Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Nickel Encapsulated in Carbon Dots Derived Nanosheets for Efficient Urea-Assisted Water Electrolysis of Hydrogen Evolution

Yichen Pan[†a], *Jiancheng Zhang*[†a], *Qian Zhang*[a], *Xin Chen*[a], *Qian Wang*[a], *Caicai Li**[a], *Zonglin Liu**[b] *and Qingfeng Sun**[a]

[a]College of Chemistry and Materials Engineering, Zhejiang A&F University, Hangzhou, Zhejiang Province, 311300, PR China.

[b]Institute for Advanced Ceramics, State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology, Harbin, 150001, China.

[†]They are equally contributed to the paper.

***Corresponding authors**: Caicai Li (ccli@zafu.edu.cn); Zonglin Liu (liuzonglin_yoo@163.com); Qingfeng Sun (qfsun@zafu.edu.cn)

Materials and chemicals

Citric acid monohydrate ($C_6H_8O_7 \cdot H_2O$) and ethylenediamine (EDA) were obtained from Sinopharm Group Chemical Reagent (Shanghai, China). Nickel(II) acetate tetrahydrate ($Ni(OAc)_2$) was purchased from Aladdin (Shanghai, China). All reagents were utilized without additional purification, and ultrapure water was utilized throughout the experiments.

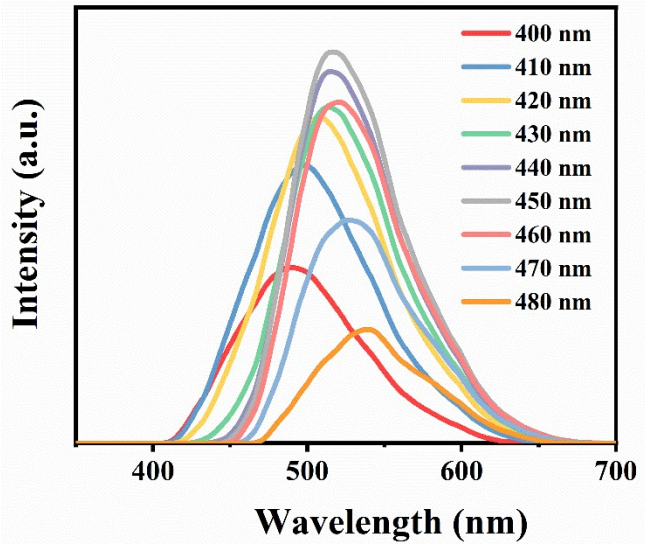

Figure S1. NCDs in ultrapure water at different excitation wavelengths (in 10 nm increments starting from 400 nm to 480 nm).

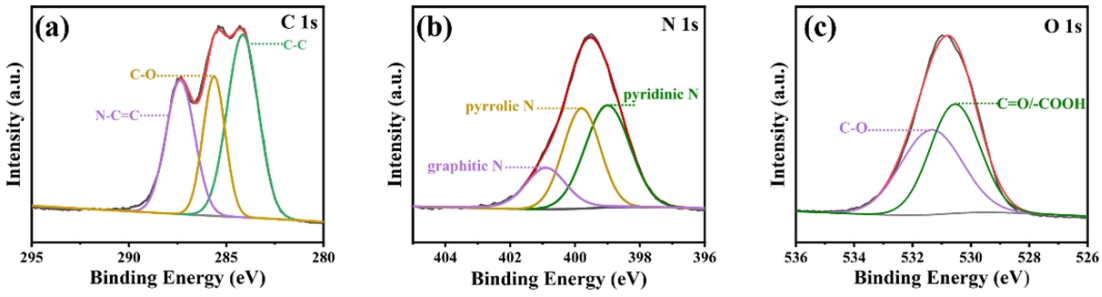

Figure S2. High XPS spectra of (a) C 1s, (b) N 1s, and (c) O 1s of NCDs.

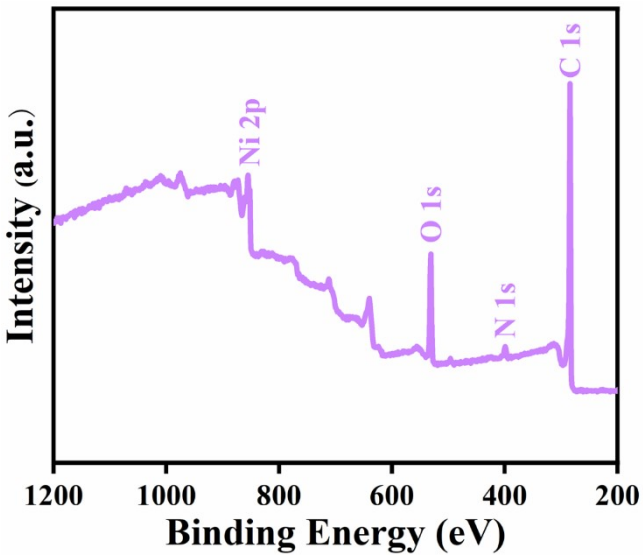

Figure S3. XPS survey spectrum of Ni@NCDs.

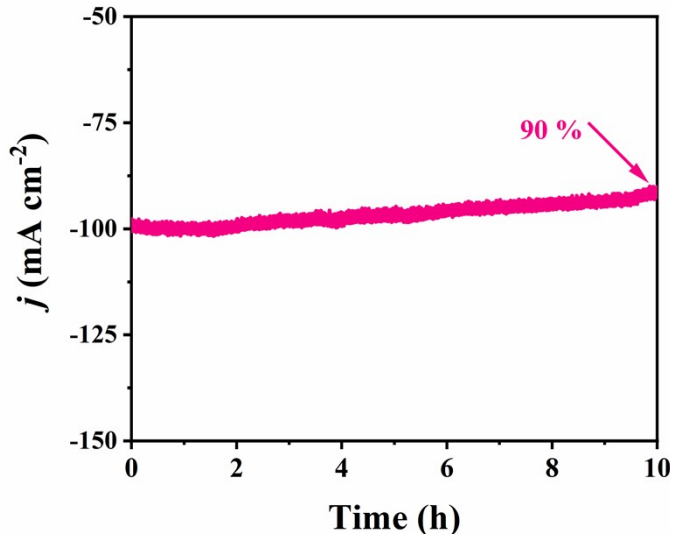

Figure S4. The i-t test at a current density of 100 cm^{-2}.

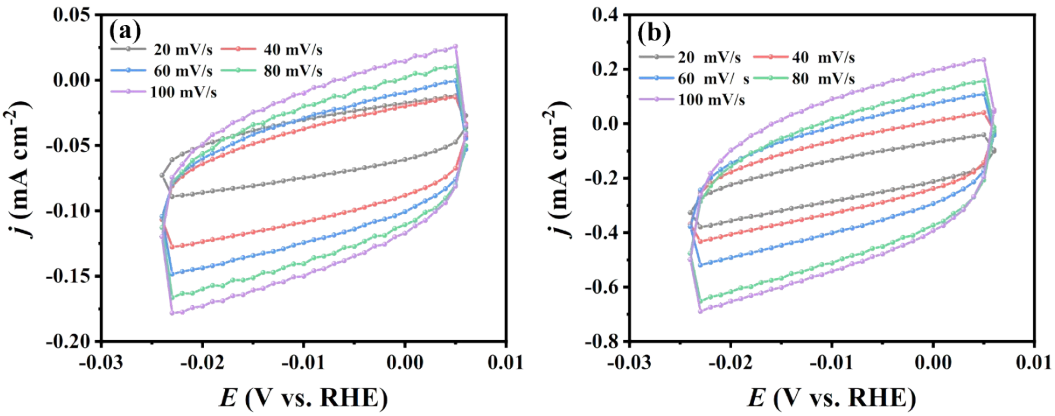

Figure S5. CV curves of NCDs-650 (a) and Ni (b) measured at different scan rates.

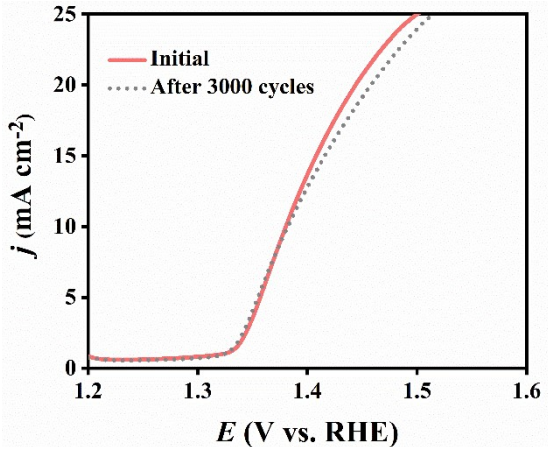

Figure S6. LSV curves for Ni@NCDs before and after 3000 CV cycles in 1.0 M KOH with 0.5 M urea.

Table S1. Comparison of the HER performance of Ni@NCDs with some recently reported Ni-based catalysts in alkaline medium.

Catalyst	η (mV)@*j* (mA cm^{-2})	Tafel slope (mV dec^{-1})	References
Ni-Cu alloy	128@10	57	[1] *Electrochim. Acta,* 2016, **215**, 609-616.
Ni-doped graphene	~180@10	45	[2] *Nat. Commun*. 2016, **7**, 10667.
NiO/Ni@CNT	80@10	82	[3] *Nat. Commun.* 2014, **5**, 4695
Ni@SNG	99.8@10	98	[4] *ACS Appl. Mater. Interfaces*, 2021, **13**, 4294-4304.
$Ni(OH)_2$/Ag hybrid	89@10	102	[5] *New J. Chem*. 2021, **45**, 13286-13292.
Ni@graphene defects	270@10	47	[6] *Chem*, 2018, **4**, 285-297.
Ni-N-C	83@10	100	[7] *ACS Appl. Mater. Interfaces*, 2022, **14**, 29822-29831.
Ni/NiFe LDH	92@10	72	[8] *J. Mater. Chem. A*, 2019, **7**, 21722-21729.
Ni/Graphene	50@10	45	[9] *Angew. Chem. Int. Ed*. 2015, **54**, 14031-14035.
Ni/NiO hybrid	105@10	55	[10] *J. Alloys Compd*. 2021, **853**, 157338.
Nanoprism NiO/oxygen vacancies	115@10	146	[11] *New J. Chem*. 2020, **44**, 1703-1706.
NiO_x@bamboo-like carbon nanotubes	79@10	119	[12] *ACS Appl. Mater. Interfaces,* 2017, **9**, 7139-7147.
Ni@NCDs	**86@10**	**78.2**	**This work**

Table S2. Comparison of the Ni@NCDs with recently reported catalysts for urea-assisted water electrolysis.

Catalyst	Cell Voltage at 10 mA cm^{-2} (V)	References
NiS/Ni_3S_4/GCW	1.44	[13] *J. Colloid Interface Sci.* 2022, **626**, 848-857.
NiS/MoS_2@CC	1.46	[14] *Chem. Eng. J.* 2022, **443**, 136321
MZS/NF-180	1.51	[15] *Renewable Energy*, 2022, **193**, 715-724.
8%Co:Ni-P-O/NF	1.48	[16] *J. Alloys Compd.* 2022, **914**, 165362.
CoS_2-Ti	1.59	[17] *Electrochim. Acta*, 2017, **246**, 776-782.
Ni@NCNT	1.56	[18] *Appl. Catal. B-Environ.* 2021, **280**, 119436.
$MnO_2/MnCo_2O_4$/Ni	1.55	[19] *J. Mater. Chem. A*, 2017, **5**, 7825-7832.
Ni/C	1.6	[20] *ACS Appl. Mater. Interfaces*, 2018, **10**, 4750-4756.
HC-NiMoS/Ti	1.59	[21] *Nano Res.* 2018, **11**, 988-996.
Ni@NCDs	**1.47**	**This work**

References

[1] M. Y. Gao, C. Yang, Q. B. Zhang, Y. W. Yu, Y. X. Hua, Y. Li and P. Dong, Electrochemical fabrication of porous Ni-Cu alloy nanosheets with high catalytic activity for hydrogen evolution, *Electrochim. Acta*, 2016, **215**, 609-616.

[2] L. Fan, P. F. Liu, X. Yan, L. Gu, Z. Z. Yang, H. G. Yang, S. Qiu and X. Yao, Atomically isolated nickel species anchored on graphitized carbon for efficient hydrogen evolution electrocatalysis, *Nat. Commun.*, 2016, **7**, 10667.

[3] M. Gong, W. Zhou, M. C. Tsai, J. Zhou, M. Guan, M. C. Lin, B. Zhang, Y. Hu, D. Y. Wang, J. Yang, S. J. Pennycook, B. J. Hwang and H. Dai, Nanoscale nickel oxide/nickel heterostructures for active hydrogen evolution electrocatalysis, *Nat. Commun.*, 2014, **5**, 4695.

[4] C. Zhang, S. Ju, T. H. Kang, G. Park, B. J. Lee, H. Miao, Y. Wu, J. Yuan and J. S. Yu, Self-Limiting Growth of Single-Layer N-Doped Graphene Encapsulating Nickel Nanoparticles for Efficient Hydrogen Production, *ACS Appl. Mater. Interfaces*, 2021, **13**, 4294-4304.

[5] T. Xu, J. Wang, M. Wang, Y. Xue, J. Liu, N. Cai, W. Chen, F. Huang, X. Li and F. Yu, $Ni(OH)_2$-Ag hybrid nanosheet array with ultralow Ag loading as a highly efficient and stable electrocatalyst for hydrogen evolution reaction, *New J. Chem.*, 2021, **45**, 13286-13292.

[6] L. Zhang, Y. Jia, G. Gao, X. Yan, N. Chen, J. Chen, M. T. Soo, B. Wood, D. Yang and A. Du, Graphene defects trap atomic Ni species for hydrogen and oxygen evolution reactions, *Chem*, 2018, **4**, 285-297.

[7] J. Guo, W. Shang, J. Hu, C. Xin, X. Cheng, J. Wei, C. Zhu, W. Liu and Y. Shi, Synergistically enhanced single-atom nickel catalysis for alkaline hydrogen evolution reaction, *ACS Appl. Mater. Interfaces*, 2022, **14**, 29822-29831.

[8] Z. Cai, X. Bu, P. Wang, W. Su, R. Wei, J. C. Ho, J. Yang and X. Wang, Simple and cost effective fabrication of 3D porous core–shell Ni nanochains@NiFe layered double hydroxide nanosheet bifunctional electrocatalysts for overall water

splitting, *J. Mater. Chem. A*, 2019, **7**, 21722-21729.

[9] H. J. Qiu, Y. Ito, W. Cong, Y. Tan, P. Liu, A. Hirata, T. Fujita, Z. Tang and M. Chen, Nanoporous graphene with single-atom nickel dopants: an efficient and stable catalyst for electrochemical hydrogen production, *Angew. Chem. Int. Ed.*, 2015, **54**, 14031-14035.

[10] H. Han, S. Park, D. Jang and W. B. Kim, N-doped carbon nanoweb-supported Ni/NiO heterostructure as hybrid catalysts for hydrogen evolution reaction in an alkaline phase, *J. Alloys Compd.,* 2021, **853**, 157338.

[11] X. Zhang and X. Du, Oxygen vacancies confined in nickel oxide nanoprism arrays for promoted electrocatalytic water splitting, *New J. Chem.*, 2020, **44**, 1703-1706.

[12] J. Wang, S. Mao, Z. Liu, Z. Wei, H. Wang, Y. Chen and Y. Wang, Dominating role of Ni^0 on the interface of Ni/NiO for enhanced hydrogen evolution reaction, *ACS Appl. Mater. Interfaces*, 2017, **9**, 7139-7147.

[13] Z. Jiang, L. Zheng, C. Sheng, H. Xu, S. Chen, Y. Liao, Y. Qing and Y. Wu, Construction of NiS/Ni_3S_4 heteronanorod arrays in graphitized carbonized wood frameworks as versatile catalysts for efficient urea-assisted water splitting, *J. Colloid Interface Sci.*, 2022, **626**, 848-857.

[14] C. Gu, G. Zhou, J. Yang, H. Pang, M. Zhang, Q. Zhao, X. Gu, S. Tian, J. Zhang, L. Xu and Y. Tang, NiS/MoS_2 Mott-Schottky heterojunction-induced local charge redistribution for high-efficiency urea-assisted energy-saving hydrogen production, *Chem. Eng. J.*, 2022, **443**, 136321.

[15] N. Chen, X. Du and X. Zhang, Controlled synthesis of MnS/ZnS hybrid material with different morphology as efficient water and urea electrolysis catalyst, *Renewable Energy*, 2022, **193**, 715-724.

[16] J. Cao, Z. Jiao, R. Zhu, H. Long, Y. Zheng, J. Pan, J. Wang, F. Luo, C. Li and Q. Wei, Enhancing hydrogen evolution through urea electrolysis over Co-doped Ni-P-O film on nickel foam, *J. Alloys Compd.*, 2022, **914**, 165362.

[17] S. Wei, X. Wang, J. Wang, X. Sun, L. Cui, W. Yang, Y. Zheng and J. Liu, CoS_2

nanoneedle array on Ti mesh: A stable and efficient bifunctional electrocatalyst for urea-assisted electrolytic hydrogen production, *Electrochim. Acta*, 2017, **246**, 776-782.

[18] Q. Zhang, F. M. D. Kazim, S. Ma, K. Qu, M. Li, Y. Wang, H. Hu, W. Cai and Z. Yang, Nitrogen dopants in nickel nanoparticles embedded carbon nanotubes promote overall urea oxidation, *Appl. Catal. B- Environ.*, 2021, **280**, 119436.

[19] C. Xiao, S. Li, X. Zhang and D. R. MacFarlane, $MnO_2/MnCo_2O_4$/Ni heterostructure with quadruple hierarchy: a bifunctional electrode architecture for overall urea oxidation, *J. Mater. Chem. A*, 2017, **5**, 7825-7832.

[20] L. Wang, L. Ren, X. Wang, X. Feng, J. Zhou and B. Wang, Multivariate MOF-Templated Pomegranate-Like Ni/C as Efficient Bifunctional Electrocatalyst for Hydrogen Evolution and Urea Oxidation, *ACS Appl. Mater. Interfaces*, 2018, **10**, 4750-4756.

[21] X. Wang, J. Wang, X. Sun, S. Wei, L. Cui, W. Yang and J. Liu, Hierarchical coral-like NiMoS nanohybrids as highly efficient bifunctional electrocatalysts for overall urea electrolysis, *Nano Res.*, 2018, **11**, 988-996.