Support information

Application of isomorphic Anion Substitution to Enhance Electrochemical Performance in Vanadium-Based NASICON Cathode Materials

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Experimental section

Material synthesis

The $NaV(PO_4)_{1-x}F(SiO_4)_x$ (x=0.05, 0.1, 0.15) was synthesized via the sol-gel method followed by high-temperature calcination. Add 3 mmol of V_2O_5 and 1.5g of $H_2C_2O_4 \cdot 2H_2O$ were added to the beaker and stirred at 70℃ for 1 h. The mixture was then supplemented with 6 mmol NaF, 6(1-x) mmol $NH_4H_2PO_4$, and a specific quantity of $(C_2H_5O)_4Si$, followed by stirring for 5 h to yield a dark green gel. Subsequently, the gel was subjected to drying at 90℃ for 12 h. The precursor was heat-treated in a tube furnace at 350℃ in an argon atmosphere for 4 h, then the temperature was raised to 750℃ for calcination for 8 h to obtain the target product $NaV(PO_4)_{1-x}F(SiO_4)_x$ (x=0.05, 0.1, 0.15). The preparation process of NVPF/C samples was the same as above, without adding $(C_2H_5O)_4Si$.

Material characterization

The crystal structure of the sample was characterized using X-ray diffraction (XRD, Cu Kα radiation, Bruker D2). The composition of functional groups in the samples was identified through Fourier transform infrared spectroscopy (FTIR, NICOLET iS50). The bandgap of the material was investigated via ultraviolet-visible diffuse reflectance spectroscopy (UV 3600I plus). Electronic conductivity of the material was evaluated using the four-point probe technique. The microstructure of the sample was analyzed by scanning electron microscopy (SEM, Thermo Scientific Apreo 2C) and high-resolution transmission electron microscopy (HR-TEM, Talos F200S G2). The oxidation states and elemental compositions were examined using X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha X).

Electrochemical measurement

The active electrode was prepared by mixing the active material, acetylene black, and polyvinylidene fluoride in an 8:1:1 mass ratio with N-methyl pyrrolidone as a solvent. After thorough grinding and homogeneous mixing, the resultant slurry was uniformly deposited onto an aluminum foil substrate. Subsequently, the aluminum foil was transferred to a vacuum drying oven set at 80 °C for 12 h. After complete drying, the foil was precision-cut into circular electrodes with a diameter of 12 mm, ensuring an active material loading of approximately 2.0 mg/cm^2. The CR2032

half-battery was assembled in a glove box under high-purity argon, and tested using GCD on the LAND system (CT210A). CV and EIS measurements were performed using a CHI760E workstation. For the full battery, hard carbon served as the anode and NVPF-SiO10 as the cathode. Hard carbon was obtained by cycling a sodium-based half-battery three times at 30 μA g^{-1}.

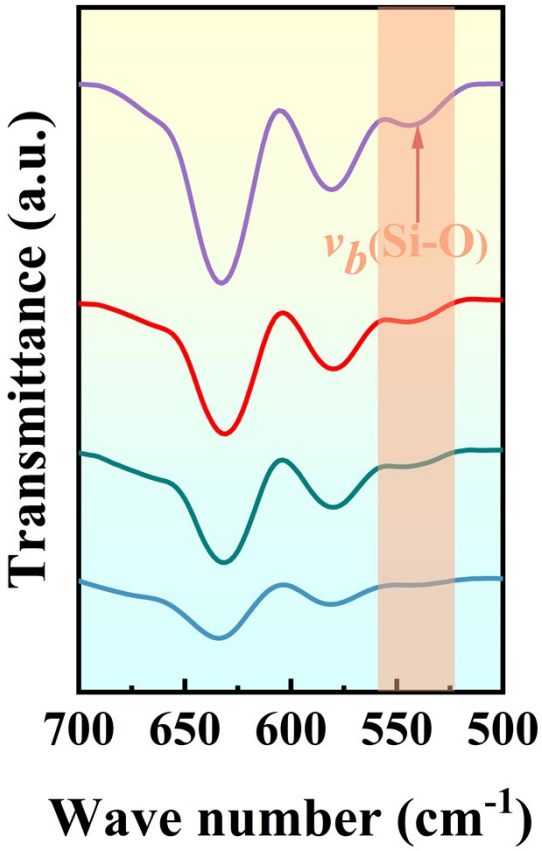

Figure S1. the FTIR local magnification of NVPF-SiOx;

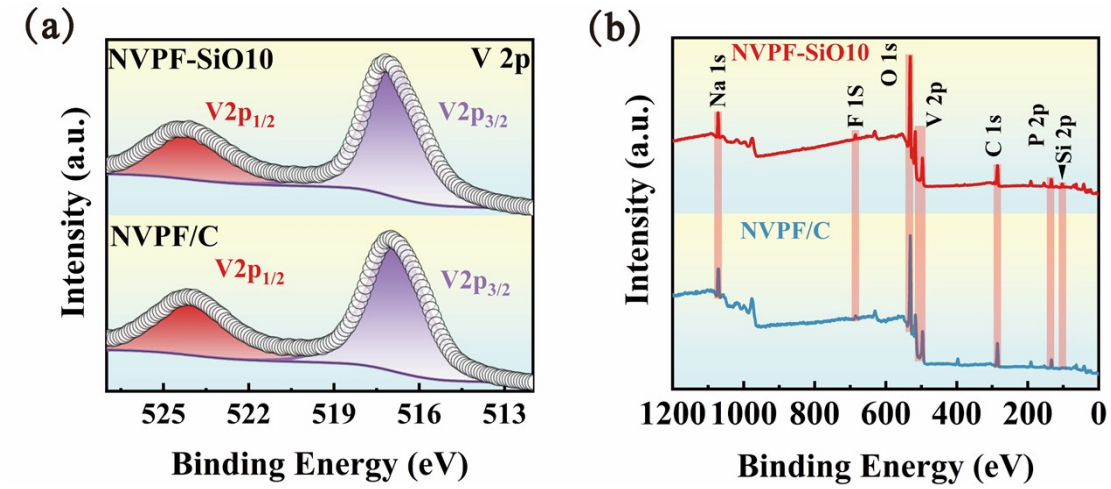

Figure S2. XPS spectra of NVPF/C and NVPF-SiO10 (a) V 2p, (b) full spectrum.

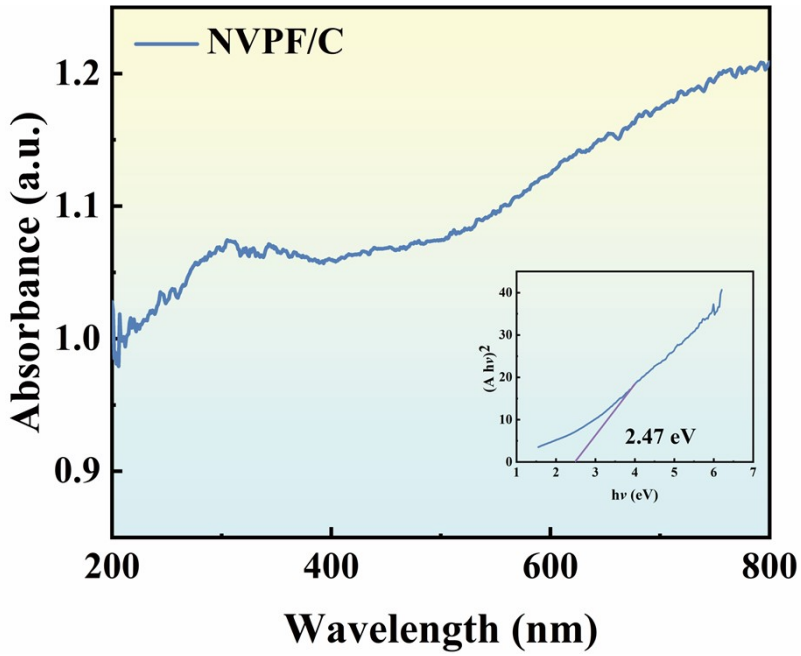

Figure S3. Uv-vis diffuse reflection spectra of NVPF/C materials

$$(\alpha h\nu)1/n=B(h\nu-E_g) \quad (S\ 1\text{-}1)$$

In the Kubelka-Munk formula, D denotes the absorbance, h represents the Planck constant, and ν signifies the frequency of light. B is a physical quantity associated with material properties, while E_g indicates the bandgap energy of the material.

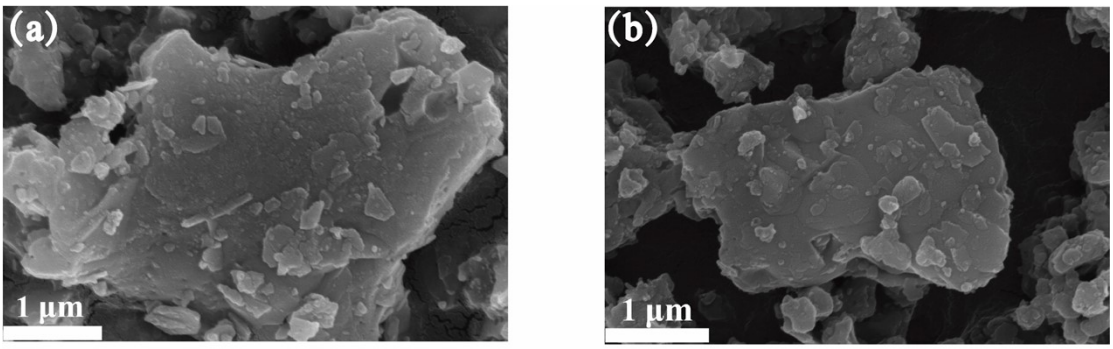

Figure S4. SEM images for (a) NVPF and (b) NVPF-SiO10

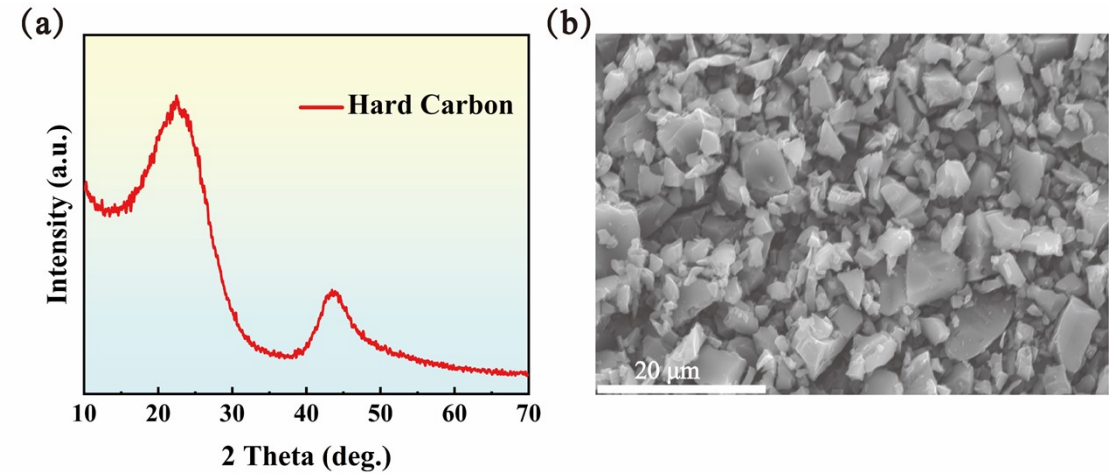

Figure S5. (a) XRD and (b) SEM of hard carbon

Table S1 Comparison of full battery electrochemical performance with recent literature results.

References	Rate (C) / Specific capacity (mAh g^{-1})							
1	1	2	5	10	20			
	97	95	93	88	68			
2	0.1	0.2	0.5	1	2	5	10	20
	130	125	122	116	110	100	70	80
3	0.1	0.5	2	10	20			
	96.6	95.4	89.4	80.5	70.3			
4	0.1	0.2	0.5	1	2	5	10	
	89.4	82.4	72.1	61.7	51	37.8	29.6	
5	0.05	0.1	0.2	0.5				
	120	104	90	65				
6	0.1	0.2	0.5	1	2	5	10	
	116	107	105	103	98	85	60	
7	0.05	0.1	0.2	0.5	1	2	5	10
	113	103	90	87	76	70	68	65.8
8	0.1	0.2	0.5	1	2	5	10	
	122	115	110	105	103	96	86	
This work	**0.5**	**1**	**3**	**5**	**10**	**20**	**30**	
	120.3	**116.6**	**112.2**	**109.6**	**103.9**	**94.6**	**89.3**	

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