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A nitridation route to construct high-activity interfaces toward

alkaline hydrogen evolution

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Fig. S1 XRD pattern of Ti foil.



Fig. S2 SEM images of $Ru/H_2Ti_2O_5$ NBs.



Fig. S3 SEM images of TiO_xN_y NBs.



Fig. S4 The XPS spectra of O1s for $Ru/TiO_xN_y,\,TiO_xN_y$ and $Ru/H_2Ti_2O_5\,NBs.$



Fig. S5 The equivalent circuits and the fitted Rs and Rct values for Ru/TiO_xN_y NBs and other electrocatalysts.



Fig. S6 CV curves of Ru/TiO_xN_y NBs and other electrocatalysts in the non-faradic regions.



Fig. S7 Electrochemical measurements of Ru/TiO_xN_y-X (X mg, X= 0, 2, 4, 6 and 8) NBs. (a) Polarization curves of as-prepared electrocatalysts in 1 M KOH solution. (b) Tafel plots of these electrocatalysts. (c) The EIS spectra and (d) the C_{dl} calculations of these electrocatalysts.



Fig. S8 CV curves of Ru/TiO_xN_y -X (X= mg X= 0, 2, 4, 6 and 8) NBs in the non-faradic regions.



Fig.S9 Electrochemical measurements of $Ru/H_2Ti_2O_5$ NBs with different nitride time (X h, X= 1, 2, 3 and 4 h) NBs. (a) Polarization curves of as-prepared electrocatalysts in 1 M KOH solution. (b) Tafel plots of these electrocatalysts. (c) The EIS spectra and (d) the C_{dl} calculations of these electrocatalysts.



Fig.S10 CV curves of $Ru/H_2Ti_2O_5$ NBs with different nitride time in the non-faradic regions.



Fig.S11 Long-term stability test of Ru/TiO_xN_y NBs at 10 mA cm⁻².



Fig. S12 High-resolution XPS of (a) Ti 2p, (b) Ru 3d, (c) O 1s and (d) N 1s for Ru/TiO_xN_y NBs after stability test.



Fig. S13 TEM (a, b) and SEM (c, d) images of Ru/TiO_xN_yNBs after stability test.

Electrocatalysts	Electrolytes	Overpotential (mV)	Tafel slope	Reference
Ru/TiO _x N _y	1.0 М КОН	16 mV at 10 mA cm ⁻²	42 mV dec⁻¹	This work
RuCr@C	1.0 M KOH	19 mV at 10 mA cm ⁻²	24 mV dec⁻¹	1
Ru-CoP/CC	1.0 M KOH	21 mV at 10 mA cm ⁻²	49 mV dec⁻¹	2
Ru@Ni-MOF	1.0 M KOH	22 mV at 10 mA $\rm cm^{-2}$	40 mV dec⁻¹	3
hybrid RuCoP clusters	1.0 M KOH	23 mV at 10 mA cm ⁻²	37 mV dec⁻¹	4
RuAu SAAs	1.0 M KOH	24 mV at 10 mA $\rm cm^{-2}$	37 mV dec ⁻¹	5
Ru MNSs	1.0 M KOH	24 mV at 10 mA cm ⁻²	~33 mV dec ⁻¹	6
Ru ₂ -GC	1.0 M KOH	25 mV at 10 mA $\rm cm^{-2}$	65 mV dec ⁻¹	7
Ru-MoS ₂ -Mo ₂ C/TiN	1.0 M KOH	25 mV at 10 mA cm ⁻²	58 mV dec ⁻¹	8
Pt-NC/Ni-MOF	1.0 M KOH	25 mV at 10 mA $\rm cm^{-2}$	41.2 mV dec ⁻¹	9
P-Ru-CoNi-LDH	1.0 M KOH	29 mV at 10 mA cm ⁻²	69 mV dec ⁻¹	10
Ru/Co₃O₄	1.0 M KOH	31 mV at 10 mA cm ⁻²	69.8 mV dec ⁻¹	11
Ru-NiCo ₂ S ₄	1.0 M KOH	32 mV at 10 mA cm ⁻²	41.3 mV dec ⁻¹	12
RuRh-Co	1.0 M KOH	32 mV at 20 mA $\rm cm^{-2}$	31 mV dec ⁻¹	13
CC@WS₂/Ru-450	1.0 M KOH	32.1 mV at 10 mA cm ⁻²	53.2 mV dec ⁻¹	14
Ru-HMT-MP-7	1.0 M KOH	33 mV at 10 mA cm ⁻²	26.4 mV dec ⁻¹	15
RuNi-NCNFs	1.0 M KOH	35 mV at 10 mA cm ⁻²	30 mV dec ⁻¹	16
A-CoPt-NC	1.0 M KOH	50 mV at 10 mA cm ⁻²	-	17
Rh/NiFeRh LDH	1.0 M KOH	57 mV at 10 mA cm ⁻²	81.3 mV dec ⁻¹	18
Sr ₂ RuO ₄	0.1 M KOH	61 mV at 10 mA cm ⁻²	51 mV dec ⁻¹	19
PtO ₂ -CoOOH/TM	1.0 M KOH	65.1 mV at 70 mA cm ⁻²	39 mV dec ⁻¹	20
Ni-MOF@Pt	1.0 M KOH	102 mV at 10 mA cm ⁻²	88 mV dec ⁻¹	21
CuPor-RuN₃	1.0 M KOH	114 mV at 10 mA cm ⁻²	-	22
Ru/NiFe LDH-F/NF	1.0 M KOH	115 mV at 10 mA cm $^{\circ}$	87.1 mV dec ⁻¹	23
Ni₅P₄-Ru	1.0 M KOH	123 mV at 10 mA cm $^{-2}$	56.7 mV dec ⁻¹	24
Pt ₁ -Mo ₂ C-C	1.0 M KOH	155 mV at 10 mA cm ⁻²	92 mV dec ⁻¹	25

Table S1. Comparison of HER performance for some recently reported electrocatalysts in alkaline electrolytes.

References

- 1 F. Bao, Z. Yang, Y. Yuan, P. Yu, G. Zeng, Y. Cheng, Y. Lu, J. Zhang and H. Huang, *Adv. Funct. Mater.*, 2021, **32**, 2108991.
- 2 X. Xiao, X. Wang, B. Li, X. Jiang, Y. Zhang, M. Li, S. Song, S. Chen, M. Wang, Y. Shen and Z. Ren, *Mater. Today Phys.*, 2020, **12**, 100182.
- 3 L. Deng, F. Hu, M. Ma, S. C. Huang, Y. Xiong, H. Y. Chen, L. Li and S. Peng, *Angew. Chem. Int. Ed. Engl.*, 2021, **60**, 22276-22282.
- 4 J. Xu, T. Liu, J. Li, B. Li, Y. Liu, B. Zhang, D. Xiong, I. Amorim, W. Li and L. Liu, *Energ. Environ. Sci.*, 2018, **11**, 1819-1827.
- 5 C. H. Chen, D. Wu, Z. Li, R. Zhang, C. G. Kuai, X. R. Zhao, C. K. Dong, S. Z. Qiao, H. Liu and X. W. Du, *Adv. Energy Mater.*, 2019, **9**, 1803913.
- 6 J. Zhang, X. Mao, S. Wang, L. Liang, M. Cao, L. Wang, G. Li, Y. Xu, X. Huang, *Angew. Chem. Int. Ed. Engl.*, 2022, e202116867.
- 7 J. Creus, S. Drouet, S. Suriñach, P. Lecante, V. Collière, R. Poteau, K. Philippot, J. García-Antón and X. Sala, ACS Catal., 2018, 8, 11094-11102.
- 8 V. H. Hoa, D. T. Tran, S. Prabhakaran, D. H. Kim, N. Hameed, H. Wang, N. H. Kim and J. H. Lee, *Nano Energy*, 2021, **88**, 106277.
- 9 C. Guo, Y. Jiao, Y. Zheng, J. Luo, K. Davey and S.-Z. Qiao, *Chem*, 2019, **5**, 2429-2441.
- 10 Q. Li, F. Huang, S. Li, H. Zhang and X. Y. Yu, *Small*, 2022, **18**, e2104323.
- 11 Z. Liu, L. Zeng, J. Yu, L. Yang, J. Zhang, X. Zhang, F. Han, L. Zhao, X. Li, H. Liu and W. Zhou, *Nano Energy*, 2021, **85**, 105940.
- 12 H. Su, S. Song, Y. Gao, N. Li, Y. Fu, L. Ge, W. Song, J. Liu and T. Ma, Adv. Funct. Mater., 2021, 2109731.
- 13 Y. Cui, Z. Xu, D. Chen, T. Li, H. Yang, X. Mu, X. Gu, H. Zhou, S. Liu and S. Mu, Nano Energy, 2021, 90, 106579.
- 14 J. Li, Y. Li, J. Wang, C. Zhang, H. Ma, C. Zhu, D. Fan, Z. Guo, M. Xu, Y. Wang and H. Ma, *Adv. Funct. Mater.*, 2022, 2109439.
- 15 Y. Zhao, X. Zhang, Y. Gao, Z. Chen, Z. Li, T. Ma, Z. Wu, L. Wang and S. Feng, Small, 2022, e2105168.
- 16 M. Li, H. Wang, W. Zhu, W. Li, C. Wang and X. Lu, *Adv. Sci.*, 2020, **7**, 1901833.
- 17 L. Zhang, Y. Jia, H. Liu, L. Zhuang, X. Yan, C. Lang, X. Wang, D. Yang, K. Huang, S. Feng and X. Yao, *Angew. Chem. Int. Ed. Engl.*, 2019, **58**, 9404-9408.
- B. Zhang, C. Zhu, Z. Wu, E. Stavitski, Y. H. Lui, T. H. Kim, H. Liu, L. Huang, X. Luan, L. Zhou, K. Jiang, W. Huang, S. Hu, H. Wang and J. S. Francisco, *Nano Lett.*, 2020, 20, 136-144.
- 19 Y. Zhu, H. A. Tahini, Z. Hu, J. Dai, Y. Chen, H. Sun, W. Zhou, M. Liu, S. C. Smith, H. Wang and Z. Shao, *Nat. Commun.*, 2019, **10**, 149.
- 20 Z. Wang, X. Ren, X. Shi, Abdullah M. Asiri, L. Wang, X. Li, X. Sun, Q. Zhang and H. Wang, *J. Mater. Chem. A*, 2018, **6**, 3864-3868.
- 21 K. Rui, G. Zhao, M. Lao, P. Cui, X. Zheng, X. Zheng, J. Zhu, W. Huang, S. X. Dou and W. Sun, *Nano Lett*, 2019, 19, 8447-8453.
- 22 J. Jiang, F. Sun, S. Zhou, W. Hu, H. Zhang, J. Dong, Z. Jiang, J. Zhao, J. Li, W. Yan and M. Wang, *Nat. Commun.*, 2018, **9**, 2885.
- Y. Wang, P. Zheng, M. Li, Y. Li, X. Zhang, J. Chen, X. Fang, Y. Liu, X. Yuan, X. Dai and H. Wang, *Nanoscale*, 2020, 12, 9669-9679.
- 24 Q. He, D. Tian, H. Jiang, D. Cao, S. Wei, D. Liu, P. Song, Y. Lin and L. Song, *Adv. Mater.*, 2020, **32**, e1906972.
- 25 S. Niu, J. Yang, H. Qi, Y. Su, Z. Wang, J. Qiu, A. Wang and T. Zhang, J. Energy Chem., 2021, 57, 371-377.