Supporting Information

Ru dopants induced tensile strain in Ni_2P for efficient urea-assisted water decomposition at an ampere-level current density

Mengmeng Wang[a,b], Yunmei Du[a,b,*], Shuangshuang Li[a,b], Yuanxiang Gu[b] and Lei Wang[a,c,*]

[a] Key Laboratory of Eco-chemical Engineering, Ministry of Education, International Science and Technology Cooperation Base of Eco-chemical Engineering and Green Manufacturing, Qingdao University of Science and Technology, Qingdao 266042, P. R. China.

[b] Shandong Engineering Research Center for Marine Environment Corrosion and Safety Protection, College of Environment and Safety Engineering, Qingdao University of Science and Technology, Qingdao 266042, P. R. China.

[c] College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Qingdao 266042, China.

*E-mail: duyunmeiqust@163.com (Yunmei Du); inorchemwl@126.com (Lei Wang)

Figures and Tables

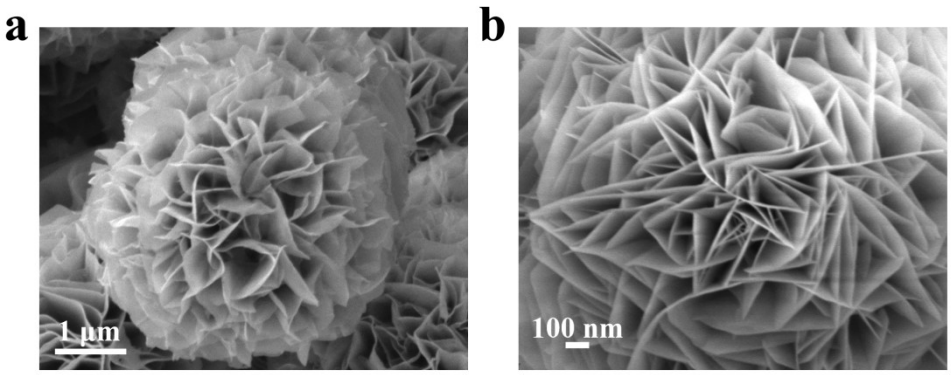

Figure S1. SEM image of N-$Ni(OH)_2$.

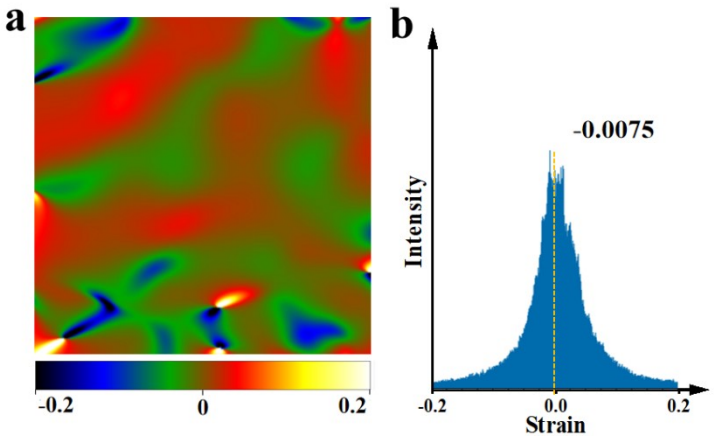

Figure S2. a) The exy strain component using geometric phase analysis (GPA) algorithm, and b) histogram of strain distribution of Ru-Ni_2P@CN.

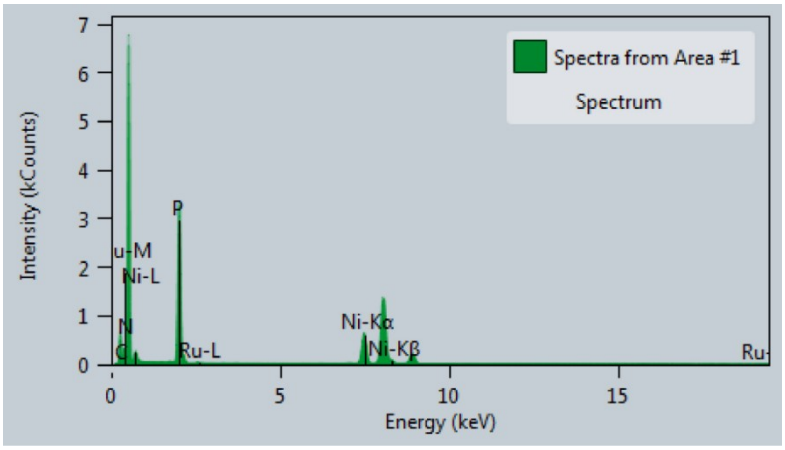

Figure S3. EDX of Ru-Ni_2P@CN catalyst.

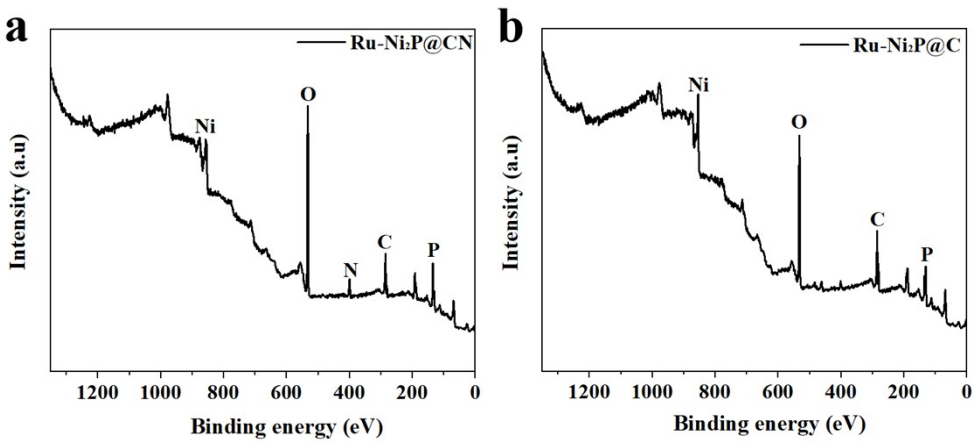

Figure S4. XPS measured the spectra of Ru-Ni_2P@CN and Ru-Ni_2P@C.

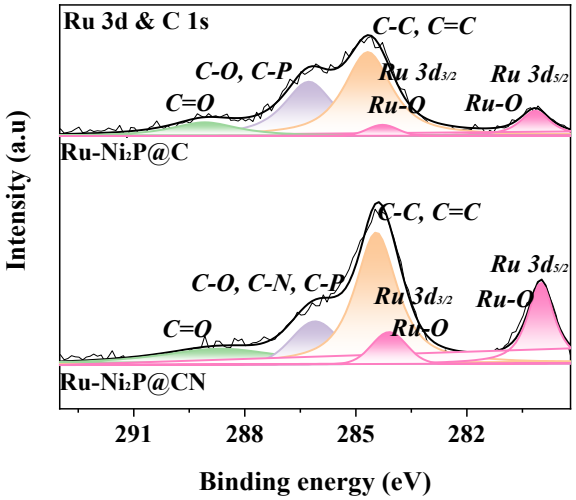

Figure S5. XPS measured the spectra of Ru-Ni_2P@CN and Ru-Ni_2P@C.

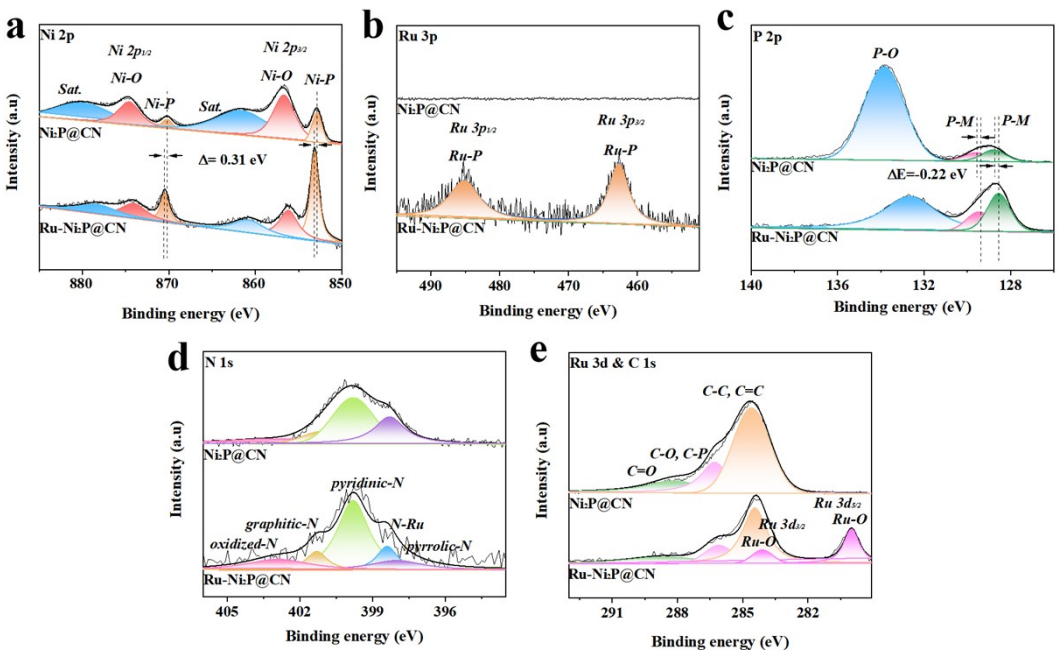

Figure S6. High-resolution spectra of (a) Ni 2p. (b) Ru 3p. (c) P 2p. (d) N 1s. (e) Ru 3d & C 1s.

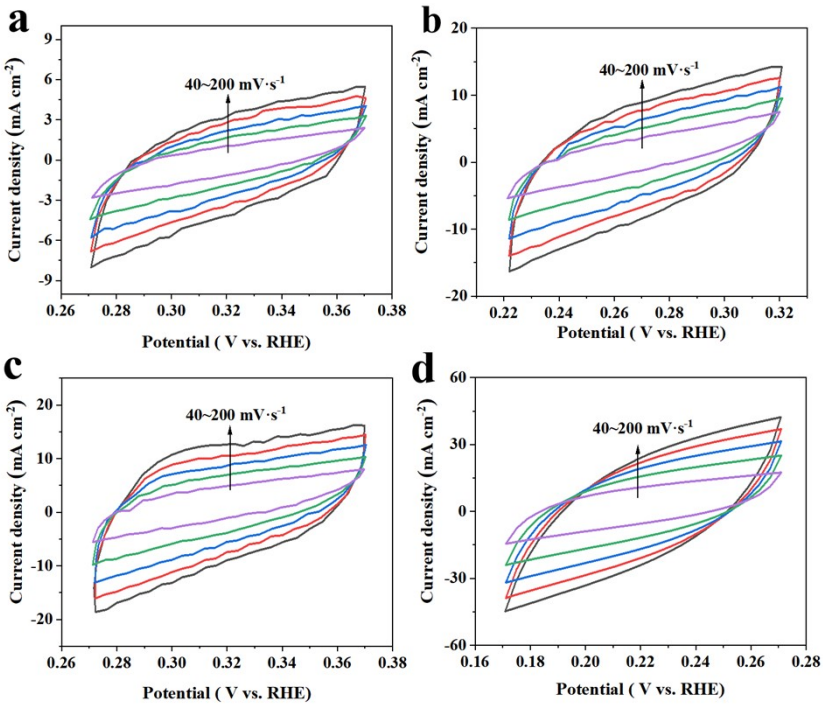

Figure S7. a) CV curves of the non-faradic region for Ni_2P@CN, (b) Ru-Ni_2P, (c) Ru-Ni_2P@CN and (d) Ru-Ni_2P@C.

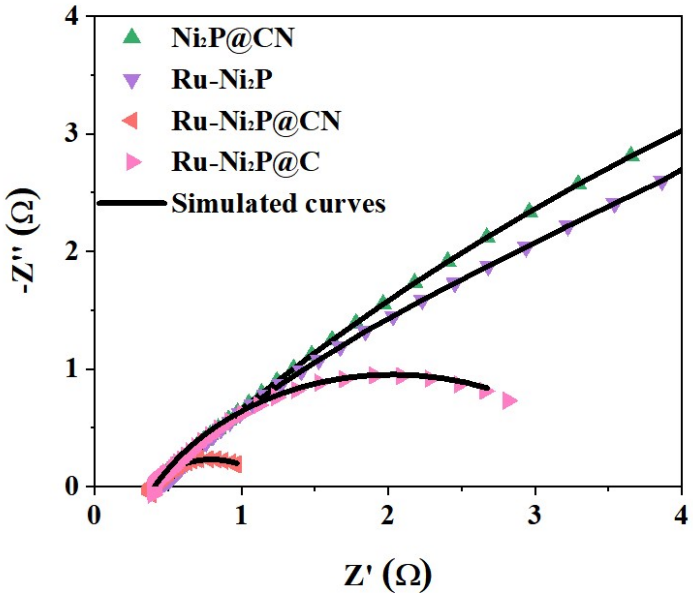

Figure S8. Nyquist and Bode plots for Ni_2P@CN, Ru-Ni_2P, Ru-Ni_2P@CN and Ru-Ni_2P@C in 1.0 M KOH.

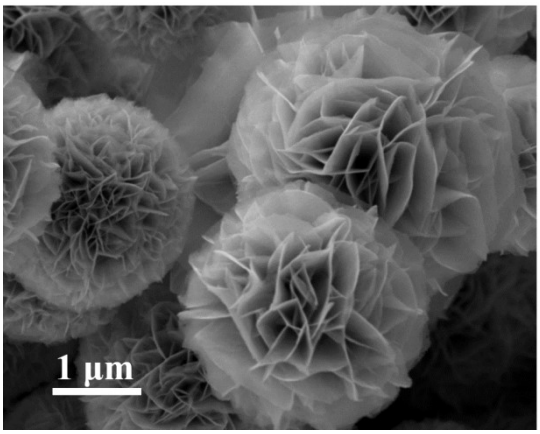

Figure S9. SEM of Ru-Ni_2P@CN after HER.

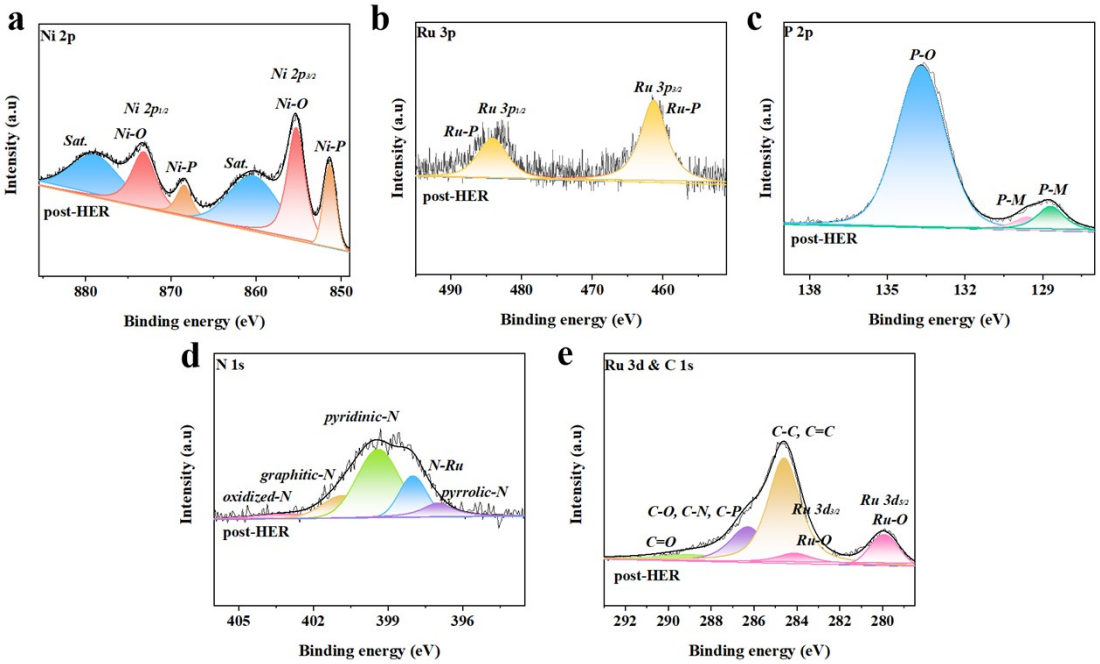

Figure S10. XPS spectra of the Ru-Ni_2P@CN after HER stability test: (a) Ni 2p, (b) Ru 3p, (c) P 2p, (d) N 1s, and (e) Ru 3d & C 1s spectrum.

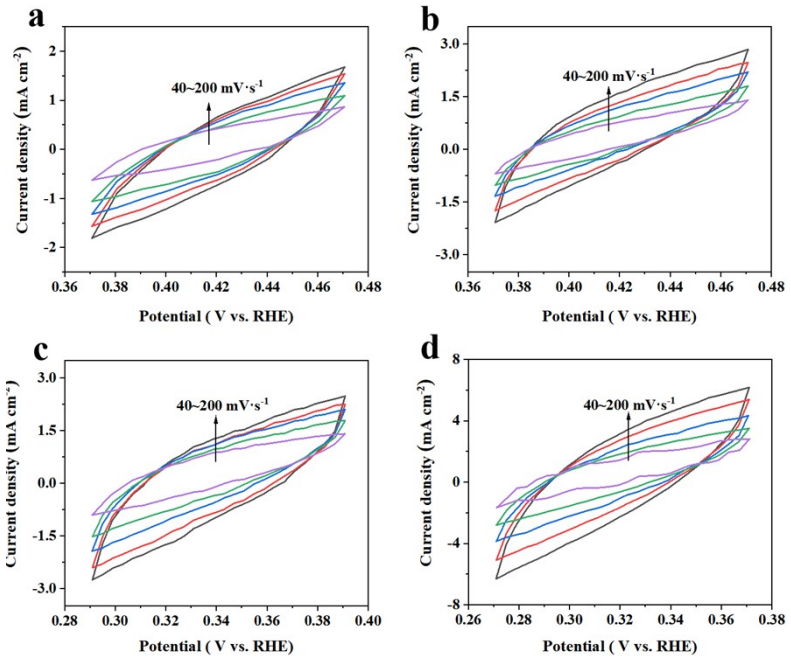

Figure S11. a) CV curves of the non-faradic region for Ni_2P@CN, (b) Ru-Ni_2P, (c) Ru-Ni_2P@CN and (d) Ru-Ni_2P@C

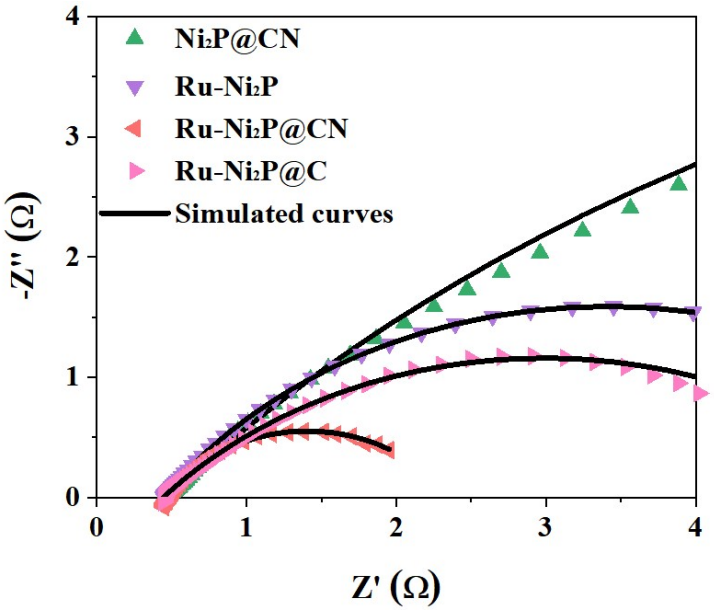

Figure S12. Nyquist and Bode plots for Ni_2P@CN, Ru-Ni_2P, Ru-Ni_2P@CN and Ru-Ni_2P@C in 1.0 M KOH and 0.5 M urea.

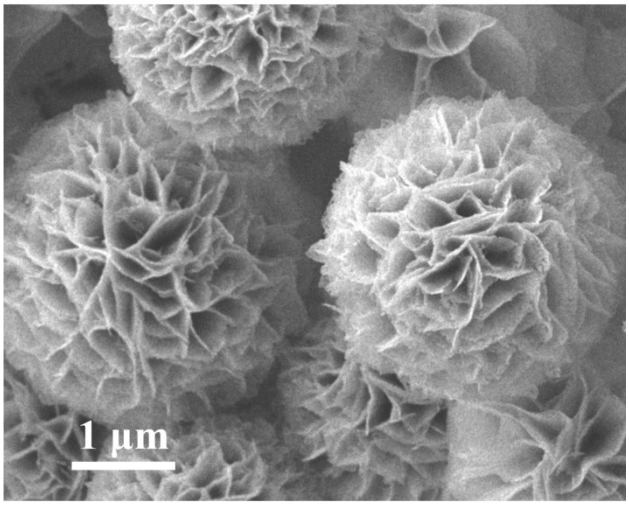

Figure S13. SEM of Ru-Ni_2P@CN after UOR.

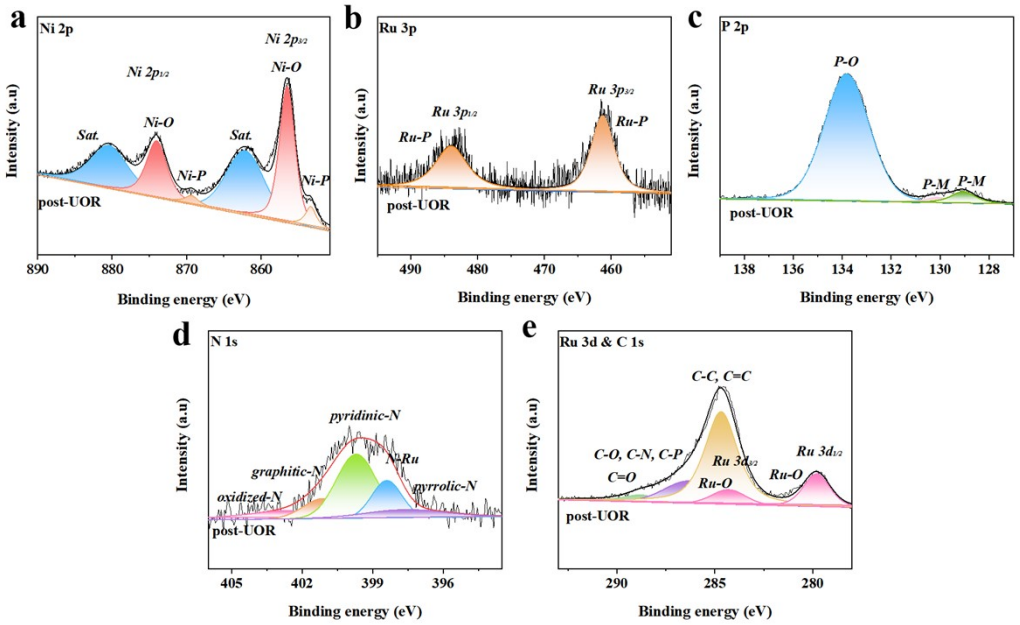

Figure S14. XPS spectra of the Ru-Ni_2P@CN after UOR stability test: (a) Ni 2p, (b) Ru 3p, (c) P 2p, (d) N 1s, and (e) Ru 3d & C 1s spectrum.

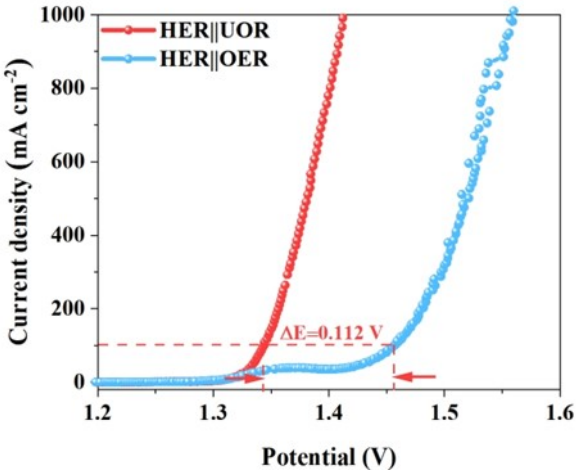

Figure S15. Electrocatalytic overall water splitting performance of Ru-Ni_2P@CN||Ru-Ni_2P@CN in 0.5 M urea solution was compared with that of Ru-Ni_2P@CN||Ru-Ni_2P@CN in 1.0 M KOH.

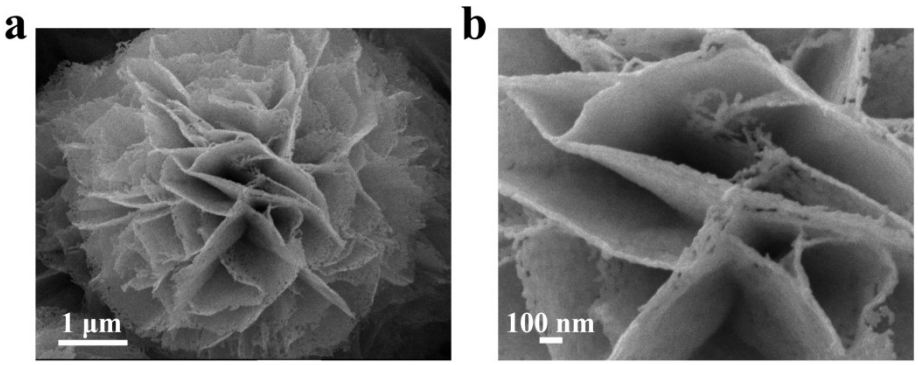

Figure S16. SEM image of Ru-Ni_2P@CN-5.

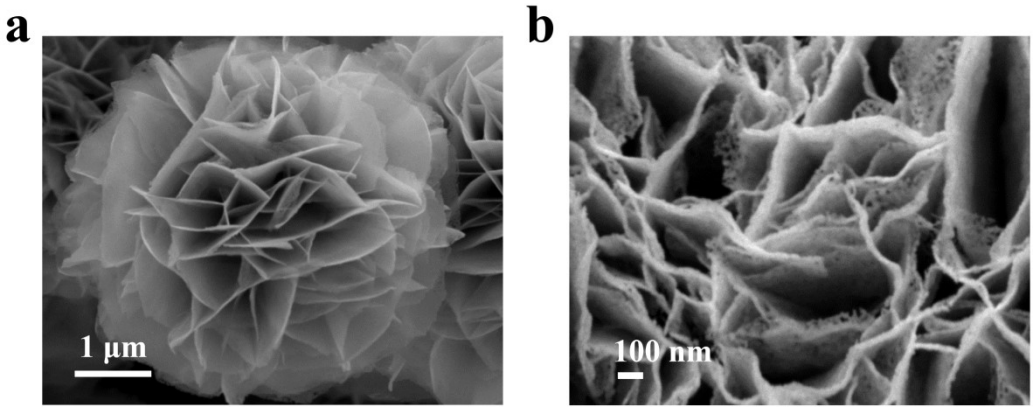

Figure S17. SEM image of Ru-Ni_2P@CN-10.

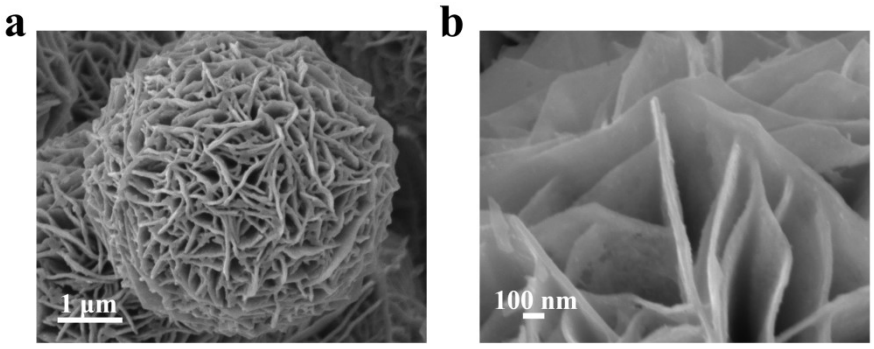

Figure S18. SEM image of Ru-Ni_2P@CN-20.

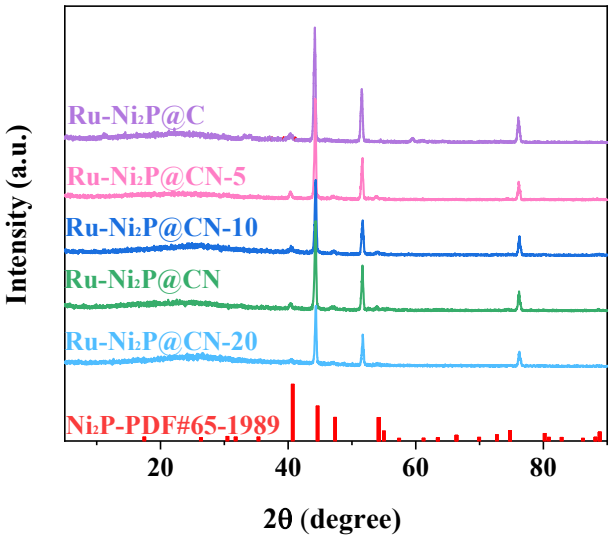

Figure S19. XRD patterns of Ru-Ni_2P@C, Ru-Ni_2P@CN-5, Ru-Ni_2P@C-10, Ru-Ni_2P@C, and Ru-Ni_2P@CN-20.

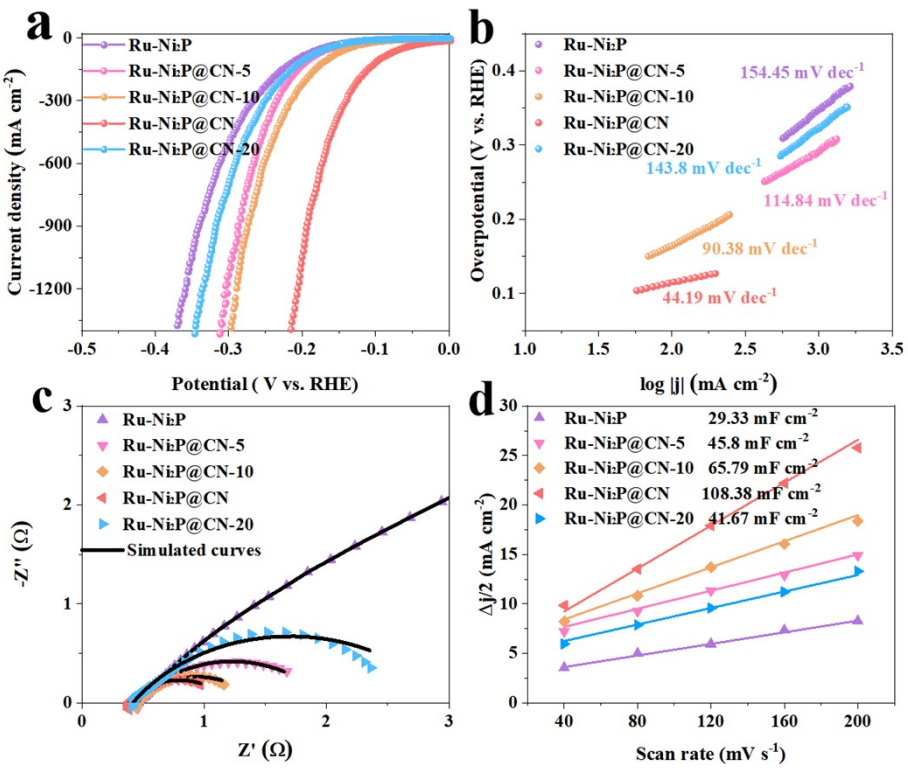

Figure S20. a) LSV curves of Ru-Ni_2P, Ru-Ni_2P@CN-5, Ru-Ni_2P@CN-10, Ru-Ni_2P@CN, and Ru-Ni_2P@CN-20 in 1.0 M KOH. b) Tafel slopes. c) EIS charts d) C_{dl} plots of Ru-Ni_2P@C, Ru-Ni_2P@CN-5, Ru-Ni_2P@CN-10, Ru-Ni_2P@CN, and Ru-Ni_2P@CN-20.

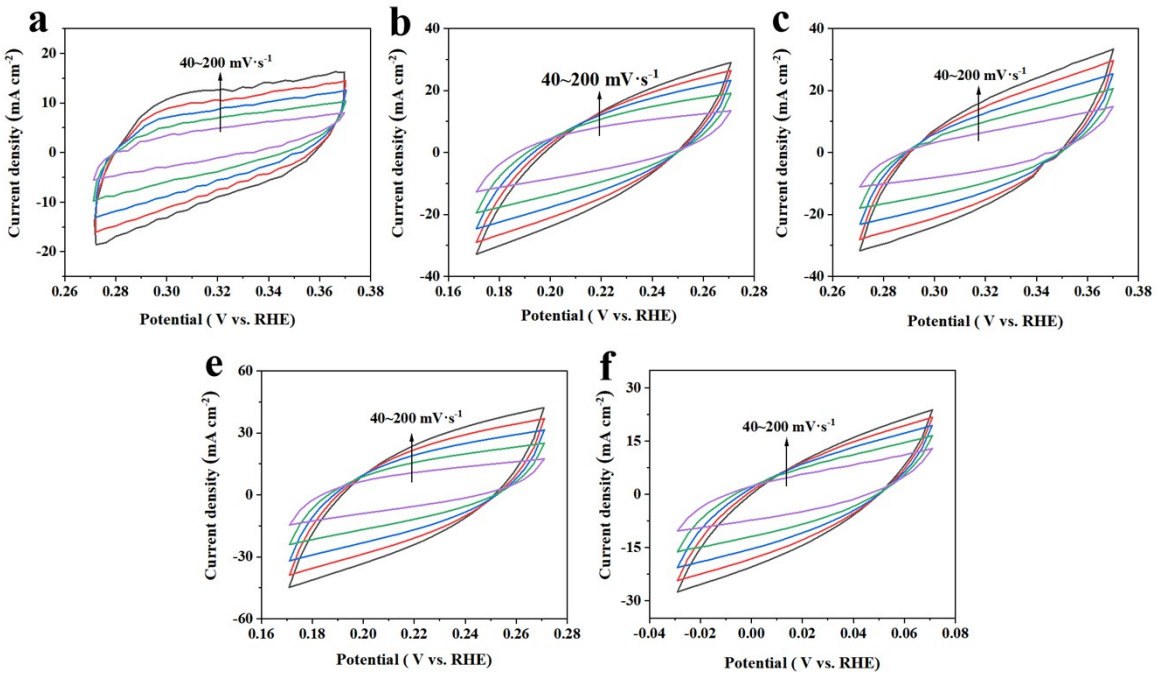

Figure S21. CV curves of the non-faradic region for (a) Ru-Ni_2P@C, (b) Ru-Ni_2P@CN-5, (c) Ru-Ni_2P@CN-10, (d) Ru-Ni_2P@CN, and (d) Ru-Ni_2P@CN-20.

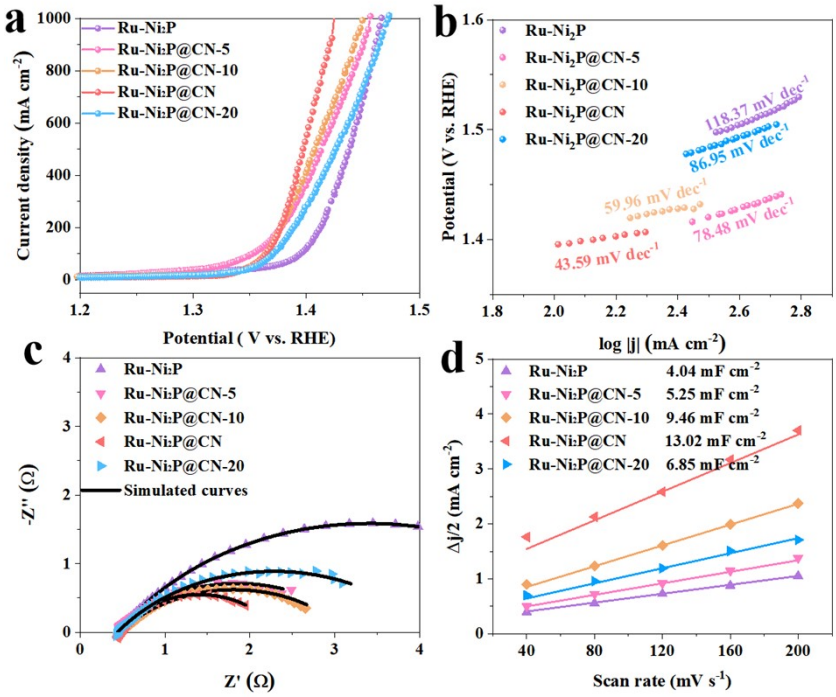

Figure S22. a) LSV curves of Ru-Ni_2P, Ru-Ni_2P@CN-5, Ru-Ni_2P@CN-10, Ru-Ni_2P@CN, and Ru-Ni_2P@CN-20 in 1.0 M KOH. b) Tafel slopes. c) EIS charts d) C_{dl} plots of RuNi_2P@C, Ru-Ni_2P@CN-5, Ru-Ni_2P@CN-10, Ru-Ni_2P@CN, and Ru-Ni_2P@CN-20.

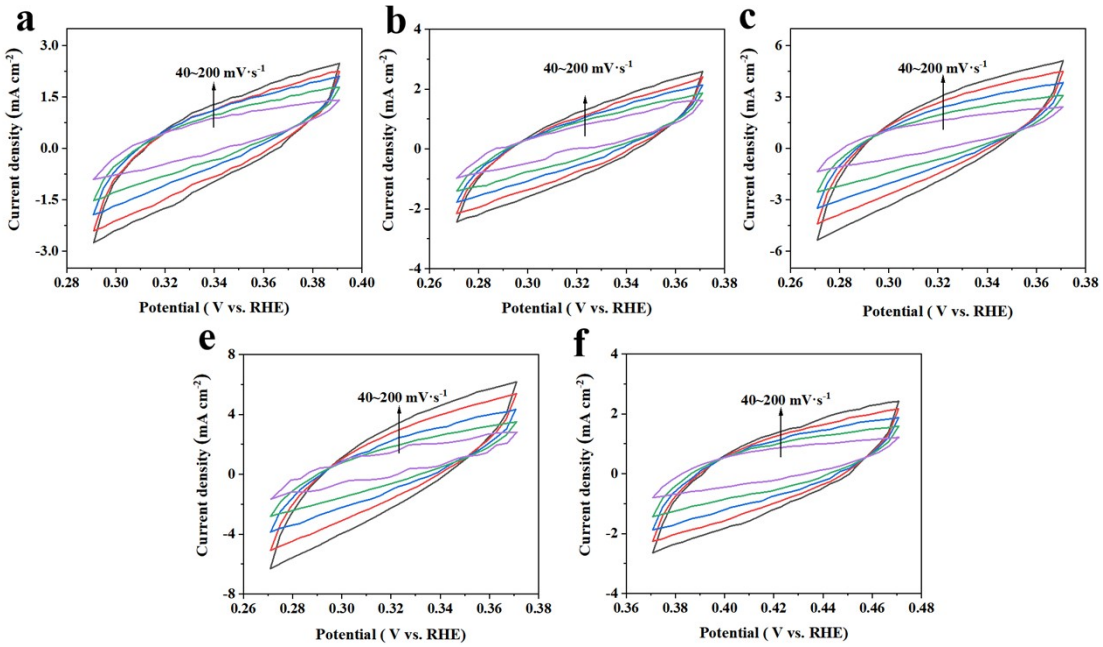

Figure S23. CV curves of the non-faradic region for (a) Ru-Ni_2P@C, (b) Ru-Ni_2P@CN-5, (c) Ru-Ni_2P@CN-10, (d) Ru-Ni_2P@CN, and (d) Ru-Ni_2P@CN-20.

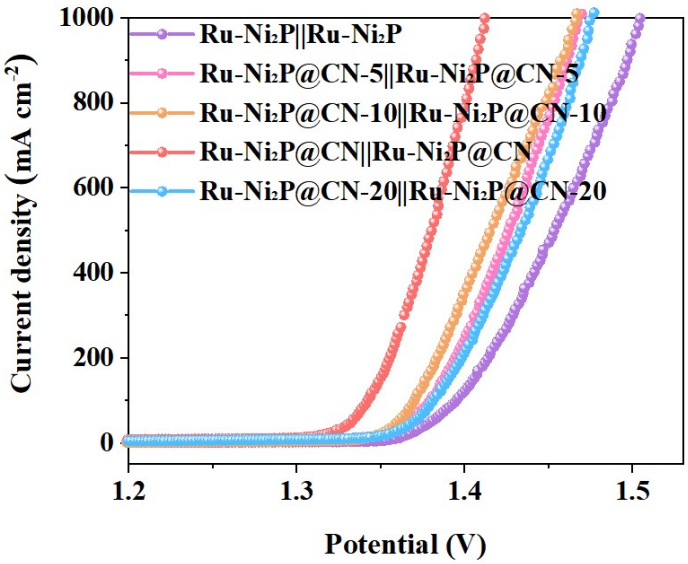

Figure S24. Electrocatalytic overall water splitting performance of Ru-Ni_2P, Ru-Ni_2P@CN-5, Ru-Ni_2P@CN-10, Ru-Ni_2P@CN, and Ru-Ni_2P@CN-20 in 0.5 M urea solution.

Table S1. Comparison of Ru, Ni, P, N, and C contents in different electrocatalysts obtained from XPS tests.

Electrocatalysts/element(at%)	Ru	Ni	P	N	C
Ru-Ni_2P@C	0.34	14.55	32.66	0	48.45
Ru-Ni_2P@CN	0.69	12.86	29.26	8.12	47.38

Table S2. Comparison of electrochemical surface area (ECSA) of Ru-Ni_2P@CN catalyst and other comparative samples for HER.

Electrocatalysts	**C_{dl} (mF cm^{-2})**	**C_{DL} (mF)**	**ECSA (cm^{-2})**
Ni_2P@CN	17.9	17.9	447.5
Ru-Ni_2P	29.33	29.33	733.25
Ru-Ni_2P@CN	108.38	108.38	2709.5
Ru-Ni_2P@C	74.28	74.28	1857

$C_{DL}=C_{dl}*S$; S=1*1 cm^2; ECSA=C_{DL}/C_s; C_s=0.04 mF cm^{-2}.

Table S3. Internal resistance (R_Ω) and charge transfer resistance (R_{ct}) of Ru-Ni_2P@CN catalyst and other comparative samples for HER

Electrocatalysts	$R_\Omega(\Omega)$	$R_{ct}(\Omega)$
Ni_2P@CN	0.43	18.16
Ru-Ni_2P	0.46	12.89
Ru-Ni_2P@CN	0.40	0.66
Ru-Ni_2P@C	0.42	2.93

Table S4. The overpotential required for excessive metal-based electrocatalysts was recently reported in an alkaline environment of 1000 $mAcm^{-2}$.

Catalyst	HER η_{1000} (mV)	References
this work	255	
Ni/MoO_2@CN	267	[1]
$Ni_2(1-x)Mo_2xP$	294	[2]
Ni_3P/MnOOH/NF	268	[3]
Ni_2P/NF	306	[4]
F, P-Fe_3O_4/IF	321.3	[5]
NiP_2-FeP_2	327	[6]
Ni2P-Fe2P/NF	333	[7]
$FeWO_4$-Ni_3S_2@C/NF	343	[8]
A-NiCo LDH/NF	384	[9]
Pt/C/NF	431	[9]
HC-Mo_2S/Mo_2C	441	[10]
$Pd_4S/Pd_3P_{0.95}$	486	[11]

Table S5. ICP results of Ru before and after HER of Ru-Ni_2P@CN

Sample	Ru content (at%)
Initial	0.72
After-HER	0.70

Table S6. Comparison of electrochemical surface area (ECSA) of N-Ru_2P@Ru catalyst and other comparative samples for UOR.

Electrocatalysts	**C_{dl} (mF cm^{-2})**	**C_{DL} (mF)**	**ECSA (cm^{-2})**
Ni_2P@CN	175.81	175.81	4395.25
Ru-Ni_2P	118.37	118.37	2959.25
Ru-Ni_2P@CN	43.59	43.59	1089.75
Ru-Ni_2P@C	62.77	62.77	1569.25

$C_{DL}=C_{dl}*S$; $S=1*1$ cm^2; $ECSA=C_{DL}/C_s$; $C_s=0.04$ mF cm^{-2}.

Table S7. Internal resistance (R_Ω) and charge transfer resistance (R_{ct}) of Ru-Ni_2P@CN catalyst and other comparative samples for UOR

Electrocatalysts	$R_\Omega(\Omega)$	$R_{ct}(\Omega)$
Ni_2P@CN	0.48	13.48
Ru-Ni_2P	0.46	5.58
Ru-Ni_2P@CN	0.46	1.76
Ru-Ni_2P@C	0.47	4.14

Table S8. The potential required for a noble metal-based electrocatalyst in 0.5 M urea solution environment at 10 mA cm^{-2} has recently been reported.

Catalyst	The electrolyte	Potential (V)	References
this work	1 M KOH+0.5M Urea	1.31	□
NiO/Ni_2P/NF-40	1 M KOH+0.33 M Urea	1.338	[12]
Co_2P/$NiMoO_4$	1 M KOH+0.5M Urea	1.34	[13]
Ni-DMAP-2/NF	1 M KOH+0.5 M Urea	1.34	[14]
MOF-Ni@ MOF-Fe–S	1 M KOH+0.33 M Urea	1.347	[15]
Ni_2P/MoO_2/NF	1 M KOH+0.5 M Urea	1.35	[16]
Fc-NiCo-BDC	1 M KOH+0.33 M Urea	1.35	[17]
P-Mo-$Ni(OH)_2$	1.0 M KOH +0.1 M urea	1.35	[18]
NiF_3/Ni_2P	1 M KOH+0.33 M Urea	1.36	[19]
Ni-MOF	1 M KOH+0.33 M Urea	1.37	[20]
Ni@NCNT	1 M KOH+0.5 M Urea	1.38	[21]
MoP@NiCo-LDH/NF-20	1 M KOH+0.5 M Urea	1.392	[22]
CoO-Co_4N@NiFe-LDH	1 M KOH+0.33 M Urea	1.393	[23]

Table S9. The potential required for a noble metal-based electrocatalyst in 0.5 M urea solution at 10 mA cm^{-2} has recently been reported.

Catalyst	Pitential (V)	References
this work	1.313	
Ru-Ni_3N@NC	1.36	[24]
Ni(OH)S/NF	1.36	[25]
$NiSe_2$-$NiMoO_4$	1.37	[26]
NiS@Ni_3S_2/$NiMoO_4$	1.4	[27]
P-$CoNi_2S_4$	1.4	[28]
Ni-Mo nanotube	1.43	[29]
$NiCo_2S_4$	1.45	[30]
Ni-S-Se/NF	1.47	[31]
Ni_2P/Fe_2P/NF	1.47	[32]
Ni_2P/CFC	1.48	[33]
$Ni(OH)_2$-PBA-P	1.5	[34]
NiF_3/Ni_2P@CC-2	1.54	[35]

Table S10. Internal resistance (R_Ω) and charge transfer resistance (R_{ct}) of Ru-Ni_2P@CN catalyst and other comparative samples for HER

Electrocatalysts	$R_\Omega(\Omega)$	$R_{ct}(\Omega)$
Ru-Ni_2P	0.46	12.89
Ru-Ni_2P@CN-5	0.46	1.40
Ru-Ni_2P@CN-10	0.44	0.82
Ru-Ni_2P@CN	0.40	0.66
Ru-Ni_2P@CN-20	0.42	2.13

Table S11 Internal resistance (R_Ω) and charge transfer resistance (R_{ct}) of Ru-Ni_2P@CN catalyst and other comparative samples for UOR

Electrocatalysts	$R_\Omega(\Omega)$	$R_{ct}(\Omega)$
Ru-Ni_2P	0.46	5.58
Ru-Ni_2P@CN-5	0.46	2.58
Ru-Ni_2P@CN-10	0.47	2.47
Ru-Ni_2P@CN	0.46	1.76
Ru-Ni_2P@CN-20	0.48	3.31

References

1. G. F. Qian, J. L. Chen, T. Q. Yu, J. C. Liu, L. Luo and S. B. Yin, *Nano-Micro Lett*., 2022, **14,** 1-15.

2. F. Yu, H. Q. Zhou, Y. F. Huang, J. Y. Sun, F. Qin, J. M. Bao, W. A. Goddard, S. Chen and Z. F. Ren, *Nat. Commun.*, 2018, **9**, 2551.

3. L. Yu, I. K. Mishra, Y. L. Xie, H. Q. Zhou, J. Y. Sun, J. Q. Zhou, Y. Z. Ni, D. Luo, F. Yu, Y. Yu, S. Chen and Z. F. Ren, *Nano Energy*, 2018, **53**, 492-500.

4. X. Y. Zhang, F. T. Li, R. Y. Fan, J. Zhao, B. Dong, F. L. Wang, H. J. Liu, J. F. Yu, C. G. Liu and Y. M.Chai, *J. Mater. Chem. A,* 2021, **21**, 15836-15845.

5. A. Kumar, V. Q. Bui, J. S. Lee, A. R. Jadhav, Y. Hwang, M. Gyu Kim, Y. Kawazoe, H. Lee. *ACS Energy Lett.* 2021, **6**, 354-363.

6. X. X. Yu, Z. Y. Yu, X. L. Zhang, Y. R. Zheng, Y. Duan, Q. Gao, R. Wu, B. Sun, M. R. Gao, G. X.Wang and S. H. Yu, *J. Am. Chem. Soc.,* 2019, **141**, 7537-7543.

7. H. H. Tang, Y. F. Qi, D. N. Feng, Y. Y. Chen, L. Y. Liu, L. Hao, K. F. Yue, D. S. Li and Y. Y. Wang, *Sustain. Energy Fuels*, 2022, **19**, 4477-4483.

8. Z. L. Wang, G. F. Qian, T. Q. Yu, J. L. Chen, F. Shen, L. Luo, Y. J. Zou and S. B. Yin, *Chem. Eng. J.,* 2022, **434**, 134669.

9. H. Y. Yang, Z. L. Chen, P. F. Guo, B. Fei, R. B. Wu, *Appl. Catal. B Environ.*, 2020, **261**, 118240.

10. C. Zhang, Y. T. Luo, J. Y. Tan, Q. M. Yu, F. N. Yang, Z. Y. Zhang, L. S. Yang, H. M. Cheng and B. L. Liu, *Nat. Commun.*, 2020, **11**, 3724.

11. G. F. Zhang, A. H. Wang, L. W. Niu, W. Gao, W. Hu, Z. H. Liu, R. M. Wang and J. B. Chen, *Adv. Energy Mater.*, 2022, **11**, 2103511.

12. X. Xu, S. J, H. Wang, X. Y. Wang, V. Linkov and R. F. Wang, *J. Colloid Interf. Sci.*, 2022, 615, 163-172.

13. M. Z. You, S. S. Yi, G. X. Zhang, W. M. Long and D. L. Chen, *J. Colloid Interface Sci.*, 2023, **5**,184.

14. H. Jiang, S. Y. Bu, Q. L. Gao, J. Long, P. F. Wang, C. S. Lee and W. J. Zhang, Mater. *Today Energy*, 2022, **27**, 101024.

15. H. Z. Xu, K. Ye, K. Zhu, J. L. Yin, J. Yan, G. L. Wang and D. X. Cao, *Dalton Trans.*, 2020, **49**, 5646-5652.

16. X. Xu, S. Ji, H. Wang, X. Y. Wang, V. Linkov and R. F. Wang, *J. Colloid Interf. Sci.*, 2022, **615**, 163-172.

17. M. Li, H. C. Sun, J. M. Yang, M. Humayun, L. F. Li, X. F. Xu, X. Y. Xue, A. Habibi-Yangjeh, K. Temst and C. D. Wang, *Chem. Eng. J.*, 2022, **430**, 132733.

18. W. H. Zhang, Y. H. Tang, L. M. Yu and X. Y. Yu, *Appl. Catal. B Environ.*, 2020, **260**, 118154.

19. K. L. Wang, W. Huang, Q. H. Cao, Y. J. Zhao, X. J. Sun, R. Ding, W. W. Lin, E. H. Liu and P. Gao, *Chem. Eng. J.*, 2022, **427**, 130865.

20. D. D. Zhu, C. X. Guo, J. L. Liu, L. Wang, Y. Du and S. Z. Qiao, *Chem. Commun.*, 2017, **53**, 10906-10909.

21. Q. Zhang, F. MD. Kazim, S. X. Ma, K. G. Qu, M. Li , Y. G. Wang, H. Hu, W. W. Cai and Z. H. Yang, Appl. *Catal. B Environ*, 2021, **280**, 119436.

22. T. Wang, H. M. Wu, C. Q. Feng, L. Zhang and J. J. Zhang, *J. Mater. Chem. A*, 2020, **8**, 18106-18116.

23. B. J. Chen, M. Humayun, Y. D. Li, H. M. Zhang, H. C. Sun, Y. Wu and C. D. Wang, ACS Sustain. *Chem. Eng.*, 2021, **9**, 14180-14192.

24. Y. B. Liu, D. B. Zheng, Y. Zhao, P. Shen, Y. X. Du, W. P. Xiao, Y. M. Du, Y. L. Fu, Z. X. Wu and L. Wang, *Int. J. Hydrogen Energy*, 2022, **47**, 25081-25089.

25. X. Jia, H. J. Kang, X. X. Yang, Y. L. Li, K. Cui, X. H. Wu, W. Qin and G. Wu, *Appl. Catal. B: Environ.*, 2022, **312**, 121389.

26. T. Q. Yu, Q. L. Xu, J. L. Chen, G. F. Qian, X. Y. Zhuo, H. F. Yang and S. B. Yin, *Chem. Eng. J.*, 2022, **449**, 137791.

27. L. Sha, T. Liu, K. Ye, K. Zhu, J. Yan, J. Yin, G. Wang, D. Cao, *J. Mater.s Chem. A*, 2020, **8**, 18055-18063.

28. X. F. Lu, S. L. Zhang, W. Sim, S. Y. Gao, X. W. David Lou, *Angew. Chem. Int. Ed*., 2021, **60**, 22885.

29. J. Y. Zhang, T. He, M. D. Wang, R. J. Qi, Y. Yan, Z. H. Dong, H. F. Liu, H. M. Wang and B. Y. Xia, *Nano Energy*, 2019, **60**, 894-902.

30. J. Wang, Y. Sun, Y. F. Qi and C. Wang, *ACS Appl. Mater. Interface*s, 2021, **13**, 57392-57402.

31. N. Chen, Y. X. Du, G. Zhang, W. T. Lu and F. F. Cao, *Nano Energy*, 2021, **81**, 105605.

32. L. Yan, Y. L. Sun, E. L. Hu, J. Q. Ning, Y. J. Zhong, Z. Y. Zhang and Y. Hu, *J. Colloid Interface Sci.*, 2019, **541**: 279-286.

33. X. Zhang, M. M. Han, G. Q. Liu, G. Z. Wang, Y. X. Zhang, H. M. Zhang and H. J. Zhao, *Appl. Catal. B: Environ.,* **2019**, 244 , 899-908.

34. H. Z. Xu, K. Ye, K. Zhu, Y. Y. Gao, J. L. Yin, J. Yan, G. L. Wang, D. X. Cao, *ACS Sustain. Chem. Eng*., 2020, **8**, 16037.

35. K. L. Wang, W. Huang, Q. H. Cao, Y. J. Zhao, X. J. Sun, R. Ding, W. W. Lin, E. H. Liu and P. Gao, *Chem. Eng. J.*, 2022, **427**, 130865.