

Supporting Information

Hierarchical $\text{Ti}_3\text{C}_2@\text{TiO}_2$ MXene Hybrids with Controllable Interlayer Distance for High Durable Lithium-ion Batteries

Li Li,^{*a,c} Gaoxue Jiang,^a Cuihua An,^{*b,c} Zhengjun Xie,^a Yijing Wang,^{*c} Lifang Jiao,^c
Huatang Yuan,^c

^aSchool of Materials Science and Engineering, University of Jinan, Jinan 250022,
Shandong, China

^bTianjin Key Laboratory of Advanced Functional Porous Materials, Institute for New
Energy Materials & Low-Carbon Technologies, School of Materials Science and
Engineering, Tianjin University of Technology, Tianjin 300384, China

^cKey Laboratory of Advanced Energy Materials Chemistry (Ministry of Education),
College of Chemistry, Nankai University, Tianjin 300071, China

^{*} *E-mail addresses*: mse_lil@ujn.edu.cn (L. Li), wangyj@nankai.edu.cn (Y. Wang)

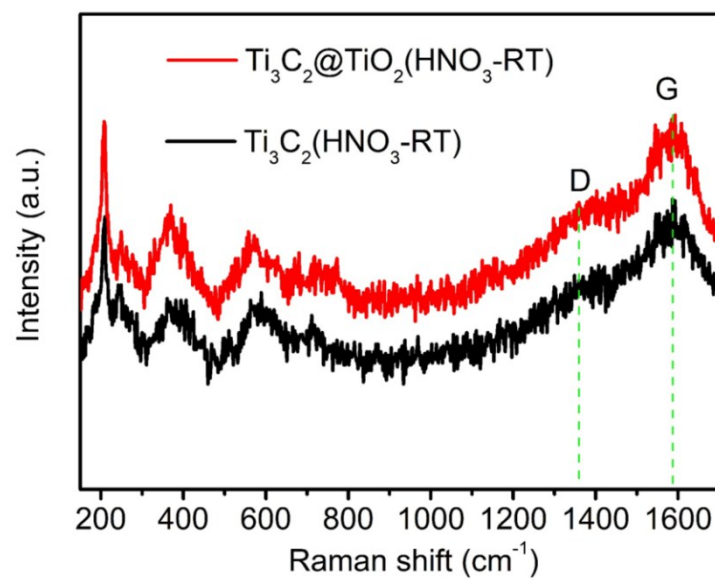


Fig. S1. Raman spectra of $\text{Ti}_3\text{C}_2(\text{HNO}_3\text{-RT})$ and $\text{Ti}_3\text{C}_2@\text{TiO}_2(\text{HNO}_3\text{-RT})$ hybrids.

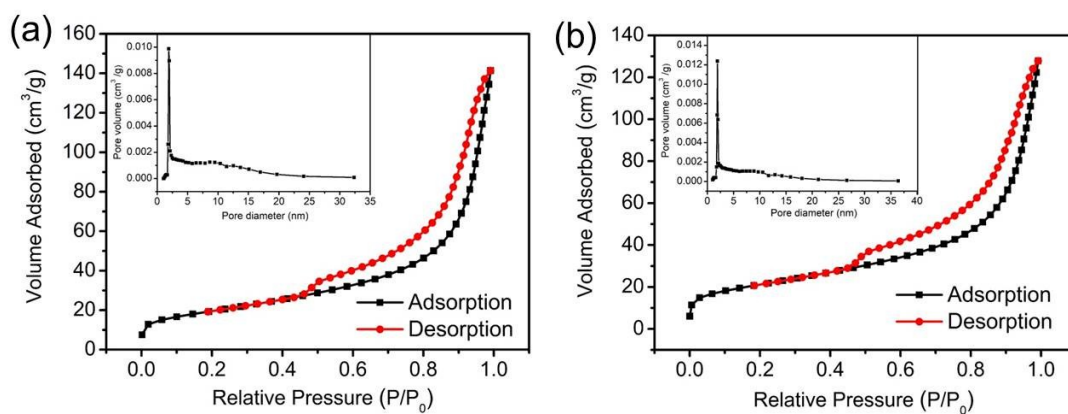


Fig. S2. N₂ adsorption/desorption isotherms of Ti₃C₂(HNO₃-RT) (a) and Ti₃C₂@TiO₂(HNO₃-RT) (b), respectively. The inserts images are the corresponding pore size distributions.

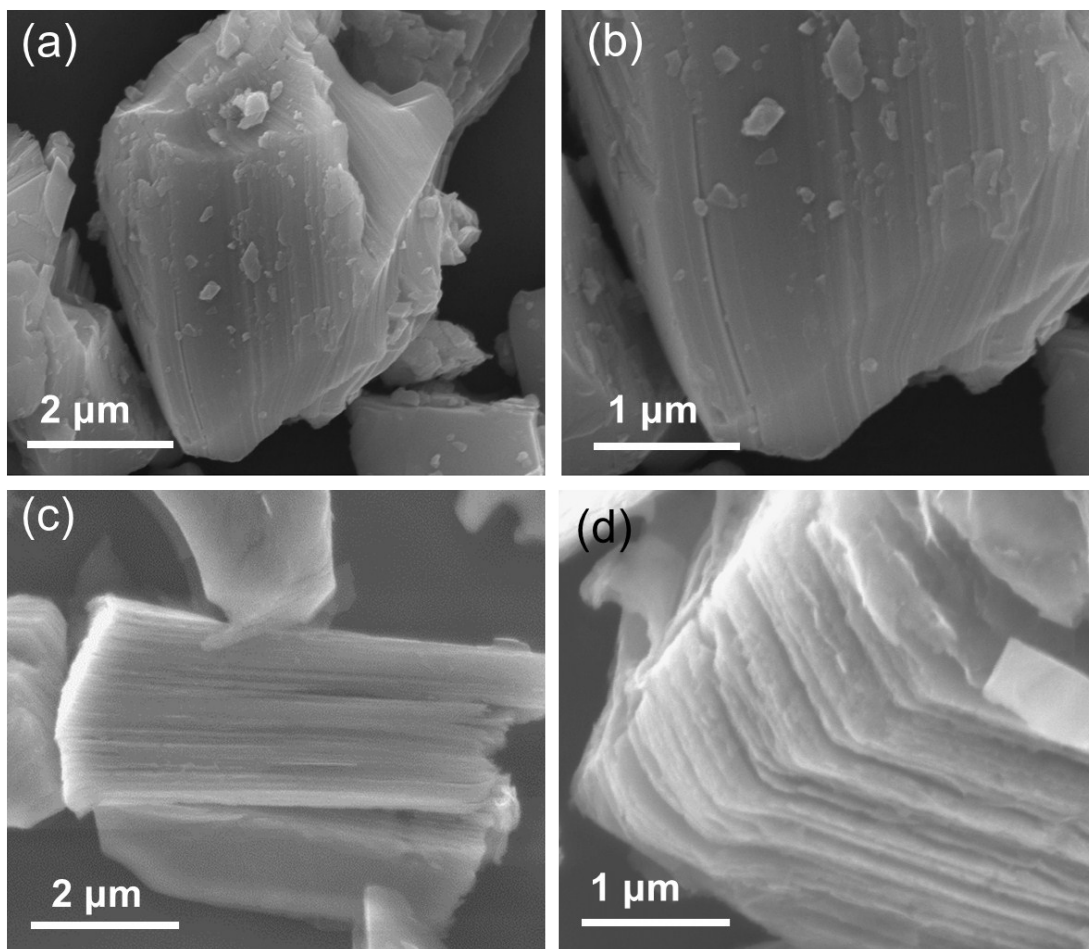


Fig. S3. SEM images of (a, b) Ti_3SiC_2 , (c-d) $\text{Ti}_3\text{C}_2(\text{H}_2\text{O}_2-40)$.

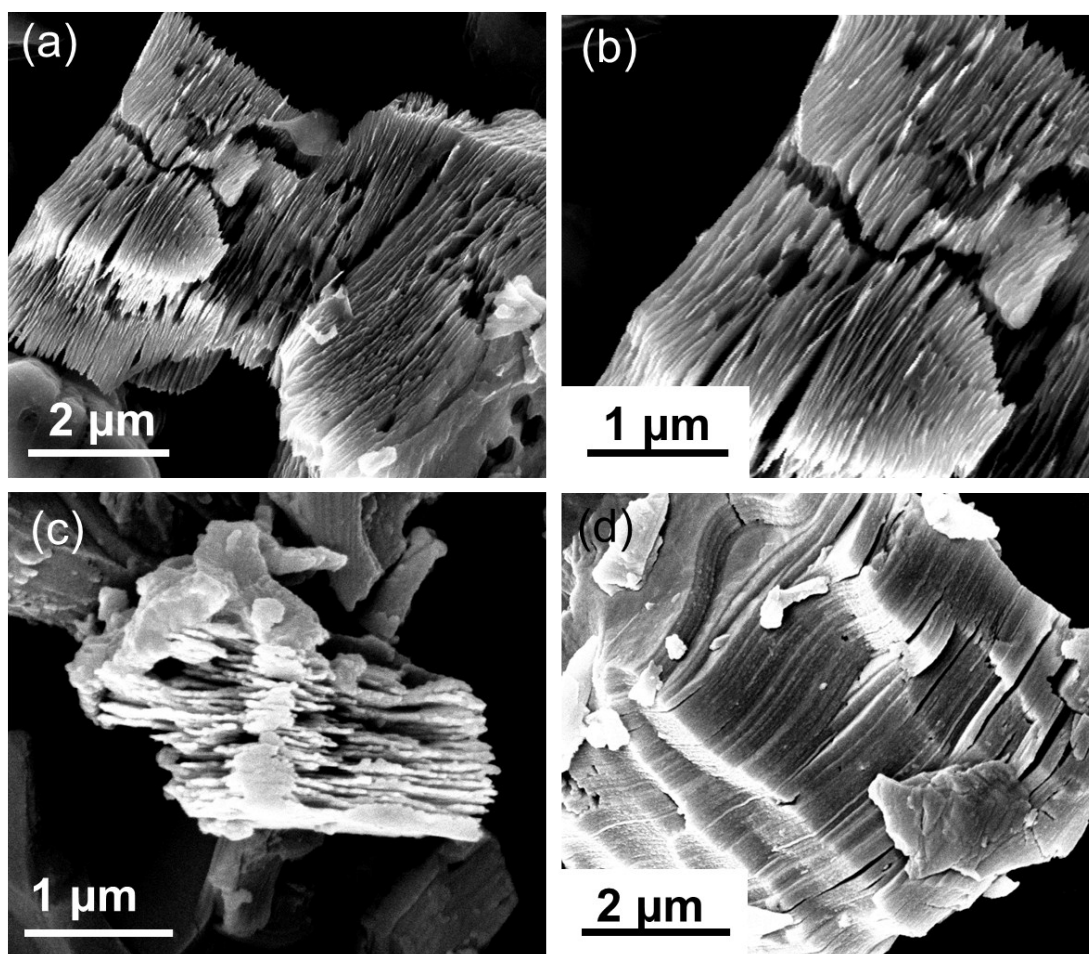


Fig. S4. SEM images of (a, b) $\text{Ti}_3\text{C}_2(\text{H}_2\text{O}_2\text{-70})$, (c) $\text{Ti}_3\text{C}_2(\text{HNO}_3\text{-40})$ and (d) $\text{Ti}_3\text{C}_2(\text{AR-RT})$.

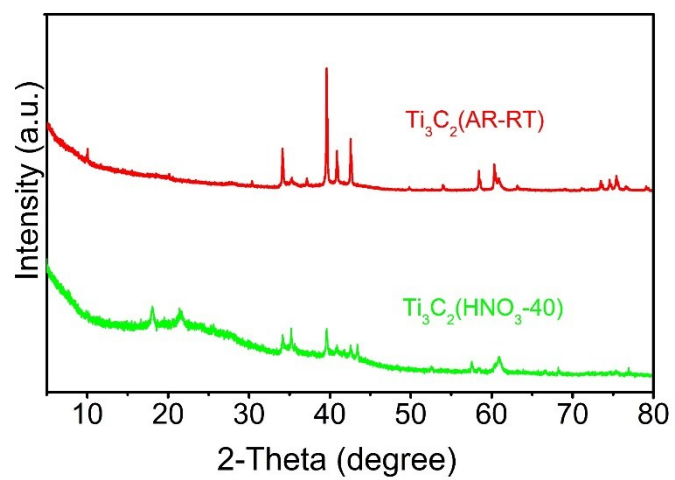


Fig. S5. XRD patterns of $\text{Ti}_3\text{C}_2(\text{HNO}_3\text{-40})$ and Ti_3C_2 (AR-RT).

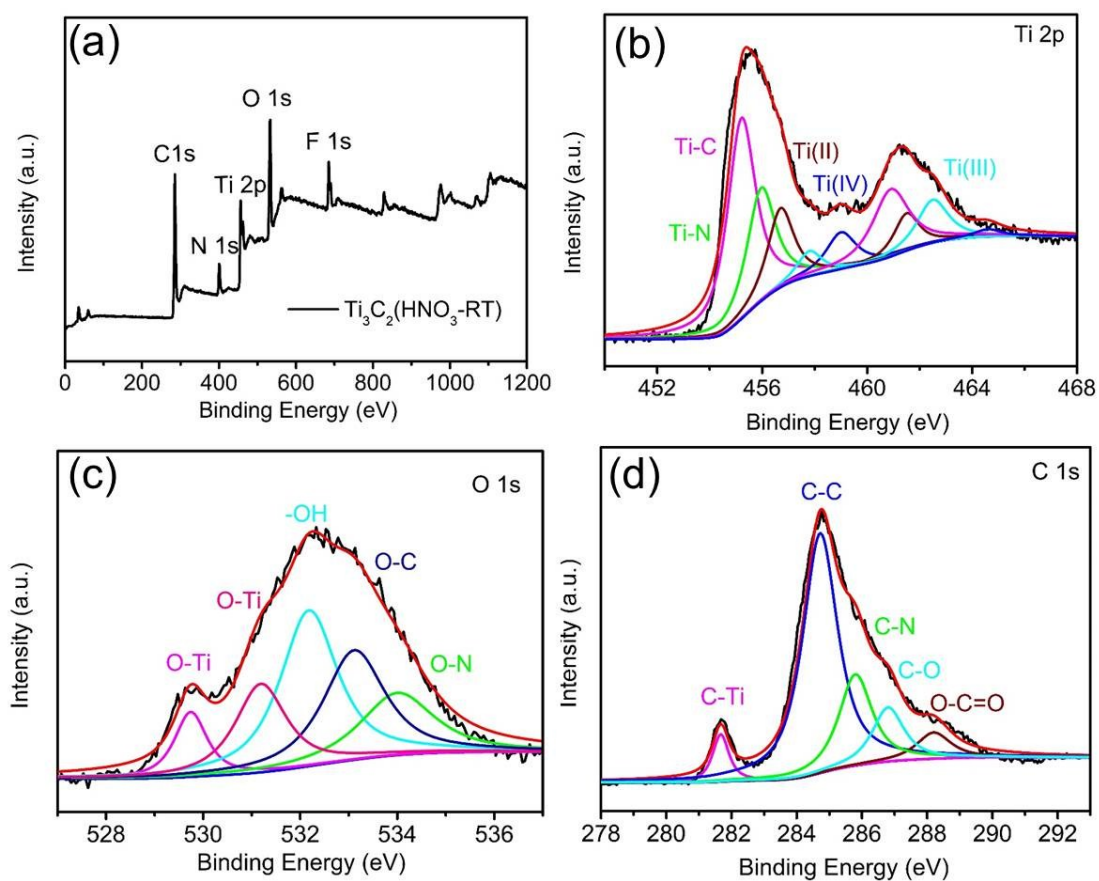


Fig. S6. (a) XPS survey scan of $\text{Ti}_3\text{C}_2(\text{HNO}_3\text{-RT})$, and high-resolution XPS spectra of (b) Ti 2p, (c) O 1s and (d) C 1s.

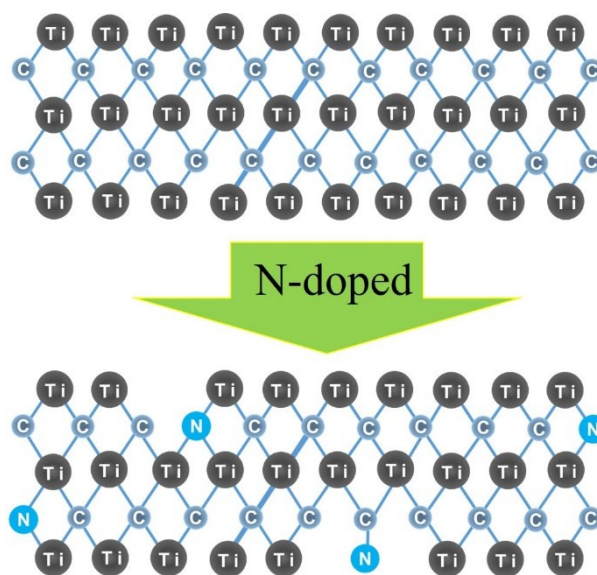


Fig. S7. Schematic diagram for the N doping process.

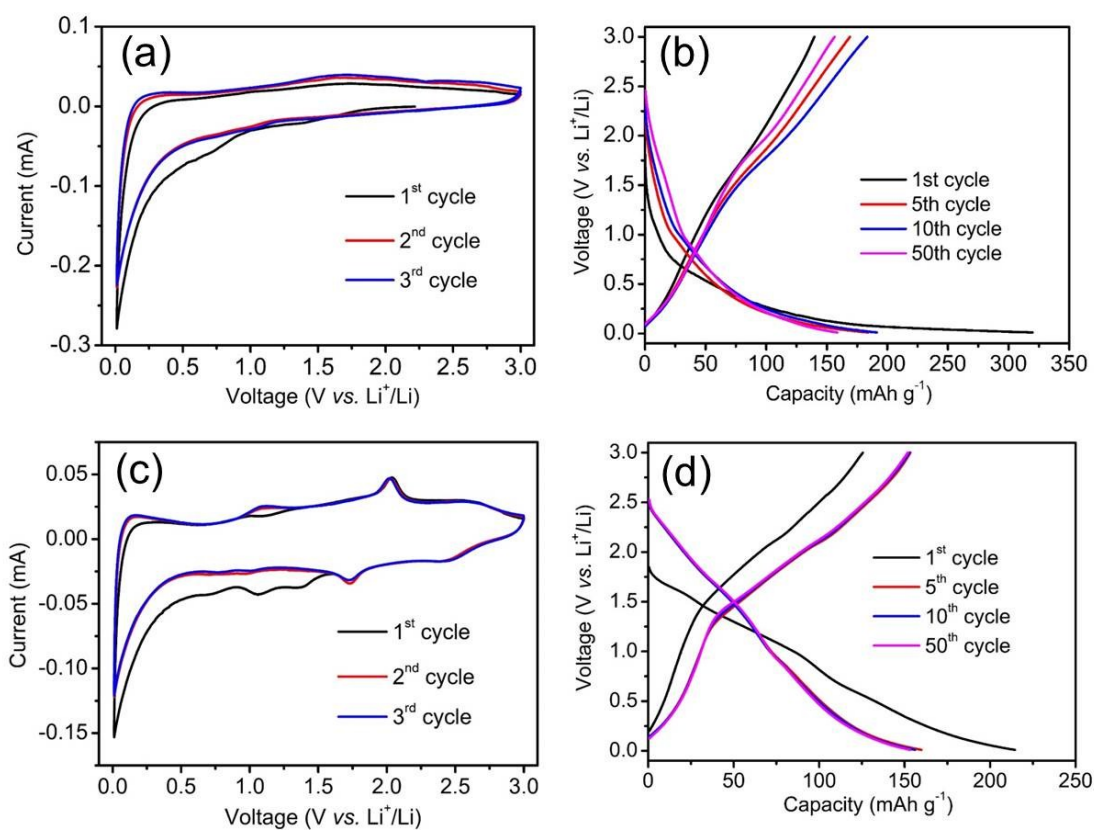


Fig. S8. Cyclic voltammogram of the $\text{Ti}_3\text{C}_2(\text{HNO}_3\text{-RT})$ (a) and $\text{Ti}_3\text{C}_2@\text{TiO}_2(\text{H}_2\text{O}_2\text{-60})$ (c) electrodes in the initial 3 cycles at a rate of 0.1 mV s^{-1} ; Charge/discharge curves of the $\text{Ti}_3\text{C}_2(\text{HNO}_3\text{-RT})$ (b) and $\text{Ti}_3\text{C}_2@\text{TiO}_2(\text{H}_2\text{O}_2\text{-60})$ (d) electrodes at different cycles, respectively.

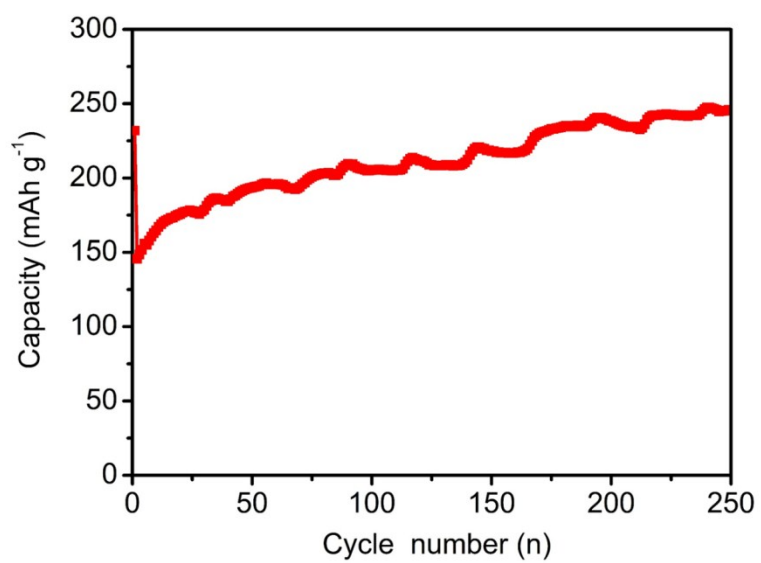


Fig. S9. Discharge capacity of N-doped $\text{Ti}_3\text{C}_2@\text{TiO}_2(\text{HNO}_3\text{-RT})$ electrodes at 500 mA g^{-1} .

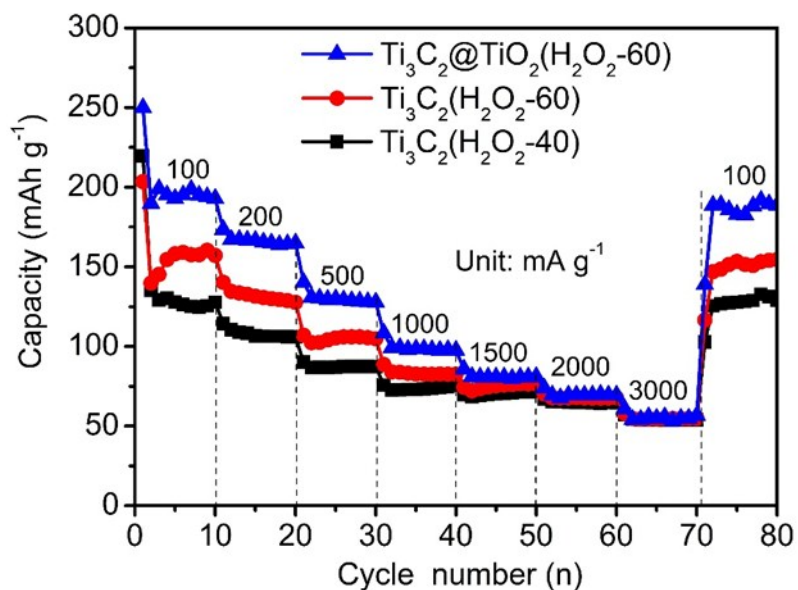


Fig. S10. Rate capability of the Ti_3C_2 and $\text{Ti}_3\text{C}_2@\text{TiO}_2$ electrodes (H_2O_2 as oxidant), respectively.

Compared with the rate capabilities of $\text{Ti}_3\text{C}_2(\text{H}_2\text{O}_2-40)$ and $\text{Ti}_3\text{C}_2(\text{H}_2\text{O}_2-60)$ electrodes, the rate capacity of $\text{Ti}_3\text{C}_2@\text{TiO}_2(\text{H}_2\text{O}_2-60)$ is higher and the discharge specific capacities are 195, 166, 129, 98, 80, 69 and 56 mA h g^{-1} at 100, 200, 500, 1000, 1500, 2000 and 3000 mA g^{-1} , respectively.

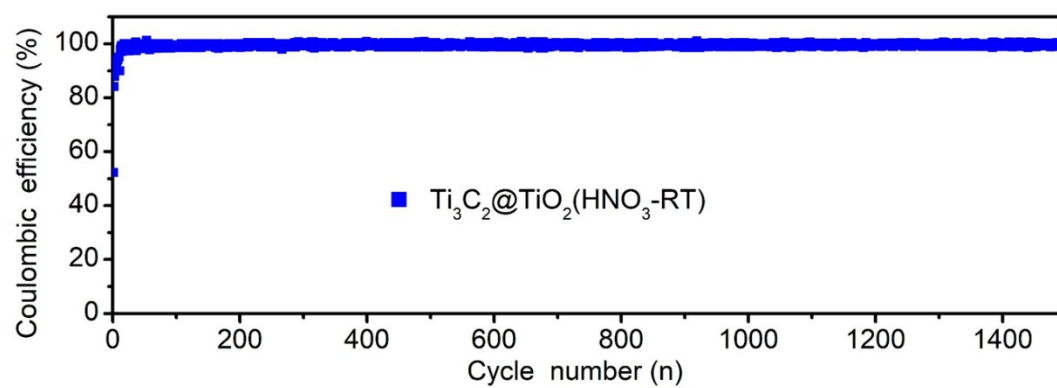


Fig. S11. The coulombic efficiency of N-doped $\text{Ti}_3\text{C}_2@\text{TiO}_2(\text{HNO}_3\text{-RT})$ electrode at 2000 mA g^{-1} .

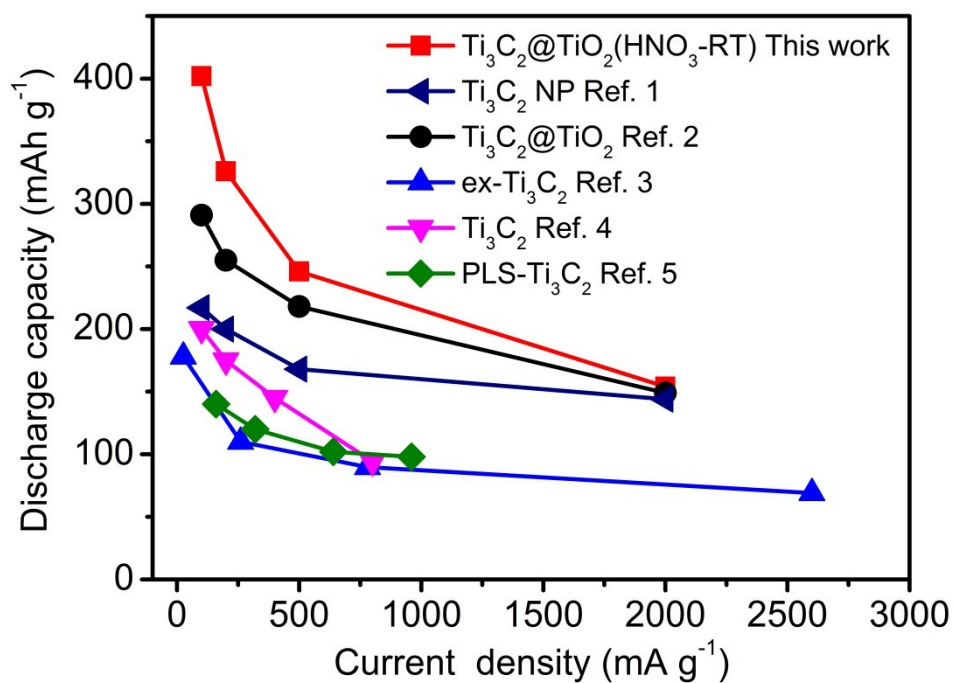


Fig. S12. Comparisons in the rate capabilities between this work and other Ti_3C_2 -based electrodes.

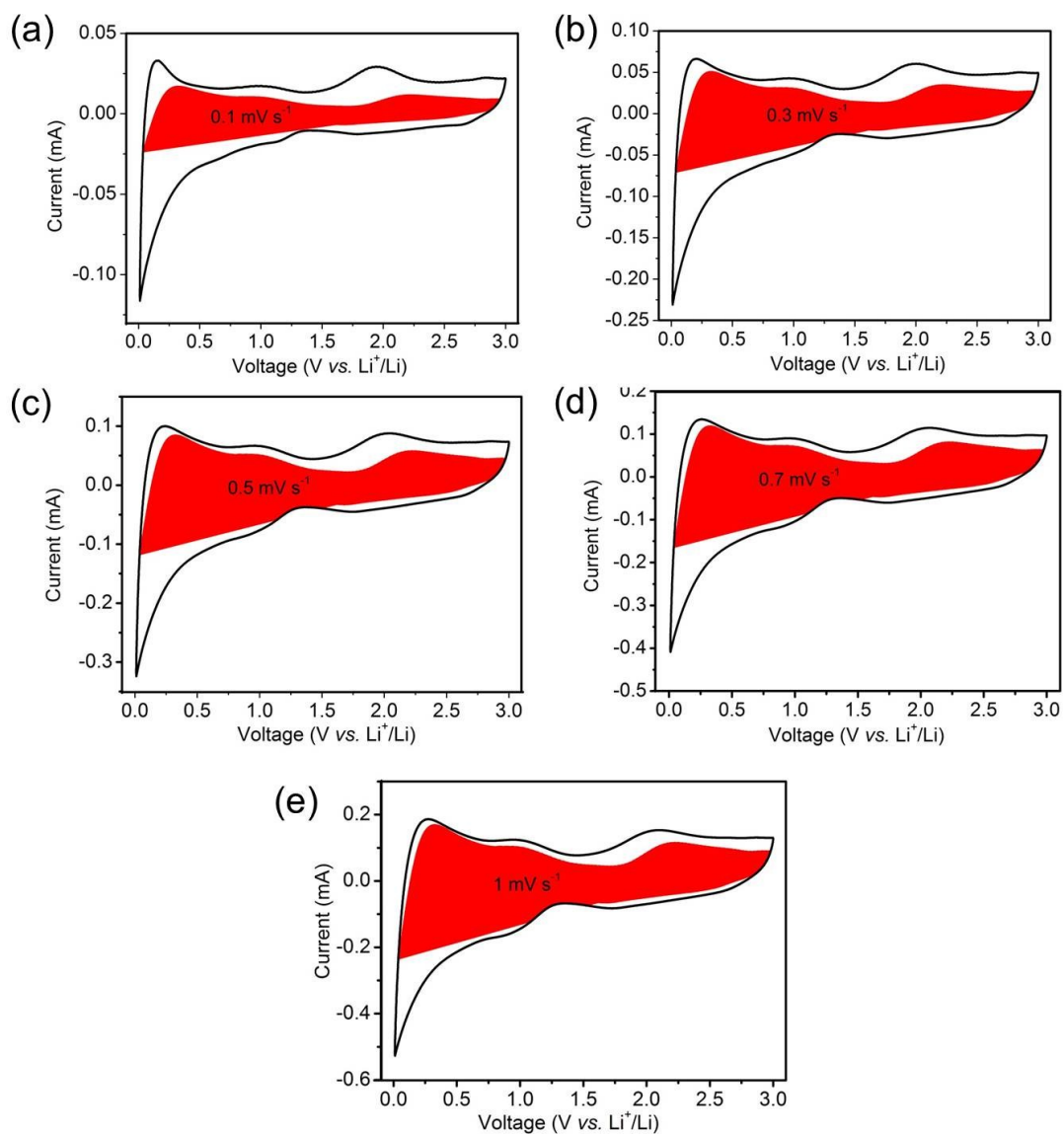


Fig. S13. CV profiles with shaded portion showing the capacitive contribution at 0.1, 0.3, 0.5, 0.7 and 1 mV s^{-1} .

Table S1 Different preparation conditions and labeling of Ti_3C_2 and $\text{Ti}_3\text{C}_2@\text{TiO}_2$,

respectively.

MAX	Etchant	T (°C)	Time (h)	Hydrothermal	Product record
Ti_3SiC_2	HF	40	48	No	$\text{Ti}_3\text{SiC}_2(\text{HF}-40)$
Ti_3SiC_2	$\text{H}_2\text{O}_2+\text{HF}$	40	48	No	$\text{Ti}_3\text{C}_2(\text{H}_2\text{O}_2-40)$
Ti_3SiC_2	$\text{H}_2\text{O}_2+\text{HF}$	60	48	No	$\text{Ti}_3\text{C}_2(\text{H}_2\text{O}_2-60)$
Ti_3SiC_2	$\text{H}_2\text{O}_2+\text{HF}$	70	48	No	$\text{Ti}_3\text{C}_2(\text{H}_2\text{O}_2-70)$
Ti_3SiC_2	$\text{H}_2\text{O}_2+\text{HF}$	60	48	Yes	$\text{Ti}_3\text{C}_2@\text{TiO}_2(\text{H}_2\text{O}_2-60)$
Ti_3SiC_2	HNO_3+HF	Room temperature	40	No	$\text{Ti}_3\text{C}_2(\text{HNO}_3\text{-RT})$
Ti_3SiC_2	HNO_3+HF	40	40	No	$\text{Ti}_3\text{C}_2(\text{HNO}_3-40)$
Ti_3SiC_2	HNO_3+HF	Room temperature	40	Yes	$\text{Ti}_3\text{C}_2@\text{TiO}_2(\text{HNO}_3\text{-RT})$
Ti_3SiC_2	AR+HF	Room temperature	40	No	$\text{Ti}_3\text{C}_2(\text{AR-RT})$

Table S2 Summary of the electrochemical performances of Ti_3C_2 -based electrodes at various current densities in LIBs.

Electrode material	Current density (mA g^{-1})	Cycle number (n)	Capacity (mA h g^{-1})	Ref.
MXene nanosheets	1000	500	139	1
Ti_3C_2	200	500	203	2
$\text{Ti}_3\text{C}_2@\text{TiO}_2$	200	500	267	2
Pure $\text{Mo}_2\text{TiC}_2\text{T}_x$	100	100	52	6
Ti_3C_2 film	1000	1000	70	7
Flash-air oxidized $\text{Ti}_3\text{C}_2\text{T}_x$	320	300	155	8
$\text{SnO}_2/\text{MXene}$	100	50	258	9
SHS- Ti_3C_2	1C	100	53	10
PLS- Ti_3C_2	1C	100	87	10
Ti_3C_2	100	100	108	11
$\text{CoO}@\text{Ti}_3\text{C}_2$	100	100	324	11
Ti_3C_2	125	1000	135	12
Ti_3C_2	100	100	125	13
Ti_3C_2	100	50	91	14
Ti_3C_2	100	200	82	15
$\text{Ti}_3\text{C}_2@\text{TiO}_2(\text{H}_2\text{O}_2\text{-60})$	2000	1500	106	This work
$\text{Ti}_3\text{C}_2(\text{HNO}_3\text{-RT})$	200	250	201	This work
$\text{Ti}_3\text{C}_2@\text{TiO}_2(\text{HNO}_3\text{-RT})$	200	250	339	This work
$\text{Ti}_3\text{C}_2@\text{TiO}_2(\text{HNO}_3\text{-RT})$	500	250	246	This work
$\text{Ti}_3\text{C}_2@\text{TiO}_2(\text{HNO}_3\text{-RT})$	2000	1500	154	This work

References

- [1] Y.T. Liu, P. Zhang, N. Sun, B. Anasori, Q.Z. Zhu, H. Liu, Y. Gogotsi and B. Xu, Self-Assembly of Transition Metal Oxide Nanostructures on MXene Nanosheets for Fast and Stable Lithium Storage, *Adv. Mater.*, 2018, **30**, 1707334.
- [2] C. Yang, Y. Liu, X. Sun, Y.R. Zhang, L.R. Hou, Q.G. Zhang and C.Z. Yuan, *In-situ* construction of hierarchical accordion-like $\text{TiO}_2\text{-Ti}_3\text{C}_2$ nanohybrid as anode material for lithium and sodium ion batteries, *Electrochim. Acta*, 2018, **271**, 165-172.
- [3] D. Sun, M. Wang, Z. Li, G. Fan, L. Z. Fan, A. Zhou, Two-dimensional Ti_3C_2 as anode material for Li-ion batteries, *Electrochem. Commun.*, 2014, 47, 80-83.
- [4] X.F. Wang, X. Shen, Y.R. Gao, Z. Wang, R. Yu and L. Chen, Atomic-Scale Recognition of Surface Structure and Intercalation Mechanism of $\text{Ti}_3\text{C}_2\text{X}$, *J. Am. Chem. Soc.*, 2015, 137, 2715-2721.
- [5] F.Y. Kong, X.D. He, Q.Q. Liu, X.X. Qi, Y.T. Zheng, Effect of Ti_3AlC_2 precursor on the electrochemical properties of the resulting MXene Ti_3C_2 for Li-ion batteries, *Ceram. Int.*, 2018, 44, 11591-11596.
- [6] C. Chen, X. Xie, B. Anasori, A. Sarycheva, T. Makaryan, M. Zhao, P. Urbankowski, L. Miao, J. Jiang and Y. Gogotsi, MoS_2 -on-MXene Heterostructures as Highly Reversible Anode Materials for Lithium-Ion Batteries, *Angew. Chem. Int. Edit.*, 2018, **57**, 1846-1850.
- [7] Z. Ma, X. Zhou, W. Deng, D. Lei and Z. Liu, 3D Porous MXene (Ti_3C_2)/Reduced Graphene Oxide Hybrid Films for Advanced Lithium Storage, *ACS Appl. Mater. Interfaces*, 2018, **10**, 3634-3643.
- [8] M. Naguib, O. Mashtalir, M.R. Lukatskaya, B. Dyatkin, C.F. Zhang, V. Presser, Y. Gogotsi and M.W. Barsoum, One-step synthesis of nanocrystalline transition metal oxides on thin sheets of disordered graphitic carbon by oxidation of MXenes, *Chem. Commun.*, 2014, **50**, 7420-7423.
- [9] B. Ahmed, D.H. Anjum, Y. Gogotsi and H.N. Alshareef, Atomic layer deposition of SnO_2 on MXene for Li-ion battery anodes, *Nano Energy*, 2017, **34**, 249-256.
- [10] F. Kong, Q.Q. Liu, X.X. Qi, Y.T. Zheng, R.G. Wang and Y.L. Bai, Effect of

Ti₃AlC₂ precursor on the electrochemical properties of the resulting MXene Ti₃C₂ for Li-ion batteries, *Ceram. Int.*, 2018, **44**, 11591-11596.

[11] X.L. Li, Y. Fang, W.J. Lv, F. Wang, Y. Liu and H. Liu, Hydrothermal preparation of CoO/Ti₃C₂ composite material for lithium-ion batteries with enhanced electrochemical performance, *J. Electroanal. Chem.*, 2018, **817**, 1-8.

[12] Y.S. Wang, Y.Y. Li, Z.P. Qiu, X.Z. Wu, P.F. Zhou, T. Zhou, J.P. Zhao, Z.C. Miao and S.P. Zhuo, Fe₃O₄@Ti₃C₂ MXene hybrids with ultrahigh volumetric capacity as an anode material for lithium-ion batteries, *J. Mater. Chem. A*, 2018, **6**, 11189-11197.

[13] J. Luo, W. Zhang, H. Yuan, C. Jin, L. Zhang, H. Huang, C. Liang, Y. Xia, J. Zhang, Y. Gan and X. Tao, Pillared Structure Design of MXene with Ultralarge Interlayer Spacing for High-Performance Lithium-Ion Capacitors, *ACS Nano*, 2017, **11**, 2459-2469.

[14] J. Luo, X. Tao, J. Zhang, Y. Xia, H. Huang, L. Zhang, Y. Gan, C. Liang and W. Zhang, Sn⁴⁺ Ion Decorated Highly Conductive Ti₃C₂ MXene: Promising Lithium-Ion Anodes with Enhanced Volumetric Capacity and Cyclic Performance, *ACS Nano*, 2016, **10**, 2491-2499.

[15] F. Wang, Z.J. Wang, J.F. Zhu, H.B. Yang, X.J. Chen, L. Wang and C.H. Yang, Facile synthesis SnO₂ nanoparticle-modified Ti₃C₂ MXene nanocomposites for enhanced lithium storage application, *J. Mater. Sci.*, 2017, **52**, 3556-3565.