3D self-supported porous vanadium-doped nickel nitride nanosheets arrays as efficient bifunctional electrocatalysts for urea electrolysis

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Fig. S1. SEM image of V-NiO/NF.







Fig. S3. Electrochemical cyclic voltammetry curves of (a) Ni₃N/NF, (b) V-Ni₃N/NF, (c) V-Ni₃N/NF-1, and (d) V-Ni₃N/NF-2 at different scan rates.



Fig. S4. SEM images of V-Ni $_3$ N/NF after HER stability tests in 1M KOH (a) and 1M PBS (b) electrolyte.



Fig. S5. XRD pattern of V-Ni₃N/NF after the HER stability test in 1M KOH electrolyte.



Fig. S6. The optimized structural models for (a) $Ni_3N(111)$, (b) V- $Ni_3N(111)$, (c) $Ni_3N(002)$, and (d) V- $Ni_3N(002)$.



Fig. S7. Tafel slopes of UOR for different catalysts.



Fig. S8. SEM image of V-Ni $_3$ N/NF after UOR stability test.



Fig. S9. XRD pattern of V-Ni₃N/NF after UOR stability test.



Fig. S10. XPS spectra of (a) Ni 2p, (b) V 2p, (c) N 1s, and (d) survey scan for V- Ni_3N/NF after UOR stability test.

Catalysts	Overpotential (mV) at	Tafel slope (mV	Deferences
	10 mA cm ⁻²	dec ⁻¹)	References
V-Ni ₃ N/NF	83	45	This work
Co-Ni ₃ N	194	156	[S1]
Ni ₃ FeN	94	90	[S2]
NiCoN/C	103		[83]
NiCu-NiCuN	93	55	[S4]
Co_4N - $VN_{1-x}O_x$	118	73.6	[85]
Mo_5N_6	94	66	[S6]
MoNiNC	110	65	[S7]
Fe-Ni ₃ S ₂	105	69	[S8]
Mn-Co-P	86	52	[89]

 Table S1 Comparison of the HER performance of V-Ni₃N/NF with other reported

 catalysts in alkaline electrolyte.

Catalysts	Potential (V) at 10 mA cm ⁻²	References
V-Ni ₃ N/NF	1.361	This work
Ni ₂ P	1.37	[S10]
MnO ₂	1.37	[S11]
Ni(OH) ₂	1.42	[S12]
NF-G-Mn	1.37	[S13]
NiMoO	1.37	[S14]
Ni ₃ Se ₄	1.38	[S15]
MnO ₂ /MnCo ₂ O ₄	1.43	[S16]
Pt/C	1.38	[S17]

Table S2 Comparison of the UOR performance of V-Ni $_3$ N/NF with other reported catalysts.

Catalysts	Voltage (V) at 10 mA cm ⁻²	References
V-Ni ₃ N/NF	1.416	This work
Ni-Mo alloy	1.43	[S18]
CoMn/CoMn ₂ O ₄	1.51	[S19]
Ni/C	1.6	[S20]
NiCoP	1.42	[S21]
MnO ₂ /MnCo ₂ O ₄	1.58	[S22]
$NiCo_2S_4$	1.49	[S23]
Ni ₂ P/Fe ₂ P	1.47	[S24]
Fe-Ni ₃ S ₂	1.46	[\$25]
Pt/C	1.68	[S26]

Table S3 Comparison of the urea electrolysis performance of V-Ni₃N/NF with other recently reported catalysts.

References

- [S1] C. Zhu, A. Wang, W. Xiao, D. Chao, X. Zhang, N. Tiep, S. Chen, J. Kang, X. Wang, J. Ding, J. Wang, H. Zhang and H. Fan, *Adv. Mater.*, 2018, **30**, 1705516.
- [S2] Y. Gu, S. Chen, J. Ren, Y. Jia, C. Chen, S. Komarneni, D. Yang and X. Yao, ACS Nano, 2018, 12, 245.
- [S3] J. Lai, B. Huang, Y. Chao, X. Chen and S. Guo, Adv. Mater., 2019, 31, 1805541.
- [S4] J. Hou, Y. Sun, Z. Li, B. Zhang, S. Cao, Y. Wu, Z. Gao and L. Sun, Adv. Funct. Mater., 2018, 28, 1803278.
- [S5] S. Dutta, A. Indra, Y. Feng, H. Han and T. Song, Appl. Catal. B: Environ., 2019,

241, 521.

- [S6] H. Jin, X. Liu, A. Vasileff, Y. Jiao, Y. Zhao, Y. Zheng and S. Qiao, ACS Nano, 2018, 12, 12761.
- [S7] F. Wang, Y. Sun, Y. He, L. Liu, J. Xu, X. Zhao, G. Yin, L. Zhang, S. Li, Q. Mao, Y. Huang, T. Zhang and B. Liu, *Nano Energy*, 2017, 37, 1.
- [S8] W. Zhang, Q. Jia, H. Liang, L. Cui, D. Wei and J. Liu, Chem. Eng. J., 2020, 396, 125315.
- [S9] T. Liu, X. Ma, D. Liu, S. Hao, G. Du, Y. Ma, A. Asiri, X. Sun and L. Chen, ACS Catal., 2017, 7, 98.
- [S10] D. Liu, T. Liu, L. Zhang, F. Qu, A. Asiri and X. Sun, J. Mater. Chem. A., 2017, 5, 3208.
- [S11] S. Chen, J. Duan, A. Vasileff and S. Qiao, Angew. Chem. Int. Ed., 2016, 55, 3804.
- [S12] X. Zhu, X. Dou, J. Dai, X. An, Y. Guo, L. Zhang, S. Tao, J. Zhao, W. Chu, X. Zeng, C. Wu and Y. Xie, *Angew. Chem. Int. Ed.*, 2016, 55, 12465.
- [S13] S. Chen, J. Duan, A. Vasileff and S. Qiao, Angew. Chem. Int. Ed., 2016, 55, 3804.
- [S14] Z. Yu, C. Lang, M. Gao, Y. Chen, Q. Fu, Y. Duan and S. Yu, *Energy Environ*. *Sci.*, 2018, **11**, 1890.
- [S15] J. Zhang, X. Tian, T. He, S. Zaman, M. Miao, Y. Yan, K. Qi, Z. Dong, H. Liu and B. Xia, *J. Mater. Chem. A.*, 2018, 6, 15653.
- [S16] C. Xiao, S. Li, X. Zhang and D. MacFarlane, J. Mater. Chem. A, 2017, 5, 7825.
- [S17] S. Chen, J. Duan, A. Vasileff and S. Qiao, Angew. Chem. Int. Ed., 2016, 55, 3804.
- [S18] J. Zhang, T. He, M. Wang, R. Qi, Y. Yan, Z. Dong, H. Liu, H. Wang and B. Xia, *Nano Energy*, 2019, **60**, 894.
- [S19] C. Wang, H. Lu, Z. Mao, C. Yan, G. Shen and X. Wang, Adv. Funct. Mater., 2020, 30, 2000556.
- [S20] L. Wang, L. Ren, X. Wang, X. Feng, J. Zhou and B. Wang, ACS Appl. Mater. Interfaces, 2018, 10, 4750.
- [S21] L. Sha, J. Yin, K. Ye, G. Wang, K. Zhu, K. Cheng, J. Yan, G. Wang and D. Cao, J. Mater. Chem. A, 2019, 7, 9078.
- [S22] C. Xiao, S. Li, X. Zhang and D. MacFarlane, J. Mater. Chem. A, 2017, 5, 7825.
- [S23] W. Zhu, M. Ren, N. Hu, W. Zhang, Z. Luo, R. Wang, J. Wang, L. Huang, Y. Suo and J. Wang, ACS Sustainable Chem. Eng., 2018, 6, 5011.
- [S24] L. Yan, Y. Sun, E. Hu, J. Ning, Y. Zhong, Z. Zhang and Y. Hu, J. Colloid Interf.

Sci., 2019, 541, 279.

[S25] W. Zhu, Z. Yue, W. Zhang, N. Hu, Z. Luo, M. Ren, Z. Xu, Z. Wei and Y. Suo, J. Wang, J. Mater. Chem. A, 2018, 6, 4346.

[S26] S. Chen, J. Duan, A. Vasileff and S. Qiao, Angew. Chem. Int. Ed., 2016, 55, 3804.