Supplementary Material

Enabling high loading of well-dispersed Ni_2CoP_2 catalysts on 3D-printed electrode for efficient electrocatalysis

Meiwen Peng[a⊥], Bo Zhao[a⊥], Danli Shi[a], Yawen Wang[a], Dong Li[a], Wenkai Liang[a], He Yang[a], Zhiqiang Liang[a], Yinghui Sun[b]*, and Lin Jiang[a]*

[a]Institute of Functional Nano & Soft Materials Laboratory (FUNSOM), Jiangsu Key Laboratory for Carbon-Based Functional Materials & Devices, Soochow University, Suzhou 215123, China

[b]Innovation Center for Chemical Sciences, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou, 215123, China

*Correspondence and requests for materials should be addressed to Lin Jiang (E-mail: ljiang@suda.edu.cn) or to Yinghui Sun (E-mail: yinghuisun@suda.edu.cn)

⊥These authors contributed equally to this work.

Supplementary Figures

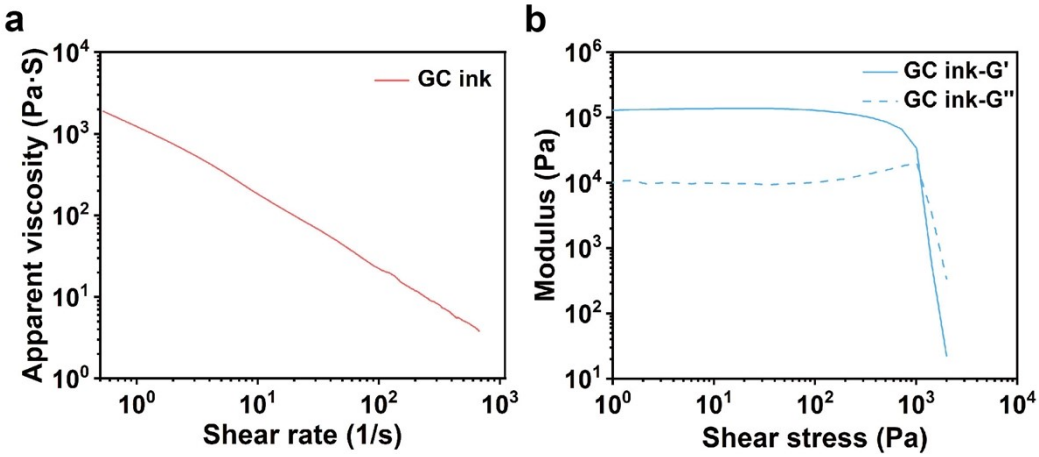

Fig. S1. (a) Apparent viscosity as a function of shear rate for GC inks. (b) Storage modulus (G') and loss modulus (G'') as a function of shear stress for GC ink.

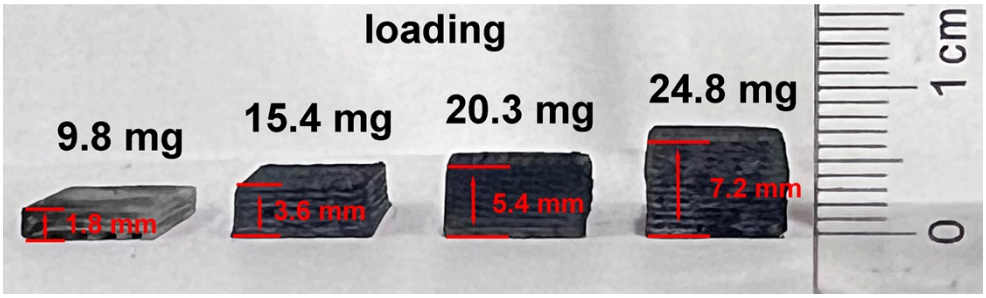

Fig. S2. The optical photo of different 3DP GC electrodes with 6, 12, 18, and 24 layers.

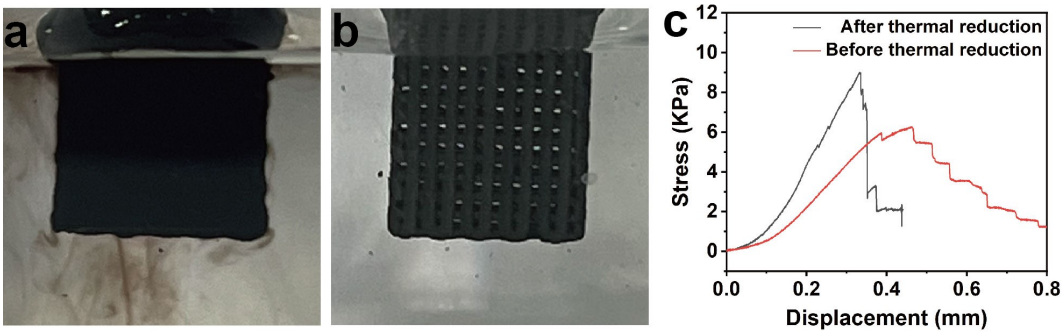

Fig. S3. (a) The 3DP GC electrode before thermal reduction, (b) The 3DP GC electrode after thermal reduction, (c) Flexural stress.

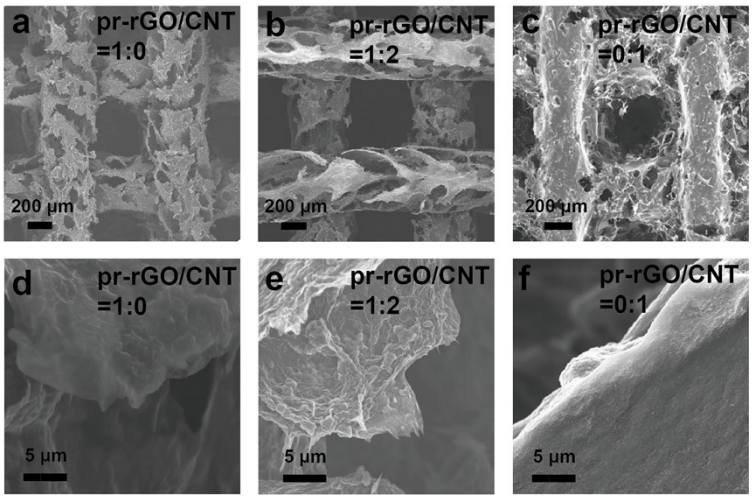

Fig. S4. SEM characterization of three electrodes with different GC proportions (a, d) pr-rGO/CNT=1:0, (b, e) pr-rGO/CNT=1:2, (c, f) pr-rGO/CNT=0:1.

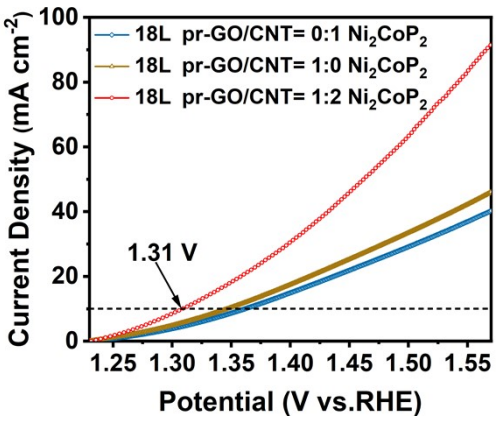

Fig. S5. The polarization curves of 18L-3DP electrodes with different ratios of CNT and pr-GO.

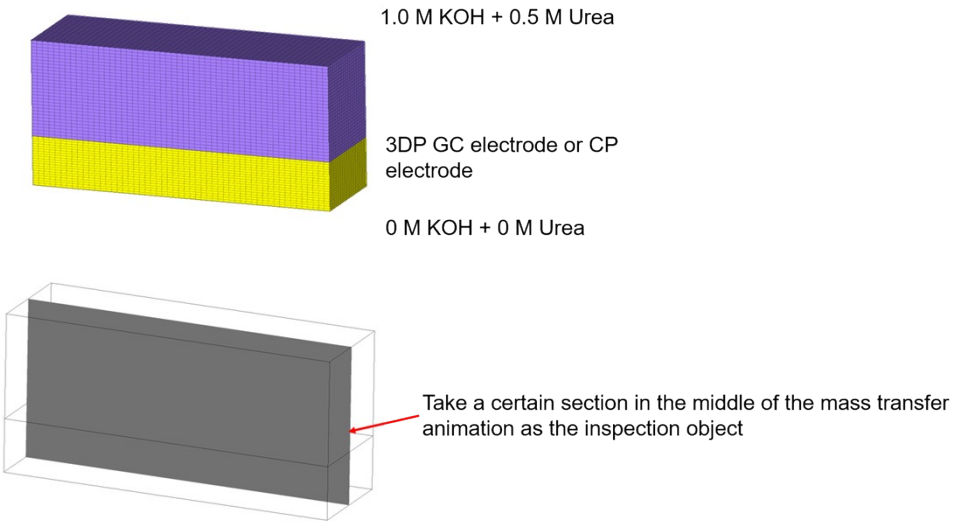

Fig. S6. The mass transport model.

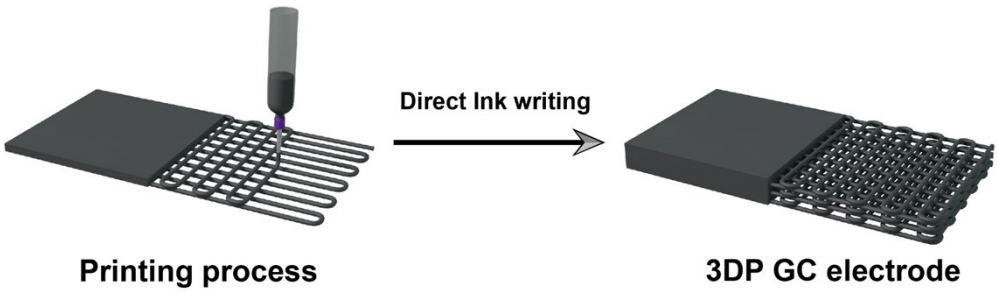

Fig. S7. The printing process of 3DP GC

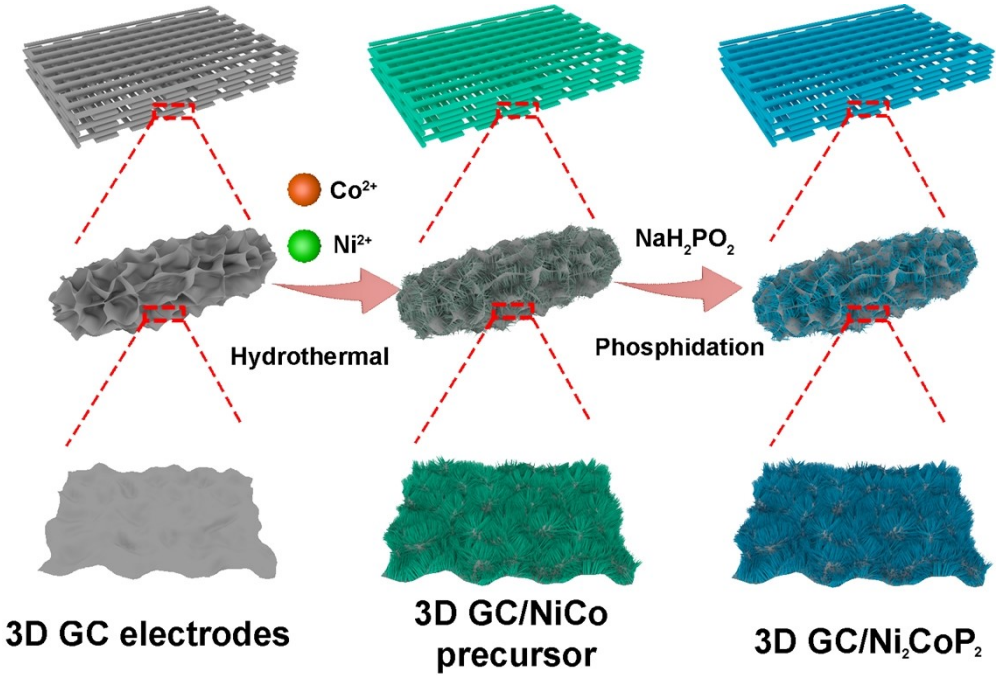

Fig. S8. The preparation of 3DP GC/Ni_2CoP_2.

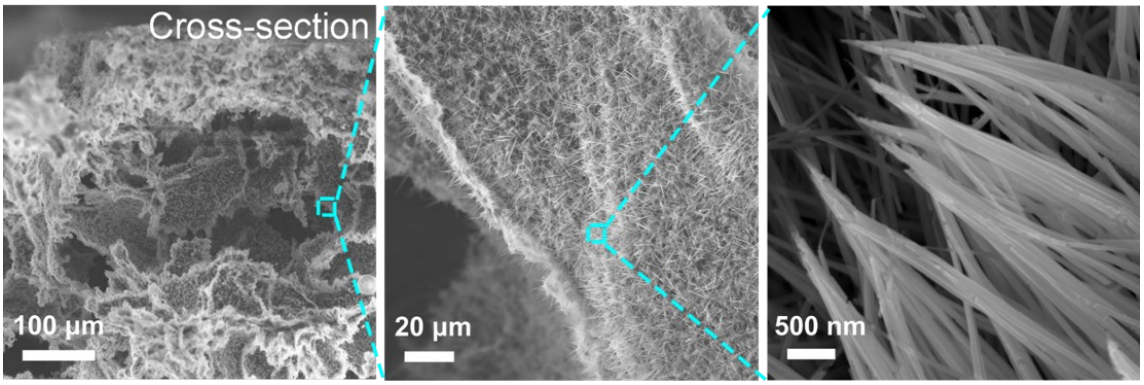

Fig. S9. The SEM images of 3DP GC/Ni_2CoP_2 (cross-section).

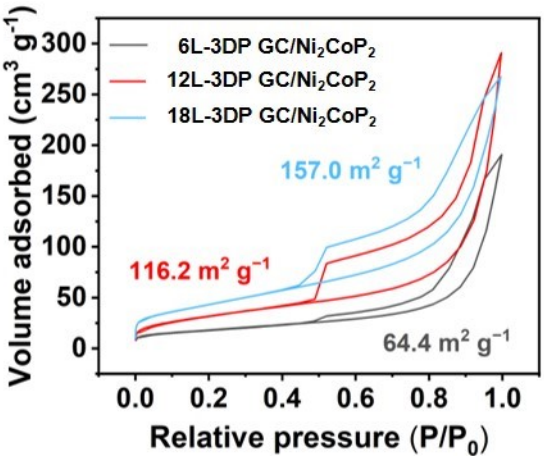

Fig. S10. N_2 sorption isotherm of 6L, 12L, 18L-3DP GC/Ni_2CoP_2.

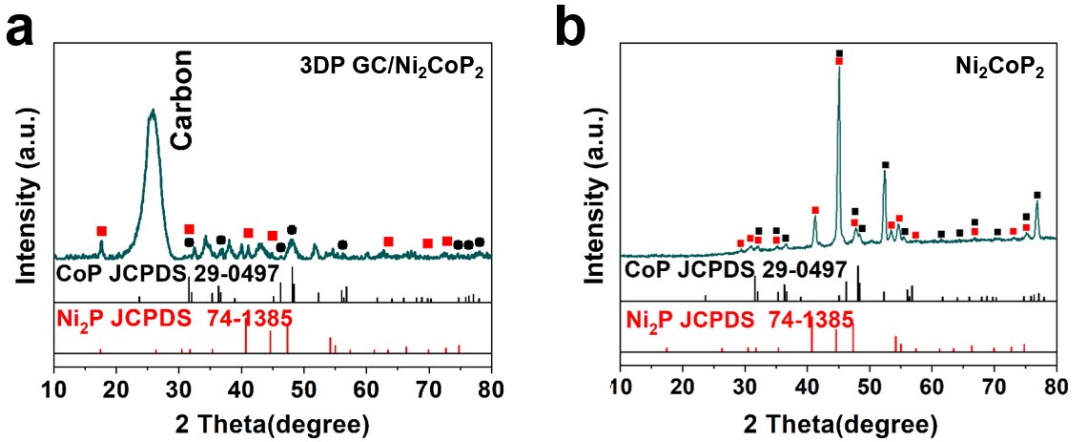

Fig. S11. XRD spectrum of a) 3DP GC/Ni_2CoP_2, b) Ni_2CoP_2. (red square for Ni_2P, black square for CoP)

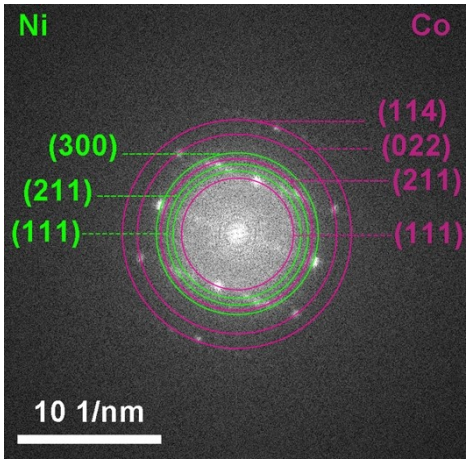

Fig. S12. The SAED pattern of Ni_2CoP_2.

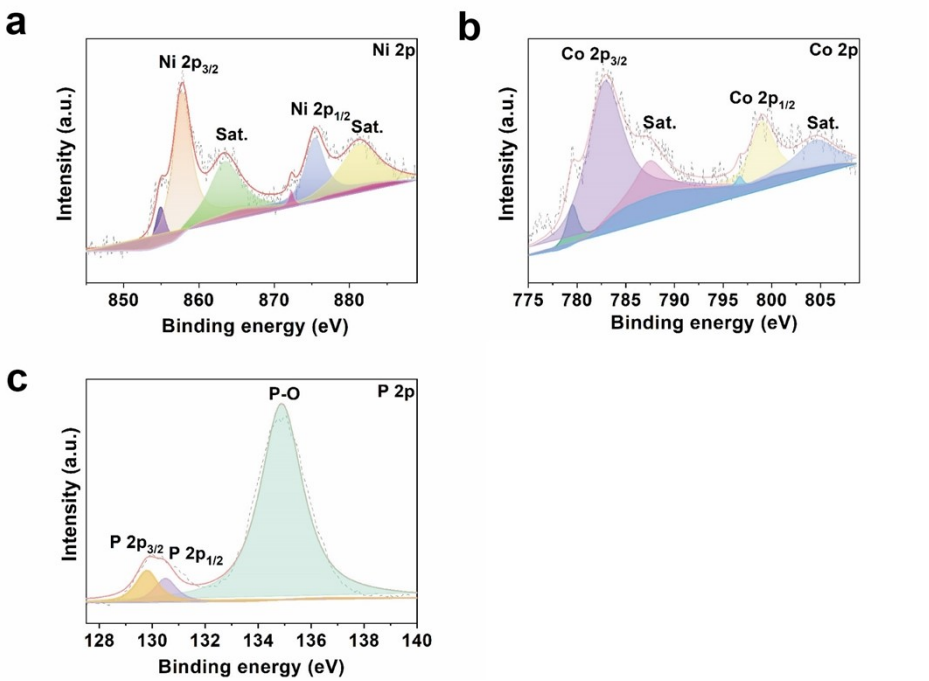

Fig. S13. High-resolution XPS spectra of 3DP GC/Ni_2CoP_2, a) Ni 2p, b) Co 2p, c) P 2p.

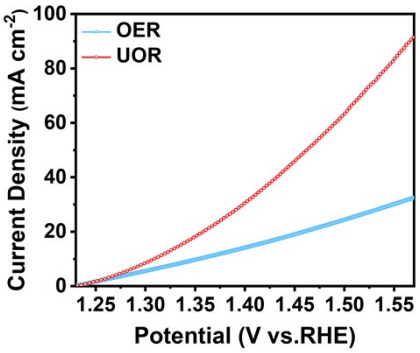

Fig. S14. UOR and OER LSV curves of 18L-3DP GC/Ni_2CoP_2.

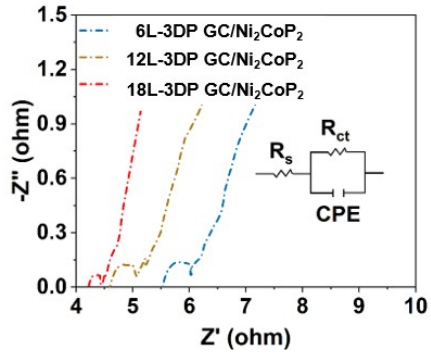

Fig. S15. Nyquist plots of different electrocatalysts for UOR.

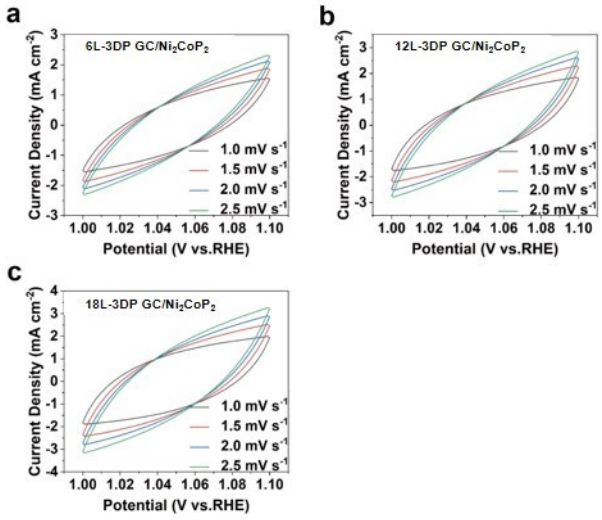

Fig. S16. CV curves of 3DP GC/Ni_2CoP_2 with different layers with different rate from 1 to 2.5 mV s^{-1} for UOR.

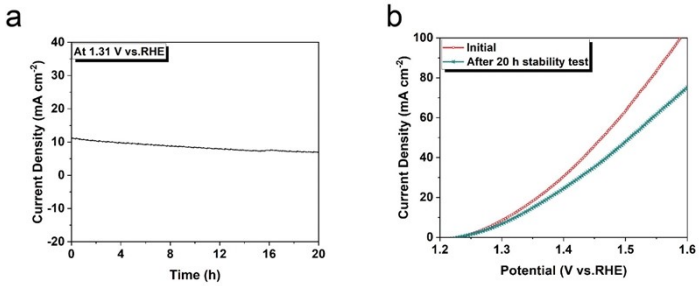

Fig. S17. a) Chronopotentiometry plots of 18L-3DP GC/Ni_2CoP_2 obtained at a constant potential of 1.31 V for UOR. b) LSV curves of 18L-3DP GC/Ni_2CoP_2 before and after 20 h stability for UOR.

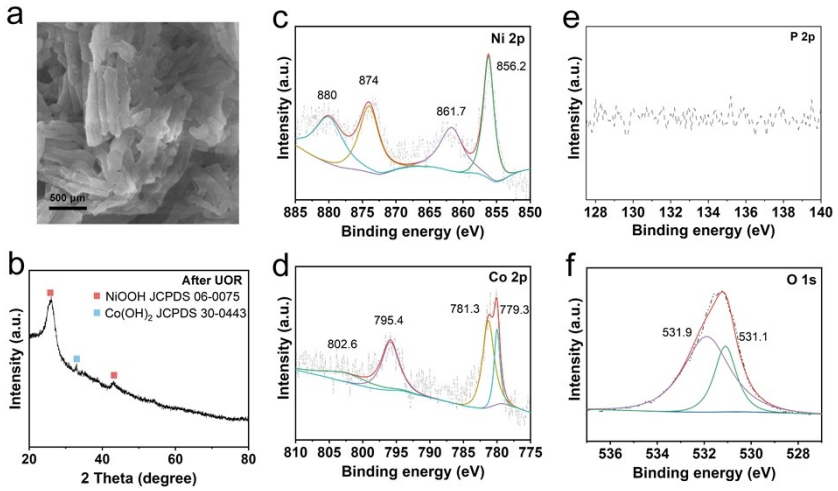

Fig. S18. a) The SEM of Ni_2CoP_2 after UOR, b) The XRD of Ni_2CoP_2 after UOR, c-f) The XPS of Ni_2CoP_2 after UOR.

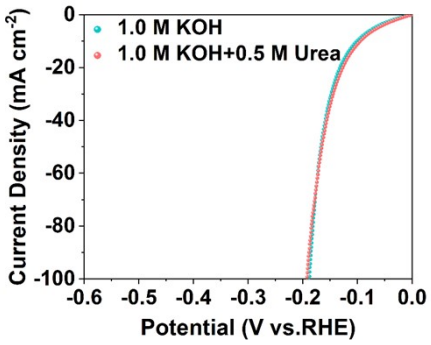

Fig. S19. HER LSV curves of 18L-3DP GC/Ni_2CoP_2 in 1.0 M KOH and 1.0 M KOH with 0.5 M urea.

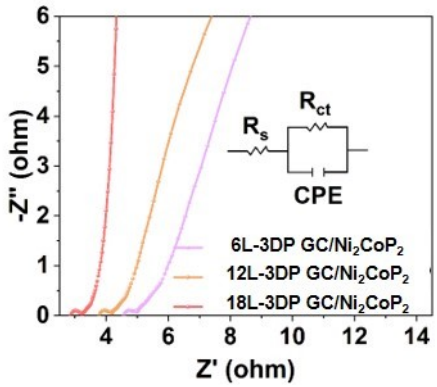

Fig. S20. Nyquist plots of different electrocatalysts for the HER.

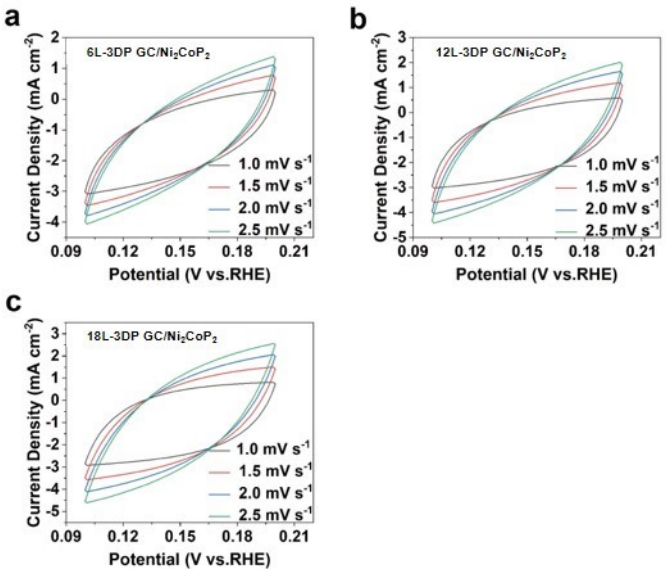

Fig. S21. CV curves of 3DP GC/Ni_2CoP_2 with different layers with different rate from 1 to 2.5 mV s^{-1} for HER.

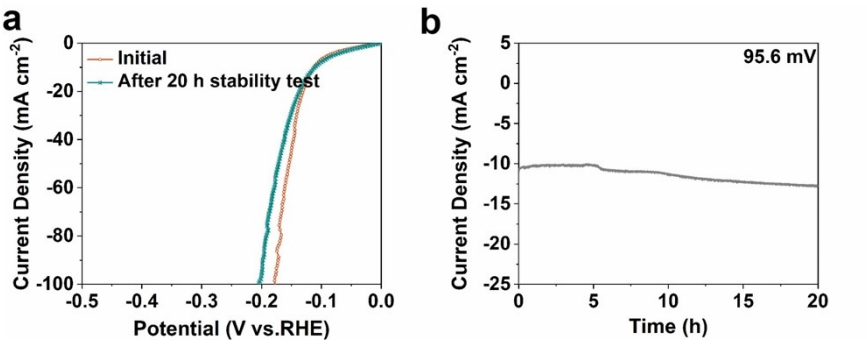

Fig. S22. a) LSV curves of 18L-3DP GC/Ni_2CoP_2 before and after 20 h stability test for the HER. b) Chronopotentiometry plots of 18L-3DP GC/Ni_2CoP_2 obtained at a constant potential of 0.0956 V for HER.

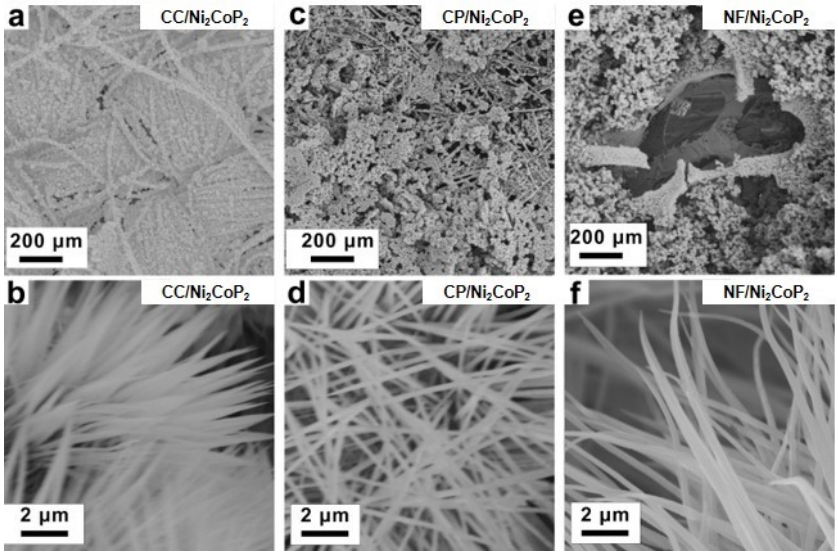

Fig. S23. The SEM images of Ni_2CoP_2 on (a,b) CC, (c,d) CP, (e,f) NF.

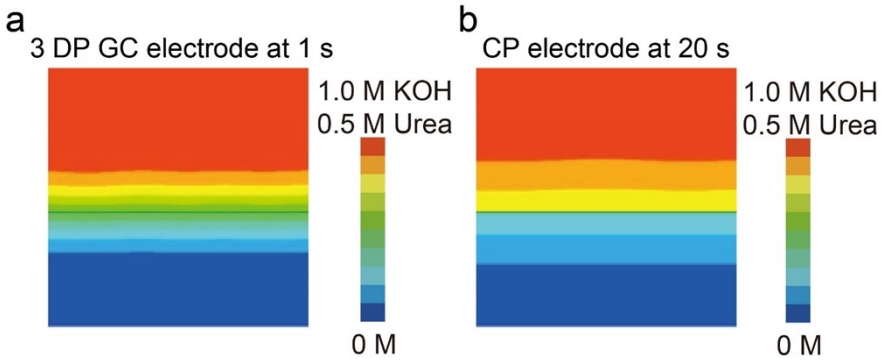

Fig. S24. Simulation of 1.0 M KOH + 0.5 M urea mass transfer under different 3D structured electrodes. a) 3DP GC electrode. b) CP electrode.

Table S1. The corresponding EIS parameters of the 6L-3DP GC/Ni_2CoP_2, 12L-3DP GC/Ni_2CoP_2 and 18L-3DP GC/Ni_2CoP_2 for UOR.

	18L-3DP GC/Ni_2CoP_2	**12L-3DP GC/Ni_2CoP_2**	**6L-3DP GC/Ni_2CoP_2**
R_s (Ω cm^2)	4.22	4.60	5.52
R_{ct} (Ω cm^2)	0.24	0.52	0.59

Table S2. The corresponding EIS parameters of the 6L-3DP GC/Ni_2CoP_2, 12L-3DP GC/Ni_2CoP_2 and 18L-3DP GC/Ni_2CoP_2 for HER.

	18L-3DP GC/Ni_2CoP_2	**12L-3DP GC/Ni_2CoP_2**	**6L-3DP GC/Ni_2CoP_2**
R_s (Ω cm^2)	2.82	3.68	4.65
R_{ct} (Ω cm^2)	0.42	0.57	0.69

Table S3. Comparison of UOR performance of 3DP GC/Ni_2CoP_2 with Ni, Co-based electrocatalysts. (*j*: current density; E: potential)

Catalysts	*j* (mA cm^{-2})	E (V)	Reference
a-MoS_2/CoS/$Co_{0.85}Se$ HNTs	50	1.38	*Nanoscale*, 2020, **12**, 991
Ni_2P/Fe_2P/NF	10	1.36	*J. Colloid Interf. Sci.,* 2019, **541**, 279-286
Co-Ni-S@NF	10	1.31	*J. Mater. Chem. A*, 2022, **10**, 24137
Co-V-NiS_2	10	1.35	*ACS Catal.,* 2022, **12**, 569-579
Co-$NiMoO_4$-Ar	10	1.324	*J. Mater. Chem. A,* 2022, **10**, 16825
Ni(OH)S/NF	10	1.34	*Appl. Catal. B Environ.,* 2022, **312**, 121389
NC-FNCP	10	1.37	*Nano Res.*, 2022, **15**, 1916-1925
CoNi LDH	10	1.32	*ACS Appl. Mater. Interfaces,* 2022, **14**, 16222-16232
Ni_3S_2/NF	10	1.34	*ACS Appl. Mater. Interfaces,* 2021, **13**, 35709-35718
3DP GC/Ni_2CoP_2	**10**	**1.31**	**This work**

Table S4 Comparison of HER performance of 3DP GC/Ni_2CoP_2 with Ni, Co-based electrocatalysts. (*j*: current density; η: overpotential)

Catalysts	*j* (mA cm^{-2})	η (mV)	Reference
a-MoS_2/CoS/$Co_{0.85}Se$ HNTs	10	127	*Nanoscale*, 2020, **12**, 991
Ni_2P/Fe_2P/NF	10	115	*J. Colloid Interf. Sci.,* 2019, **541**, 279-286
Ni-Co-P HNBs	10	107	*Energy Environ. Sci.,* 2018, **11**, 872
Fe-CoP HTPAs	10	98	*Small,* 2018, **14**, 1704233
NiCoP/NF	10	95	*J Mater. Chem. A,* 2023, **11**, 1256
NiCoP-90	10	93	*Adv. Energy Mater.,* 2023, **12**, 2300499
$Ni_{0.2}S/Cu_5FeS_4$	10	140	*J. Colloid Interf. Sci.,* 2020, **578**, 668-676
r-NiS/h-NiS	10	101	*J. Colloid Interf. Sci.,* 2023, **633**, 640-648
Ni NDs_{45}	10	204	*Mol. Catal.,* 2021, **516**, 112006
$Co_{0.9}Ni_{0.1}Se$ with vacancies	10	185.7	*Mol. Catal.,* 2022, **525**, 112339
Ni-SA/NC	10	102	*Angew. Chem. Int. Ed.,* 2020, **59**, 22743-22748
$NiCo_2$-P	10	183	*Adv. Mater.,* 2020, **33**, 2003846
HC NiCo/C	10	99	*ACS Appl. Mater. Interfaces,* 2021, **13**, 9932-9941
NiCo DASs/N-C	10	189	*Adv. Funct. Mater.,* 2023, **33**, 2210867
NiCoO-NiCo/C	10	123	*Appl. Catal. B Environ.,* 2021, **292**, 120170
3DP GC/Ni_2CoP_2	10	95.6	This work

Video S1. Electrolyte transmission behaviour of 3DP GC electrode.

Video S2. Electrolyte transmission behaviour of CP electrode.