Supporting Information For

Substituting Innocent Phosphate with Redox-active Silicate Towards Advanced Polyanion-type Cathode Materials for Sodium-ion Batteries

Ruimin Sun[1], Mingyue Dou[1], Yuxiang Zhang[1], Jingyu Chen[1], Yuhao Chen[1], Bo Han[1], Kaisheng Xia[1], Qiang Gao[1], Xiaoxiao Liu[2], Zhao Cai[1,*], and Chenggang Zhou[1,*]

[1] Faculty of Materials Science and Chemistry, China University of Geosciences (Wuhan), Wuhan 430074, China

[2] Wuhan National Laboratory for Optoelectronics, Huazhong University of Science and Technology, Wuhan 430074, China

* E-mail: caizhao@cug.edu.cn (Z. Cai); cgzhou@cug.edu.cn (C. Zhou).

Supplementary Figures

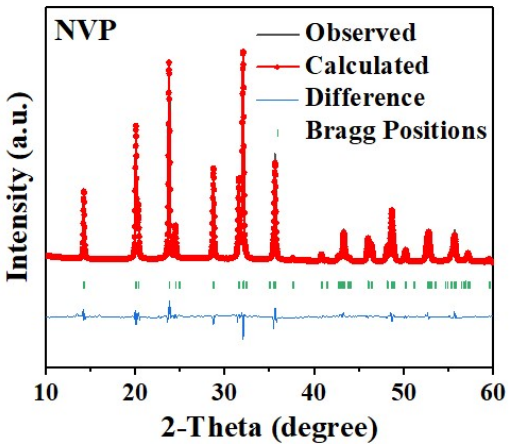

Figure S1. XRD Rietveld refinement results of pristine NVP materials.

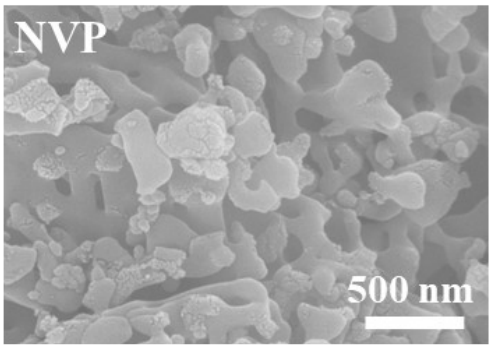

Figure S2. SEM image of pristine NVP materials.

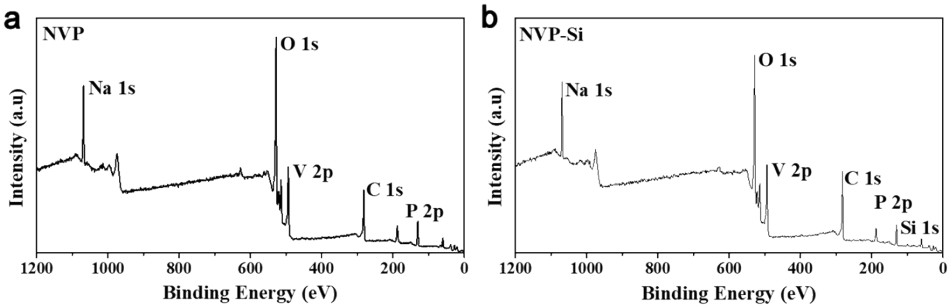

Figure S3. XPS full spectra of as-prepared (a) NVP and (b) NVP-Si materials.

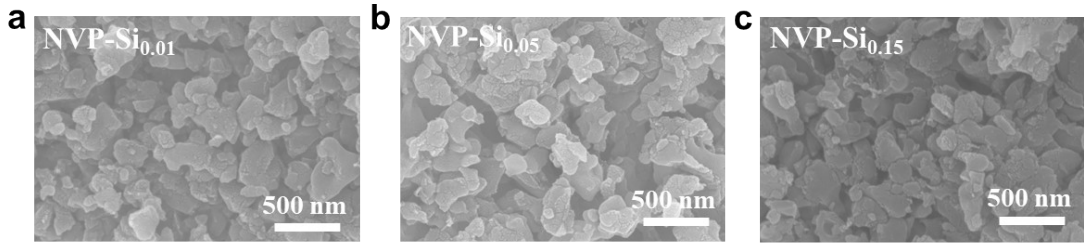

Figure S4. SEM images of as-prepared (a) $Na_3V_2(PO_4)_{2.99}(SiO_4)_{0.01}$ (i.e. NVP-$Si_{0.01}$), (b) $Na_3V_2(PO_4)_{2.95}(SiO_4)_{0.05}$ (i.e. NVP-$Si_{0.05}$), and (c) $Na_3V_2(PO_4)_{2.85}(SiO_4)_{0.15}$ (i.e. NVP-$Si_{0.15}$) materials.

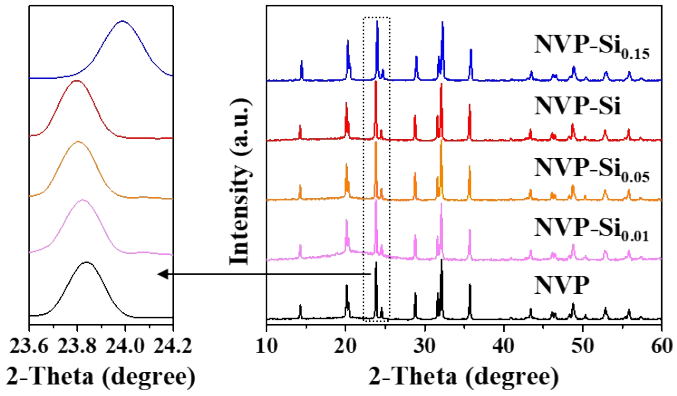

Figure S5. XRD patterns of as-prepared NVP, NVP-$Si_{0.01}$, NVP-$Si_{0.05}$, NVP-Si, and NVP-$Si_{0.15}$ materials.

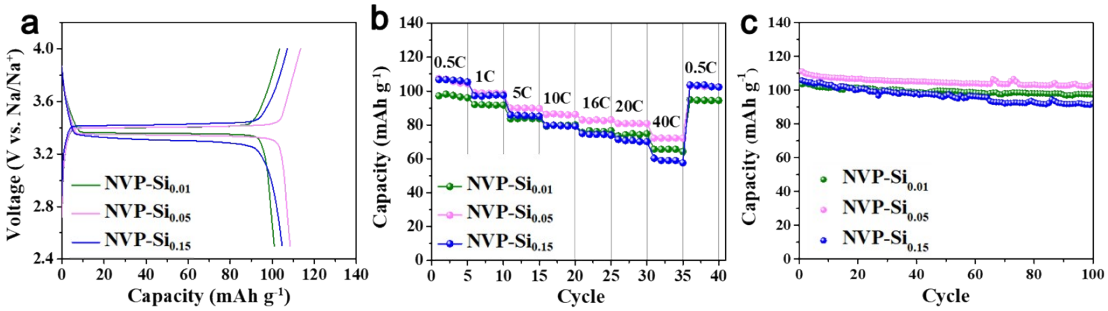

Figure S6. (a) Charge/discharge curves at 0.5 C, (b) rate performance from 0.5 C to 40 C, and (c) cycling performance at 0.5 C of the NVP-$Si_{0.01}$, NVP-$Si_{0.05}$, and NVP-$Si_{0.15}$ cathodes.

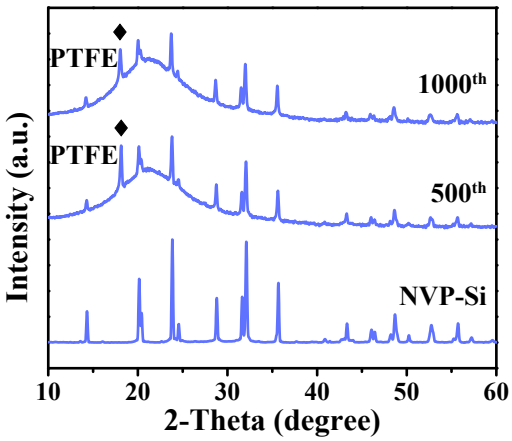

Figure S7. The XRD patterns of the NVP-Si cathodes before cycling and after 500/1000 electrochemical cycles at 10 C.

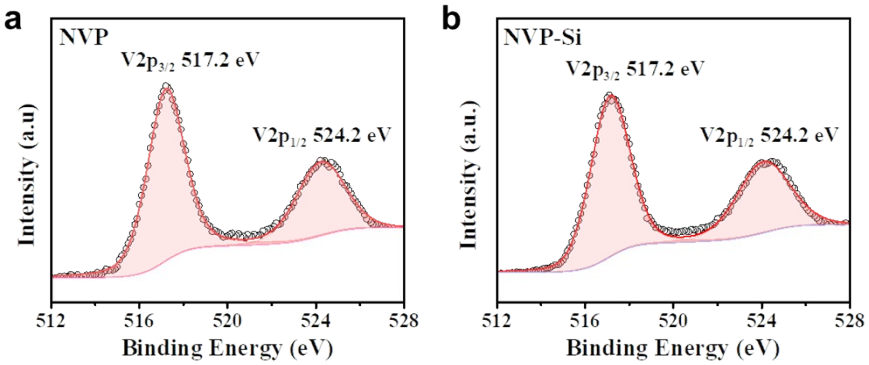

Figure S8. The V 2p XPS analysis of the (a) NVP and (b) NVP-Si cathodes.

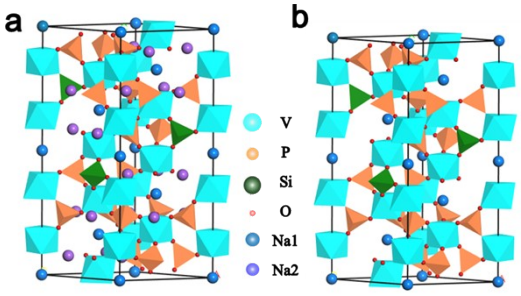

Figure S9. Crystal structures of NVP-Si (a) after discharging with a formula of $Na_3V_2(PO_4)_{2.9}(SiO_4)_{0.1}$ and (b) after charging with a formula of $Na_1V_2(PO_4)_{2.9}(SiO_4)_{0.1}$.

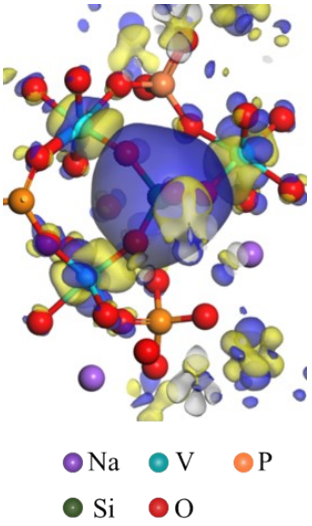

Figure S10. Differential charge simulation result of $Na_1V_2(PO_4)_{2.9}(SiO_4)_{0.1}$ (i.e. NVP-Si after charging).

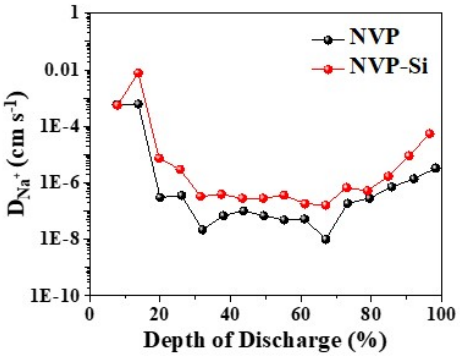

Figure S11. Diffusion coefficient of Na^+ for NVP and NVP-Si cathodes at different depth of discharge based on GITT measurements.

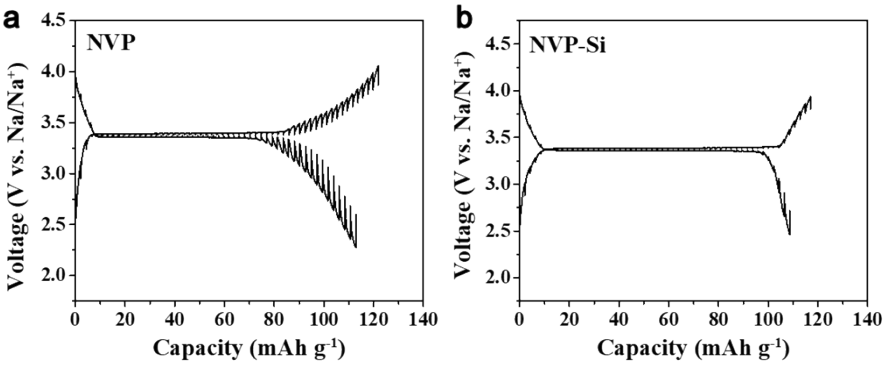

Figure S12. GITT measurement results of the (a) NVP and (b) NVP-Si cathodes.

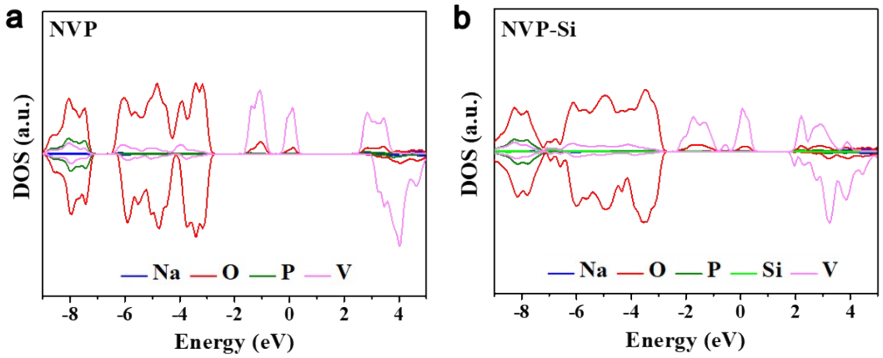

Figure S13. Partial density of states for the (a) NVP and (b) NVP-Si materials.

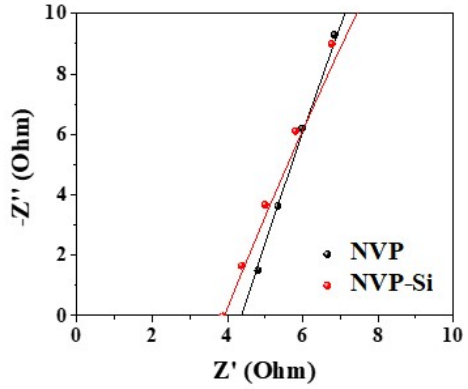

Figure S14. Enlarged Nyquist plots of the NVP and NVP-Si cathodes, suggesting the lower solution resistance for NVP-Si.

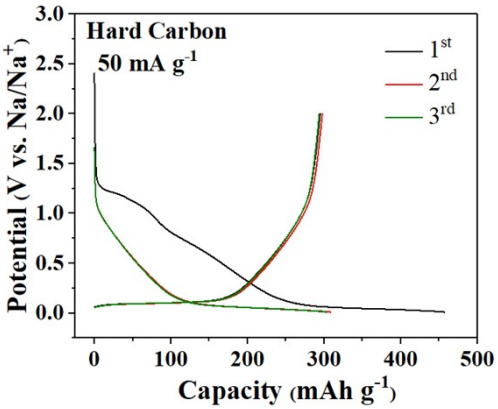

Figure S15. Charge/discharge curves of HC anode in sodium cells.

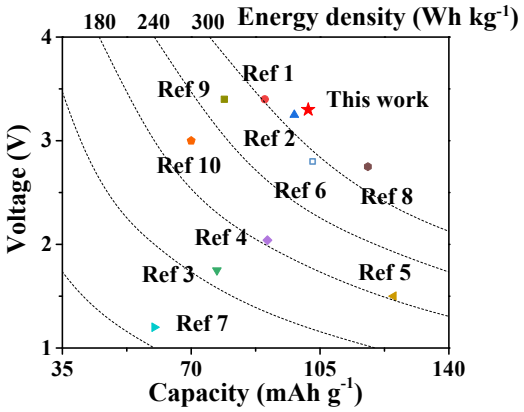

Figure S16. The electrochemical performances of the NVP-Si cathode in full cell configuration, compared with the reported NVP-based cathodes in recent publications [1-10].

Supplementary Tables

Table S1. Comparisons for the refined crystallographic data of NVP and NVP-Si materials based on XRD Rietveld refinement results in **Figure 1b** and **S1**.

	Rwp / %	a	c	Na1	Na2	P-O1/Å	V-O1/Å
NVP	12.1	8.722103	21.787947	0.14844	0.34889	1.52234(0)	2.07243(0)
NVP-Si	13.1	8.726444	21.794979	0.16639	0.36519	1.53839(0)	2.02566(0)

Table S2. The calculated diffusion activation energy and discharged potentials for NVP and NVP-Si materials.

Materials	**Energy (eV)**	**Potential (V)**
NVP/charged	-814.585	
NVP/discharged	-855.964	3.675
NVP-Si/charged	-814.953	
NVP-Si/discharged	-857.182	3.746

References

[1] C. Xu, R. Xiao, J. Zhao, F. Ding, Y. Yang, X. Rong, X. Guo, C. Yang, H. Liu, B. Zhong, Y. Hu, *ACS Energy Lett.*, 2022, **7**, 97-107.

[2] C. Xu, J. Zhao, E. Wang, X. Liu, X. Shen, X. Rong, Q. Zheng, G. Ren, N. Zhang, X. Liu, X. Guo, C. Yang, H. Liu, B. Zhong, Y. Hu, *Adv. Energy Mater.* 2021, **11**, 2100729.

[3] A. Das, S. B. Majumder, A. Chaudhuri. *J. Power Sources*, 2020, **461**, 228149.

[4] Y. Subramanian, W. Oh, W. Choi, H. Lee, M. Jeong, R. Thangavel, W. Yoon, *Chem. Eng. J.*, 2021, **403**, 126291.

[5] Q. Deng, Q. Cheng, X. Liu, C. Chen, Q. Huang, J. Li, W. Zhong, Y. Li, J. Hu, H. Wang, L. Wu, C. Yang, *Chem. Eng. J.*, 2022, **430**, 132710.

[6] H. Li, L. Peng, Y. Zhu, D. Chen, X. Zhang, G. Yu, *Energy Environ. Sci.*, 2016, **9**, 3399-3405.

[7] X. Rui, X. Zhang, S. Xu, H. Tan, Y. Jiang, L. Gan, Y. Feng, C. Li, Y, Yu, *Adv. Funct. Mater.* 2021, **32**, 2009458.

[8] H. Wang, M. Gu, J. Jiang, C. Lai, X. Ai. *J. Power Sources*, 2016, **327**, 653-657.

[9] B. Peng, Z. Sun, L. Zhao, J. Li, G. Zhang. *Energy storage Mater.*, 2021, **35**, 620-629.

[10] J. Deng, W. Luo, X. Lu, Q. Yao, Z. Wang, H. Liu, H. Zhou, S. Dou, *Adv. Energy Mater.,* 2017, **8**, 1701610.