# Supporting Information

## Single-Atom Ru Anchored in Nitrogen-Doped MXene ($Ti_3C_2Tx$) as Efficient Catalyst for the Hydrogen Evolution Reaction at All pH Values

Haigang Liu[a, b, +], Zhe Hu[c, +], Qinglei Liu[b], Peng Sun[b], Yongfei Wang[a,b, *], Shulei Chou[c, *], Zhizhi Hu[b], Zhiqiang Zhang[b,*]

[a]School of Materials and Metallurgy University of Science and Technology Liaoning Anshan, Liaoning 114051, P. R. China

[b]Key Laboratory for Functional Material School of Chemical Engineering University of Science and Technology Liaoning 185 Qianshan Zhong Road, Anshan 114051, P. R. China

[c]Institute for Superconducting and Electronic Materials University of Wollongong Squires Way, North Wollongong, NSW 2519, Australia

[+]These author contributed equally to this work.

E-mail: wyf8307@ustl.edu.cn, shulei@uow.edu.au, zzq@ustl.edu.cn

## Table of contents

**Fig. S1–S11**

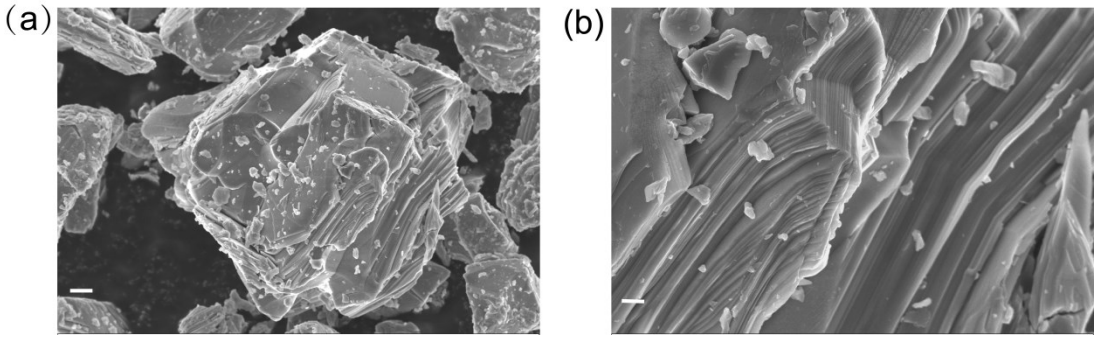


**Fig. S1** SEM image of $Ti_3AlC_2$, scale bara (a)1μm and (b) 200 nm.

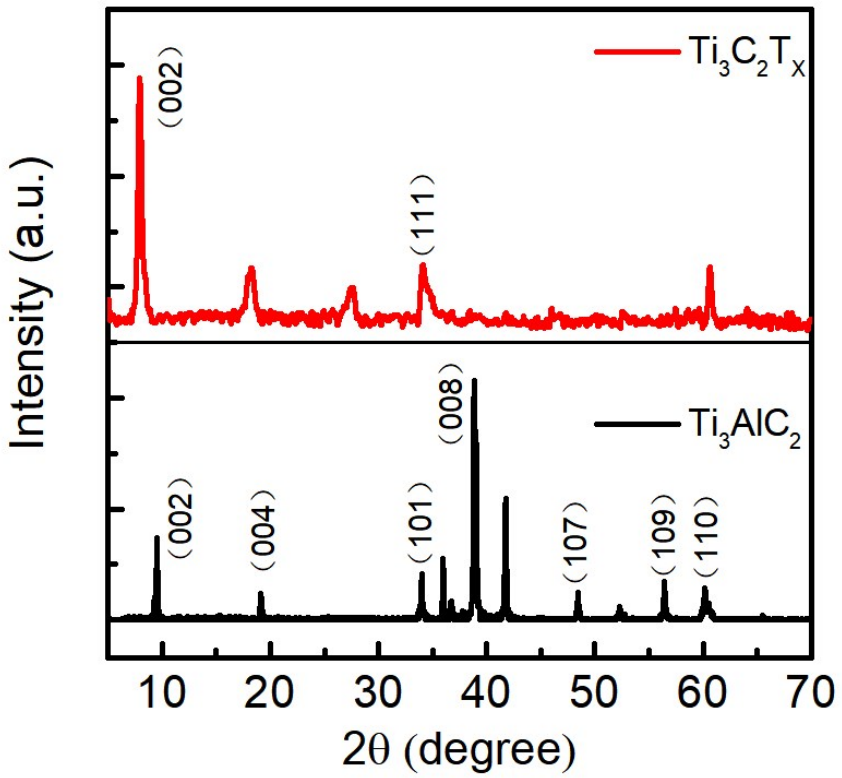


**Fig. S2** XRD patterns of the MAX phase $Ti_3AlC_2$ and $Ti_3C_2Tx$ MXene.

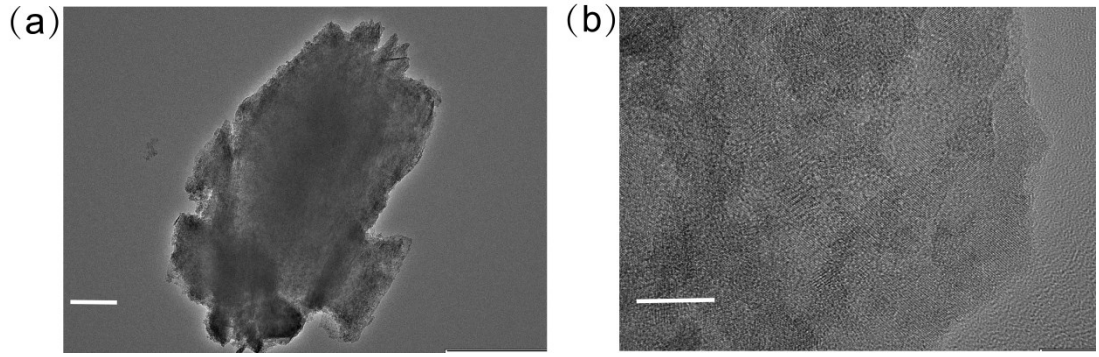


**Fig. S3** (a) TEM image of the $Ti_3C_2Tx$ (scale bar, 200 nm). (b) High-resolution TEM image of the $Ti_3C_2Tx$ (scale bar, 10 nm)

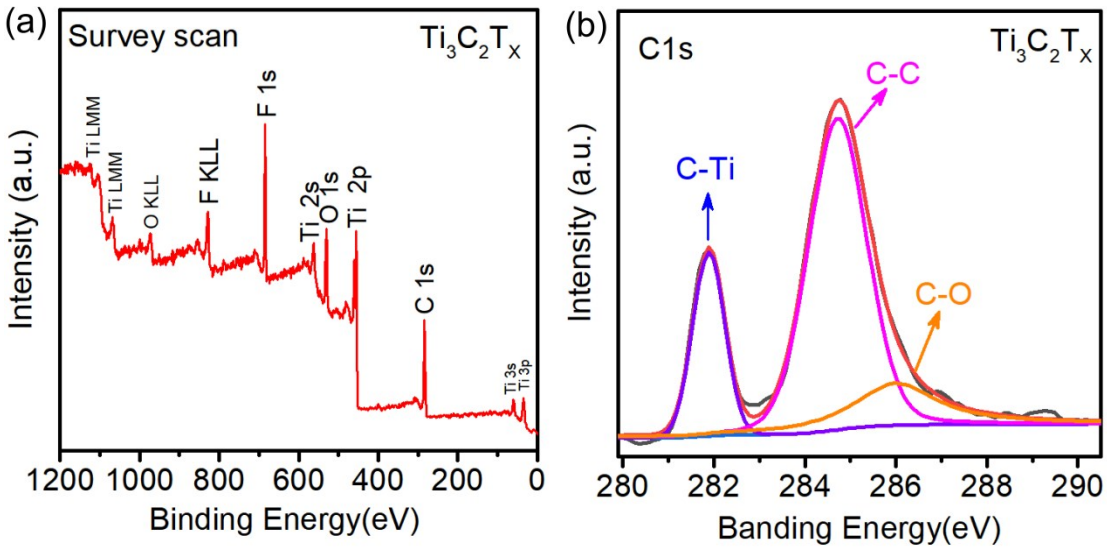


**Fig. S4** (a) Survey scan and (b) high resolution C1s XPS spectra of $Ti_3C_2Tx$.

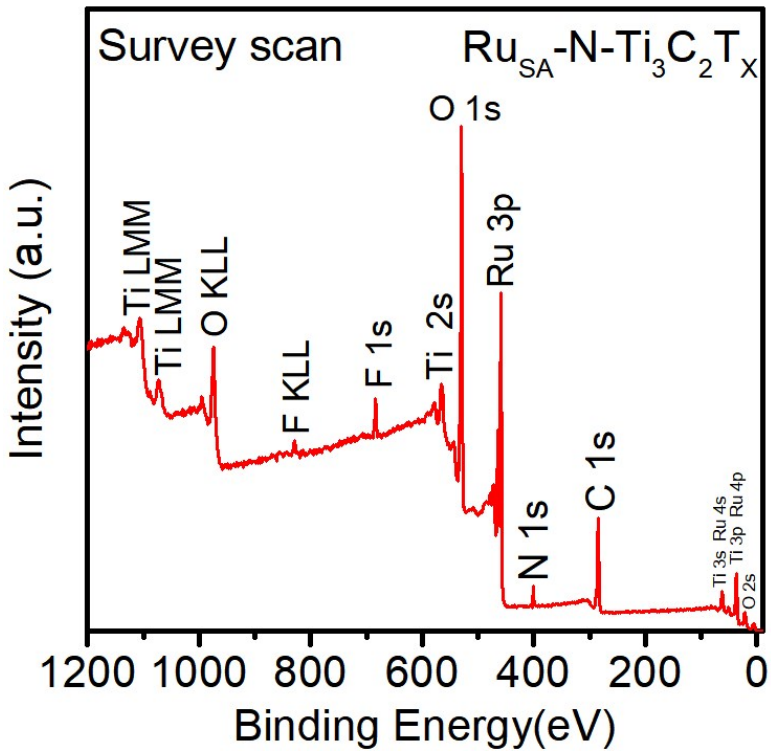


**Fig. S5** Survey scan XPS spectra of the $Ru_{SA}$-N-$Ti_3C_2T_x$ catalyst.

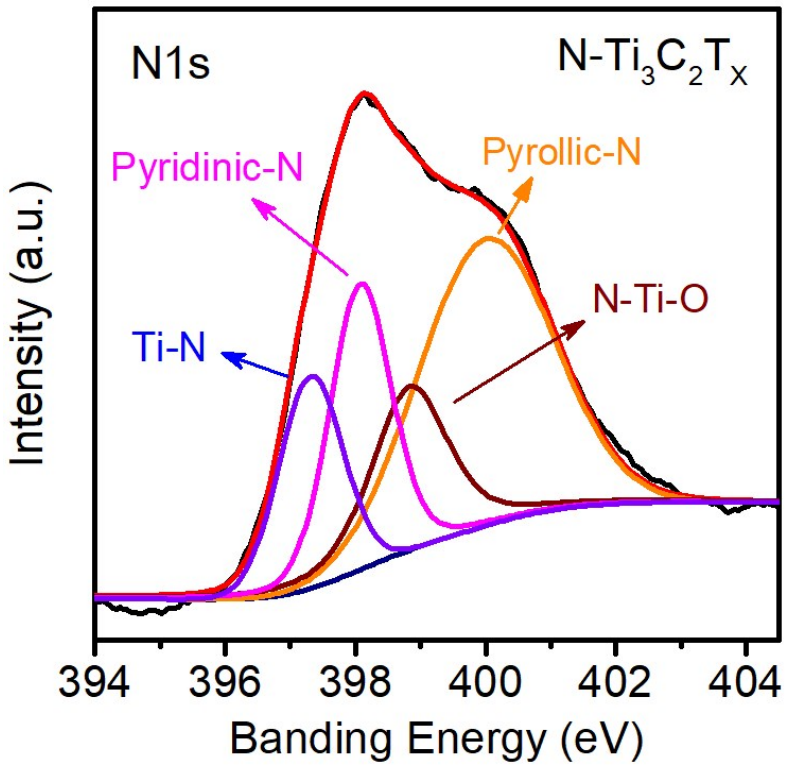


**Fig. S6** High resolution N1s XPS spectra of N-$Ti_3C_2T_x$.

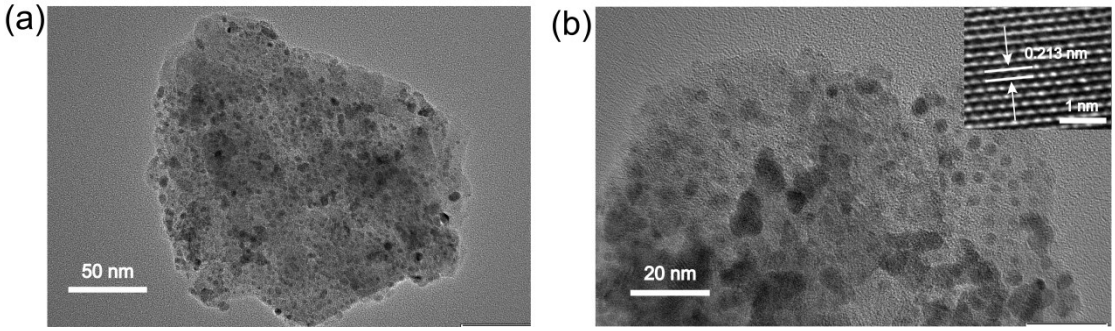


**Fig. S7** TEM image of the $Ru_{NC}$-$Ti_3C_2Tx$, (a) (scale bar, 50 nm) and (b) (scale bar, 20 nm, inset: HRTEM image)

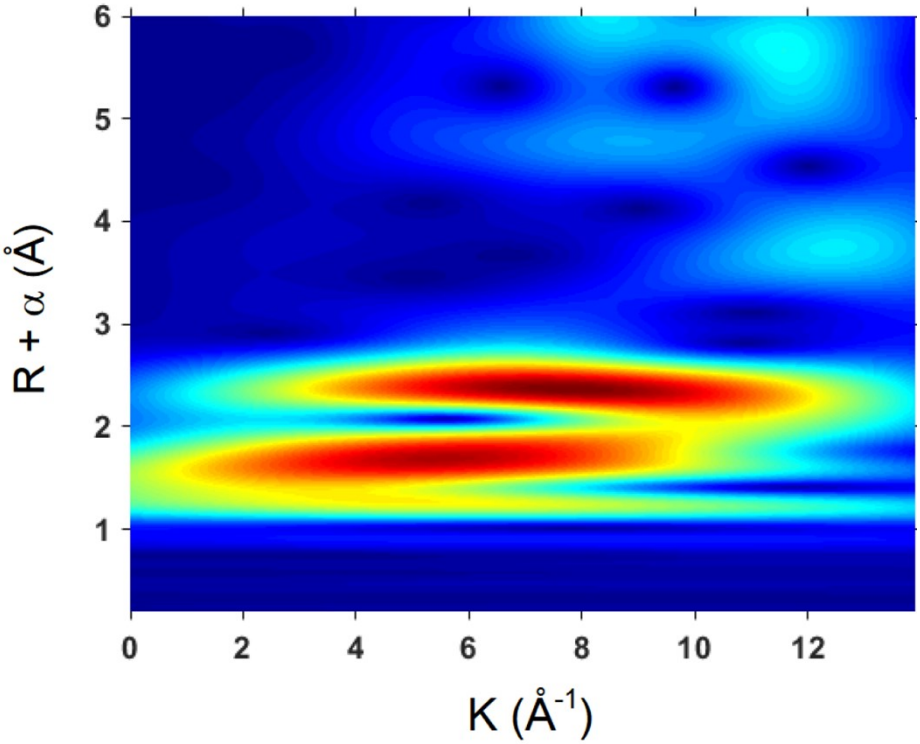


**Fig. S8** The wavelet transform for the $k^2$-weighted Ru-edge EXAFS of $Ru_{NC}$-$Ti_3C_2Tx$.

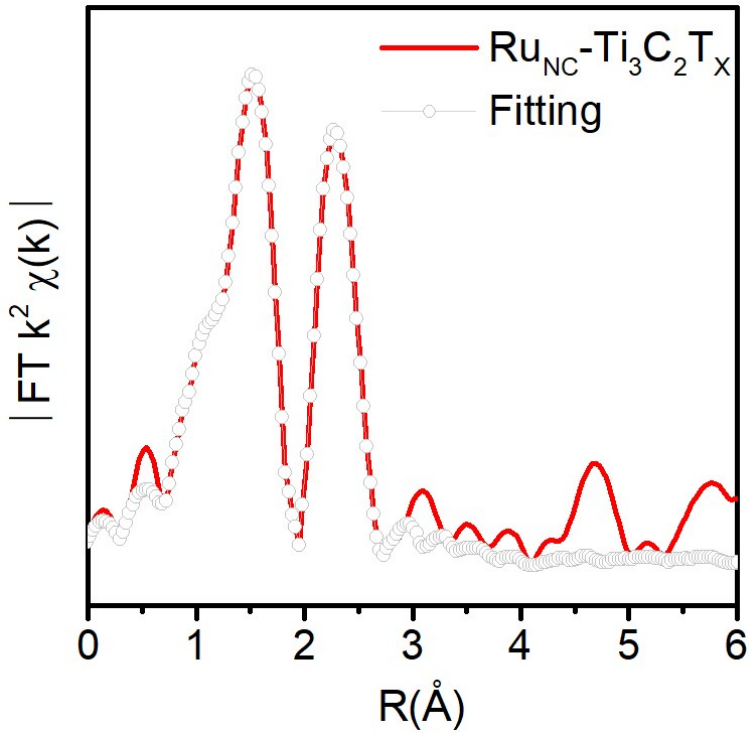


**Fig. S9** EXAFS fitting results for $Ru_{NC}$-$Ti_3C_2Tx$.

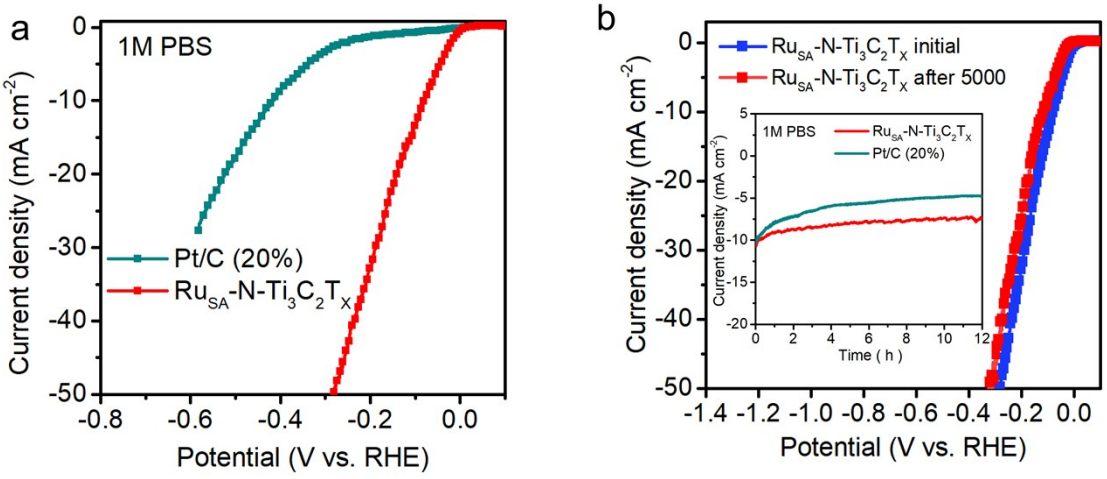


**Fig. S10** (a) HER polarization curves for $Ru_{SA}$-N-$Ti_3C_2Tx$ and Pt/C in 1 M PBS. (b) Durability of $Ru_{SA}$-N-$Ti_3C_2Tx$ before and after 5000 CV cycles in 1 M PBS. (inset: chronoamperometry curve of $Ru_{SA}$-N-$Ti_3C_2Tx$ and Pt/C).

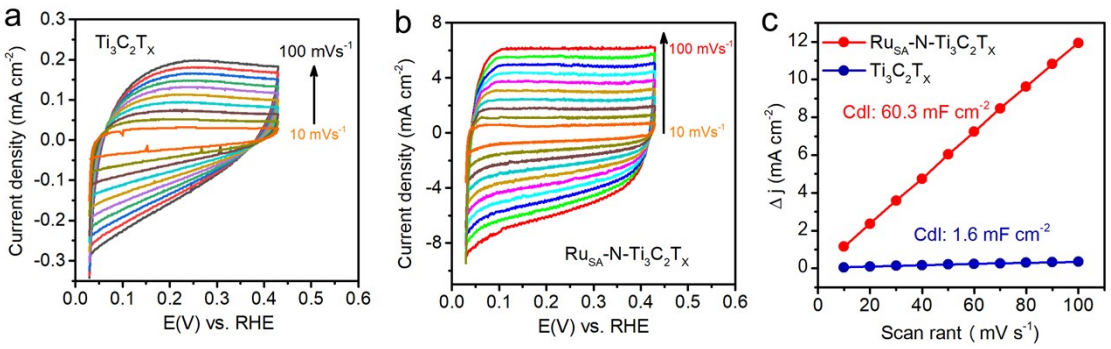


**Fig. S11** CV curves of (a) $Ti_3C_2Tx$ and (b) $Ru_{SA}$-N-$Ti_3C_2Tx$ at different scan rates in 0.5 M $H_2SO_4$. (C) The double-layer capacitance value ($C_{dl}$) of $Ti_3C_2Tx$ and $Ru_{SA}$-N-$Ti_3C_2Tx$ .

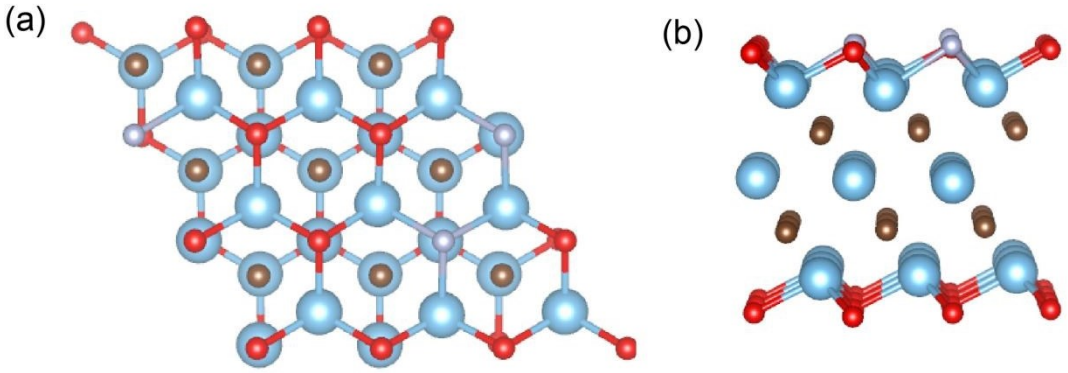


**Fig. S12** (a) Top and (b) side views of the $Ti_3C_2Tx$ layer atomic model. Blue: Ti; red: O; brown: C, and cyan : F.

## Tables S1-S2

**Table S1.** EXAFS curve Fitting Parameters of the Ru K-edge ($S0^2$=0.95)

| Sample | shell | $N^a$ | R(Å) | $\sigma^2(10^{-3}Å^2)$ | R factor |
|---|---|---|---|---|---|
| $Ru_{SA}$-N-$Ti_3C_2T_X$ | Ru-N/O | 3.4 | 2.09 | 5.3 | 0.0068 |
| $Ru_{NC}$-$Ti_3C_2T_X$ | Ru-C | 3.8 | 2.03 | 8.7 | 0.0076 |
| | Ru-Ru | 4.2 | 2.60 | 9.2 | |
| Ru foil | Ru-Ru | 12* | 2.68 | 4.0 | 0.0020 |
| $RuO_2$ | Ru-O | 4* | 1.90 | 4.5 | 0.0025 |
| | Ru-O | 2* | 2.02 | 3.8 | |

$S0^2$ is the amplitude reduction factor; $N^a$ is the coordination number; R is interatomic distance (the bond length between central atoms and surrounding coordination atoms); $\sigma^2$ is Debye-Waller factor (a measure of thermal and static disorder in absorber-scatterer distances); R factor is used to value the goodness of the fitting. Error bounds that characterize the structural parameters obtained by EXAFS spectroscopy were estimated as $N^a$±20%; R±1%; $\sigma^2$±20%.

* This value was fixed during EXAFS fitting, based on the known structure of standard crystal.

**Table S2.** Comparison of HER performance in alkaline/acid/neutral media for $Ru_{SA}$-N-$Ti_3C_2T_X$ with other HER electrocatalysts.

| Catalyst | Catalyst Loading ($mg/cm^2$) | Electrolytes | Overpotential @10 $mA/cm^2$ (mV) | Tafel slop ($mV\ dec^{-1}$) | Ref |
|---|---|---|---|---|---|
| Ru-N-$Ti_3C_2Tx$ | 1.0 | 1 M KOH | 27 | 29 | This work |
| | | 0.5 M $H_2SO_4$ | 23 | 35 | |
| | | 1 M PBS | 81 | - | |
| Mxene@Pt/SWCT | - | 0.5 M $H_2SO_4$ | 62 | 78 | [1] |

| s | | | | | |
|---|---|---|---|---|---|
| $Mo_2TiC_2Tx$-$Pt_{SA}$ | 1.0 | 0.5 M $H_2SO_4$ | 30 | 30 | [2] |
| $Ru_{SA}$-N-S-$Ti_3C_2Tx$ | 1.0 | 1 M KOH | 99 | - | [3] |
| | | 0.5 M $H_2SO_4$ | 76 | 90 | |
| | | 1 M PBS | 275 | - | |
| Ru@Co-SAS/N-C | 0.285 | 1 M KOH | 7 | 30 | [4] |
| | | 0.5 M $H_2SO_4$ | 57 | 55 | |
| | | 1 M PBS | 55 | 82 | |
| $Co_1$/PCN | 0.5 | 1 M KOH | 138 | 89 | [5] |
| | | 0.5 M $H_2SO_4$ | 151 | 52 | |
| RuSA@PN | 1.0 | 0.5 M $H_2SO_4$ | 42 | 38 | [6] |
| $RuP_2$@NPC | 1.0 | 1 M KOH | 52 | 69 | [7] |
| | | 0.5 M $H_2SO_4$ | 38 | 38 | |
| | | 1 M PBS | 57 | 87 | |
| Ru@CN-0.16 | 0.048 | 1 M KOH | 32 | 53 | [8] |
| | | 0.1 M $H_2SO_4$ | 126 | - | |
| | | 1 M PBS | 100 | - | |
| Ru@MWCNT | 0.16 | 1 M KOH | 17 | 27 | [9] |
| | 0.7 | 0.5 M $H_2SO_4$ | 13 | 27 | |
| | - | 1 M PBS | - | - | |
| Ru/$C_3N_4$/C | 0.204 | 1 M KOH | 79 | - | [10] |
| | | 0.5 M $H_2SO_4$ | ~75 | - | |
| CoP/CC | 0.92 | 1 M KOH | 209 | 129 | [11] |
| | | 0.5 M $H_2SO_4$ | 67 | 51 | |
| | | 1 M PBS | 65 | 93 | |
| Ru–$MoO_2$ | 0.285 | 1 M KOH | 29 | 31 | [12] |
| | 0.57 | 0.5 M $H_2SO_4$ | 55 | 44 | |
| 1D-$RuO_2$-$CN_x$ | 0.17 | 0.5 M KOH | 95 | 70 | [13] |

| | | | | | |
|---|---|---|---|---|---|
| | | 0.5 M $H_2SO_4$ | 93 | 40 | |
| | | 0.1 M PBS | 356 | 135 | |
| CoP@BCN | 0.4 | 1 M KOH | 215 | 52 | [14] |
| | | 0.5 M $H_2SO_4$ | 87 | 46 | |
| | | 1 M PBS | 122 | 59 | |
| $NiCo_2P_x$/CF | 5.9 | 1 M KOH | 58 | 34.3 | [15] |
| | | 0.5 M $H_2SO_4$ | 104 | 59.6 | |
| | | 1 M PBS | 63 | 63.3 | |
| Mn-CoP/Ti | 5.61 | 1 M KOH | 76 | 52 | [16] |
| | | 0.5 M $H_2SO_4$ | 49 | 55 | |
| | | 1 M PBS | 86 | 82 | |
| CoNC/GD | - | 1 M KOH | 284 | 115 | [17] |
| | | 0.5 M $H_2SO_4$ | 340 | 138 | |
| | | 1 M PBS | 368 | 207 | |
| $Zn_{0.3}Co_{2.7}S_4$ | 0.285 | 1 M KOH | 85 | - | [18] |
| | | 0.5 M $H_2SO_4$ | 80 | 47.5 | |
| | | 1 M PBS | 90 | - | |

**References**.


1 C. Cui, R. Cheng, H. Zhang, C. Zhang, Y. Ma , C. Shi, B. Fan, H. Wang, X. Wang*, Adv*. *Funct*. *Mater.*, 2020, 2000693.

2 J. Zhang, Y. Zhao, X. Guo, C. Chen, C. Dong, R. Liu, C. Han, Y. Li, Y. Gogotsi,G. Wang, *Nat. Catal.,* 2018, **1**, 985.

3 V. Ramalingam, P. Varadhan, H. Fu, H. Kim, D. Zhang, S. Chen, L. Song, D. Ma,

Y. Wang, H. N. Alshareef, J. H. He. *Adv. Mater.,* 2019, ***31***, 1903841.

4 S. Yuan, Z. Pu, H. Zhou, J. Yu, I. S. Amiinu, J. Zhu, Q. Liang, J. Yang, D. He, Z. Hu, G. V. Tendeloo, S. Mu, *Nano Energy,* 2019, **59**, 472.

5 L. Cao, Q. Luo, W. Liu, Y. Lin, X. Liu, Y. Cao, W. Zhang, Y. Wu, J. Yang, T. Yao, S. Wei, *Nat. Catal.,* 2018, **2**, 134.

6 J. Yang, B. Chen, X. Liu, W. Liu, Z. Li, J. Dong, W. Chen, W. Yan, T. Yao, X. Duan, Y. Wu, Y. Li, *Angew. Chem. Int. Ed.,* 2018, **57**, 9495.

7 Z. Pu, I. S. Amiinu, Z. Kou, W. Li, S. Mu, *Angew. Chem. Int. Ed*., 2017*,* **56**, 11559.

8 J. Wang, Z. Wei, S. Mao, H. Li, Y. Wang, *Energ. Environ. Sci.,* 2018, **11**, 800.

9 Do Hyung Kweon1 Mahmut Sait Okyay , Seok-Jin Kim , Jong-Pil Jeon, Hyuk-Jun Noh ,Noejung Park, Javeed Mahmood& Jong-Beom Baek, *Nat. Com.,* 2020, **11**, 1278.

10 Y. Zheng, Y. Jiao, Y. Zhu, L. H. Li, Y. Han, Y. Chen, M. Jaroniec, S.-Z. Qiao, *J. Am. Chem. Soc.,* 2016, **138**, 16174.

11 J. Tian, Q. Liu, A. M. Asiri, X. Sun, *J. Am. Chem. Soc.,* 2014, **136**, 7587.

12 P. Jiang, Y. Yang, R. Shi, G. Xia, J. Chen, J. Su, Q. Chen, *J. Mater. Chem. A,* 2017, **5** , 5475.

13 T. Bhowmik, M. K. Kundu, S. Barman, *ACS Appl. Mater. Inter.,* 2016, **8**, 28678.

14 H. Tabassum, W. Guo, W. Meng, A. Mahmood, R. Zhao, Q. Wang, R. Zou, *Adv. Energy Mater.,* 2017, **7**, 1601671.

15 R. Zhang, X. Wang, S. Yu, T. Wen, X. Zhu, F. Yang, X. Sun, X. Wang, W. Hu, *Adv. Mater.,* 2017, **29**.

16 T. Liu, X. Ma, D. Liu, S. Hao, G. Du, Y. Ma, A. M. Asiri, X. Sun, L. Chen, *ACS Catal.* 2016, **7***,* 98.

17 Y. Xue, J. Li, Z. Xue, Y. Li, H. Liu, D. Li, W. Yang, Y. Li, *ACS Appl. Mater. Inter.,* 2016**, 8**, 31083.

18 Z. F. Huang, J. Song, K. Li, M. Tahir, Y. T. Wang, L. Pan, L. Wang, X. Zhang, J. J. Zou, *J. Am. Chem. Soc*., 2016, **138***,* 1359.