Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Crossing-linked $Na_2VTi(PO_4)_3$@C Hierarchical Nanofibers as High-Performance Bi-Functional Electrodes for Symmetric Aqueous Rechargeable Sodium Batteries

Jing Dong,[a] *Guoming Zhang,*[a] *Xiaoguang Wang,*[a] *Sen Zhang,*[b,*] *Chao Deng*[a,*]

[a]Key Laboratory for Photonic and Electronic Bandgap Materials, Ministry of Education; Key Laboratory of Photochemical Biomaterials and Energy Storage Materials, Heilongjiang Province; Harbin Normal University, Harbin, 150025, Heilongjiang, China.

[b]Key Laboratory of Superlight Material and Surface Technology, Ministry of Education; College of Material Science and Chemical Engineering, Harbin Engineering University, Harbin, 150001, Heilongjiang, China.

Corresponding Author

E-Mail: chaodenghsd@sina.com (C. Deng); senzhang@hrbeu.edu.cn (S. Zhang)

S-1: Calculation process for sodium intercalation coefficients

The diffusion coefficient of sodium-ion (D_{Na}) can be calculated on the basis of the Randles-Sevcik equation,

$$i_p = 0.4463\left(\frac{F}{RT}\right)^{1/2} n^{3/2} A D_{Na}^{1/2} C^* v^{1/2} \quad (1)$$

Where i_p, n, A, C^* and v are the peak current, number of exchanged electrons, surface area, sodium concentration and sweep rate, respectively.

S-2: Optimized Design of hybrid nanofiber

Based on above results, the crossing-linked nanofiber exhibits superior properties than the reference ones. Therefore, we optimize the carbon content to further optimize its composition. A series carbon contents, *i. e.* 0.5, 1, 3, 5, 7, 9, 12, 18, 36 wt.% were employed. In our study, the carbon content corresponds to the ratio of the weight of the carbon to the weight of hybrid composite.

Firstly, the evolution of the morphology for the composites is discussed. As displayed in Figure S1(*a*), when the carbon content is lower than 1 wt.%, only microscale spheres are obtained and no fiber is observed. As it is increased to 3 wt.%, the 1D structure begins to appear. The 1D structure increases and the 3D sphere decreases as increasing the carbon content. When it reaches 7 wt.%, well-defined nanofibers are obtained. Then the good 1D structure is maintained as the carbon content is further increased. Therefore, the results indicate that the well-defined nanofibers can be constructed as the carbon content is higher than 7 wt.%. Too low carbon amount (<3 wt.%) in the composite are not sufficient to build perfect 1D nanofiber architecture, which leads to different architectures.

Next, we investigated the electrochemical properties of all the samples that have different carbon contents. Figure S1(*b*) exhibits their discharge capacities at low (0.5 *C*), moderate (4 *C*) and high (40 *C*) current densities during employed as cathodes. Slight difference is observed between the samples as the current density is as low as 0.5 *C*. When the current is increased to 4 *C*, obvious differences are observed between the samples. As the carbon content increases, the capacity initially increases and then turns to decreases. The maximum value is achieved when the carbon content is in the range 9~12 wt.%. As the current density is further increased to 40 *C*, the differences between the samples become more significant. In all cases, the maximum value is obtained for the sample with carbon content of 9~12 wt.%.

Combine above results, the carbon content plays an important role on the electrode design. It greatly influences both the structure and the electrochemical properties of the $Na_2VTi(PO_4)_3$ composite. On the one hand, when the carbon content is too low (<5 wt.%), the large microspheres with insufficient electron pathways are

constructed, which leads to inferior properties especially at high rate. On the other hand, when too much carbon is employed (>12 wt.%), thick surface layer is constructed surrounding the particles inside the nanofiber, which also restricts fast sodium intercalation and affects the high rate capabilities of $Na_2VTi(PO_4)_3$. Therefore, only moderate carbon content will result in both well-defined 1D architecture and the superior electrochemical properties. In preset study, we employ the carbon content of 9 wt.% as the optimized value to construct crossing-linked nanofiber, which is based on the consideration of well-defined architecture, fast sodium intercalation, superior high rate capability and high efficiency.

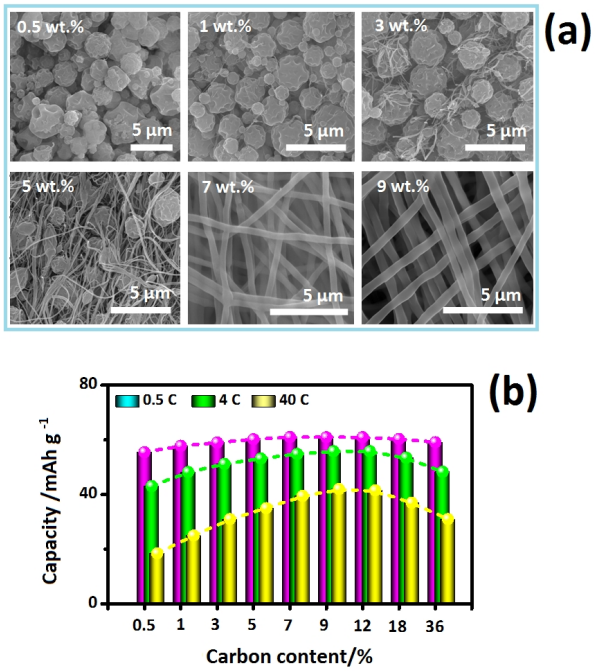

Figure S1 (a) Morphology evolution of the composites with the different carbon content. (b) Rate capability of the hybrid nanofibers with different carbon content.

Figure S2

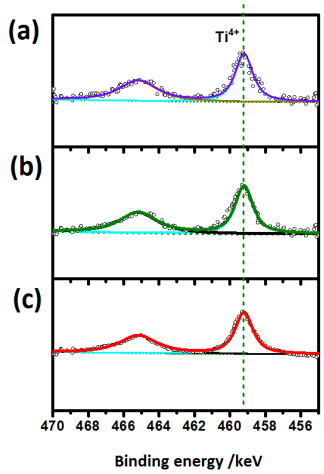

Figure S2 XPS spectra of the titanium element in the cathode potential (0~0.6 V vs. Ag/AgCl) range at pristine (c), fully charge (b) and fully discharged states (a).

Figure S3

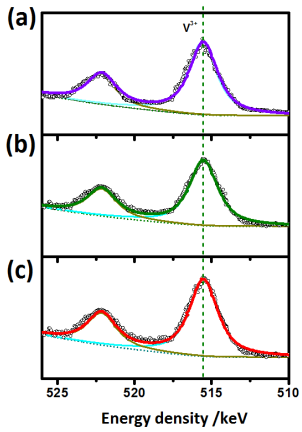

Figure S3 XPS spectra of the vanadium element in the anode potential range (-1~0 V vs. Ag/AgCl) at pristine (c), fully charge (b) and fully discharged states (a).

Table S1: Physical characteristics (BET area, pore volume and carbon content) of the crossing-linked nanofiber (iii), random arranged nanofiber (ii) and aggregated powder (i).

Materials	BET area /m^2g^{-1}	Pore volume/m^3g^{-1}	Carbon content/%
iii	126.7	0.811	8.92
ii	98.6	0.673	8.68
i	4.2	0.029	0.12