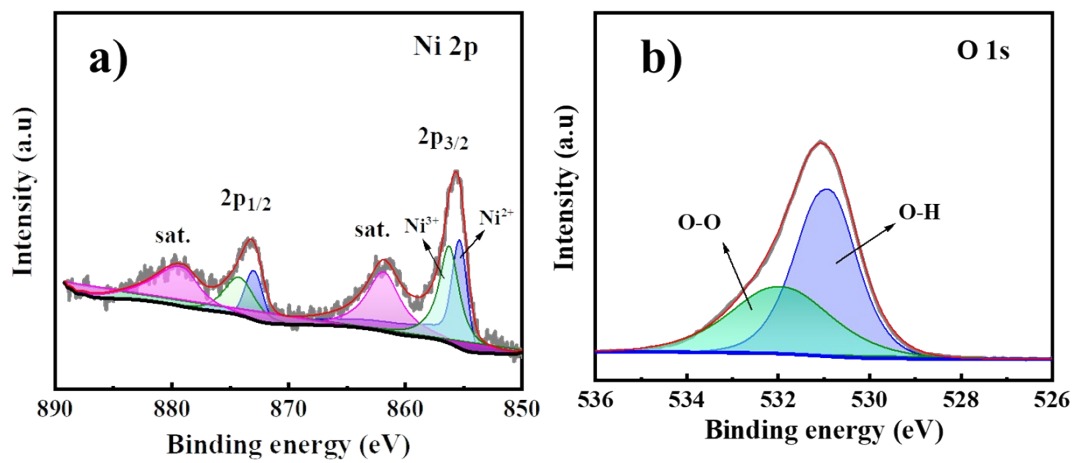
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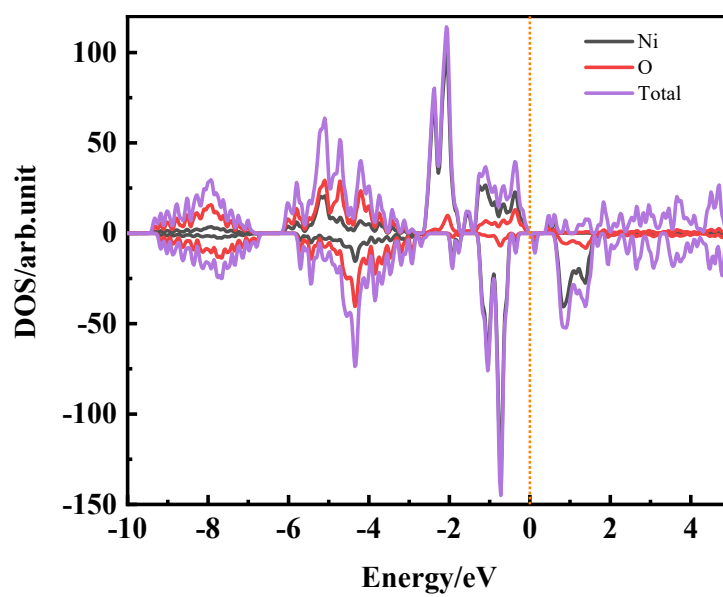
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88 Fig. S9. XPS spectra of a) Ni 2p and b) O 1s of the Co/Mn-Ni(OH)<sub>2</sub> after stability test.

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92 Fig. S10. The DOS of pure Ni(OH)<sub>2</sub> sample.

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94 Table. S1 Comparison of this work with other catalysts.

Materials	Electrolyte		Potential (V vs. RHE)	Tafel	Ref
	(KOH + urea)			slopes (mV dec <sup>-1</sup> )	
O <sub>vac</sub> -V-Ni(OH) <sub>2</sub> /NF	1 M	0.33 M	1.47 @100 mA cm <sup>-2</sup>	29.12	[1]
SS-NiCo	1 M	0.33 M	1.34 @100 mA cm <sup>-2</sup>	48.2	[2]
Ni/NiMoO <sub>x</sub>	1 M	0.33 M	1.355 @20 mA cm <sup>-2</sup>	24.3	[3]
Ni-S-Se	1 M	0.5 M	1.6 @100 mA cm <sup>-2</sup>	-	[4]
Ce-Ni <sub>2</sub> P	1 M	0.3 M	1.473 @100 mA cm <sup>-2</sup>	78.4	[5]
Ni, N-NiMoO <sub>4</sub> /NF	1 M	0.5 M	1.444 @100 mA cm <sup>-2</sup>	120	[6]
CoN/Ni(OH) <sub>2</sub>	1 M	0.5 M	1.39 @50 mA cm <sup>-2</sup>	64	[7]
Ni <sup>0</sup> -rich Ni/NiO	1 M	0.33 M	1.49 @10 mA cm <sup>-2</sup>	85	[8]
NiS/MoS <sub>2</sub> @FCP	1 M	0.4 M	1.43 @100 mA cm <sup>-2</sup>	70	[9]
NiCo-WO <sub>x</sub>	1 M	0.33 M	1.38 @100 mA cm <sup>-2</sup>	28	[10]
This work	1 M	0.33 M	1.38 @100 mA cm <sup>-2</sup>	35	

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## 96 Reference

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98 [1] Qin H, Ye Y, Li J, Jia W, Zheng S, Cao X, et al. Synergistic Engineering of Doping and

99 Vacancy in Ni(OH)<sub>2</sub> to Boost Urea Electrooxidation. *Advanced Functional Materials*. 2022;33.

100 [2] Zhang Z, Yang J, Liu J, Gu Z-G, Yan X. Sulfur-doped NiCo carbonate hydroxide with

101 surface sulfate groups for highly enhanced electro-oxidation of urea. *Electrochimica Acta*.

102 2022;426.

103 [3] Liu G, Sun Z, Liu D, Li Y, Zhang W. Enhancing the surface polarization effect via

104 Ni/NiMoO<sub>x</sub> heterojunction architecture for urea-assisted hydrogen generation. *Journal of*  
105 *Colloid and Interface Science*. 2023;629:1012-20.

106 [4] Chen N, Du Y-X, Zhang G, Lu W-T, Cao F-F. Amorphous nickel sulfoselenide for efficient  
107 electrochemical urea-assisted hydrogen production in alkaline media. *Nano Energy*.  
108 2021;81:105605.

109 [5] Xiong K, Yu L, Xiang Y, Zhang H, Chen J, Gao Y. Cerium-incorporated Ni<sub>2</sub>P nanosheets  
110 for enhancing hydrogen production from overall water splitting and urea electrolysis. *Journal*  
111 *of Alloys and Compounds*. 2022;912:165234.

112 [6] Wang T, Wu H, Feng C, Ding Y, Mei H. Ni, N - codoped NiMoO<sub>4</sub> grown on 3D nickel  
113 foam as bifunctional electrocatalysts for hydrogen production in urea - water electrolysis.  
114 *Electrochimica Acta*. 2021;391:138931.

115 [7] Cheng Y, Liao F, Dong H, Wei H, Geng H, Shao M. Engineering CoN/Ni(OH)<sub>2</sub>  
116 heterostructures with improved intrinsic interfacial charge transfer toward simultaneous  
117 hydrogen generation and urea-rich wastewater purification. *Journal of Power Sources*.  
118 2020;480:229151.

119 [8] Zhang B, Wang S, Ma Z, Qiu Y. Ni<sup>0</sup>-rich Ni/NiO nanocrystals for efficient water-  
120 to-hydrogen conversion via urea electro-oxidation. *Applied Surface Science*. 2019;496:143710.

121 [9] Zheng Y, Tang P, Xu X, Sang X. POM derived UOR and HER bifunctional NiS/MoS<sub>2</sub>  
122 composite for overall water splitting. *Journal of Solid State Chemistry*. 2020;292.

123 [10] Roh H, Lim C, Kim D, Park T, Yong K. Hierarchically nanostructured Ni(Mo,Co)-WO<sub>x</sub>  
124 electrocatalysts for highly efficient urea electrolysis. *Applied Surface Science*.

125 2023;610:155520.

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