Supporting Information

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Ice-Templated, Sustainable Carbon Aerogels with Hierarchically Tailored Channels for Sodium- and Potassium-Ion Batteries

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1. Calculations and Equations

The apparent density ($\rho$) of the aerogels was calculated using the equation:

$$\rho = \frac{m}{\pi r^2 h}$$

(S1)

where $m$ is the mass, $r$ is the radius and $h$ is the height of cylindrical aerogels.

The average interlayer spacing ($d$-spacing) was determined from Bragg’s law as follows:[1]

$$d = \frac{\lambda}{2 \sin \theta}$$

(S2)

where $\theta$ is the X-ray diffraction angle, and $\lambda$ is the X-ray wavelength ($\lambda = 0.154$ nm).

In this regime (stage 1), $I_D$ is proportional to the total number of defects probed by the laser spot. For an average defect distance ($L_D$) and laser spot size ($L_L$), there are on average defects in the area probed by the laser - $(L_L/L_D)^2$, thus $I_D \propto (L_L/L_D)^2$. On the other hand, $I_G$ is proportional to the total area probed by the laser ($I_G \propto L_L^2$), giving $I_D/I_G \propto 1/L_D^2$.

However, if two defects are closer than the average distance an e-h pair travels before scattering with a phonon, then their contributions will not sum independently anymore. For an increasing number of defects (stage 2), where $L_D < 3$ nm ($v_F/\omega_D \sim 3$ nm),[2] $I_D/I_G \propto M$ ($M$ being the number of ordered hexagons), $I_D/I_G \propto L_D^2$.[3]

For the high defect density regime (stage 2, with $L_D < 3$ nm), the average defect distance ($L_D$) can be calculated by the following equation:[4]
where $E_L$ (eV) is the laser excitation energy, $I_D/I_G$ is the intensity ratio of the D-peak to G-peak. For the light wavelength of 532 nm, $E_L$ is 2.33 eV.

The contribution ratio of the two mechanisms can be qualitatively analyzed by the power-law equation:[5]

$$i = a v^b$$

where $i$ is the peak current, $v$ is scan rate, and $a$ and $b$ are adjustable parameters; when $b = 0.5$, implying a Faradaic insertion/extraction, namely, the diffusion-controlled process; $b = 1.0$, revealing a capacitive-controlled process. Therefore, a $b$-value between 0.5 and 1.0 suggests the presence of mixed mechanisms during the charge storage process.

According to typical Randles circuits, the Nyquist plot can be fitted:[6]

$$Z = R_s + \frac{1}{j\omega C_{dl} + \frac{1}{R_{ct} + W_0}} + \frac{1}{j\omega C_t + \frac{1}{R_{leak}}}$$

where $Z$ is the impedance, $R_s$ is the inner resistance, $R_{ct}$ is the charge-transfer resistance; the sum of $R_s$ and $R_{ct}$ is the equivalent series resistance (ESR) of the device. Furthermore, $C_{dl}, C_t,$
$W_0$ and $R_{\text{leak}}$ represent the double-layer capacitance, the low-frequency mass capacitance, the Warburg element and the low-frequency leakage resistance, respectively.

The charge/discharge specific capacity values of the working electrodes were calculated from GCD according to Equation S6 as follows:

$$Q_{\text{electrode}} = \frac{I \Delta t}{3.6m}$$

(S6)

where $Q_{\text{electrode}}$ is the charge/discharge specific capacity, $I$ is the constant charge/discharge current, $\Delta U$ ($= U_{\text{max}} - IR_{\text{drop}} - U_{\text{min}}$) is the working voltage window, $m$ is the mass of active material loaded on the working electrodes, and $\Delta t$ is the charge/discharge time.

The power/energy density values of the full cells were obtained using Equation S7 and S8, respectively, as follows:

$$E_{\text{device}} = \frac{I}{3.6M} \int_{t_1}^{t_2} U(t) dt$$

(S7)

$$P_{\text{device}} = \frac{3600E}{\Delta t}$$

(S8)

where $E_{\text{device}}$ is the energy density of devices, and $P_{\text{device}}$ is the power density. $I$ is the constant charge/discharge current, $M$ is the total mass of active materials in both anodes and cathodes, and $\Delta t$ is the charge/discharge time. $U$ is the voltage that changes with time under
galvanostatic discharging or charging, $t_1$ is the start time of charge/discharge processes, and $t_2$ is the end time.

The average pore diameter ($D_{Avg}$) was obtained by the Gurwitch rule:\cite{8}

$$D_{Avg} = \frac{4V_{Total}}{S_{BET}}$$

(S9)

2. Results and Discussion

**Figure S1.** Top-view SEM images of a) VCA-U, b) VCA-3, c) VCA-5 and d) VCA-7.
Figure S2. TEM image of cellulose nanocrystal (CNC) suspensions showing the ordering of rod-like CNCs.
Figure S3. a) Typical FTIR spectra, and b) TGA results for CNC/PEO nanocomposite aerogels.

Characterization: Fourier-transform infrared spectra (FTIR) of PEO, CNCs and CNC/PEO aerogels were acquired using FT-IR spectrometer (Spectrum 100, PerkinElmer) fitted with a universal ATR accessory. The thermal stability of CNC/PEO aerogels (5-10 mg) was studied by thermogravimetric analysis (TGA)/differential scanning calorimetry (DSC) STA (449 F3, Jupiter) at a heating rate of 5 K min\(^{-1}\) from 30 °C to 800 °C under a nitrogen environment (50 mL min\(^{-1}\)).

FTIR: CNCs exhibit a characteristic absorbance band centered at \(~3341\) cm\(^{-1}\) due to a stretching vibration of the \(–OH\) groups. The characteristic band of CNCs located at 2880 cm\(^{-1}\) attributed to C–H bonds stretching.\[^9\] A band observed at \(~1033\) cm\(^{-1}\) is thought to result from stretching vibration of the C–O group at the C\(_6\) position of the cellulose structure. A typical absorption band of pure PEO is observed at \(~957\) cm\(^{-1}\), which corresponds to CH\(_2\) rocking and twist.\[^10\] Two vibrational bands of PEO located at \(~1146\) and \(~1342\) cm\(^{-1}\), attributed to C–O–C stretching and CH\(_2\) wagging, respectively.\[^11\] The change in the intensity ratio of 1146 cm\(^{-1}\) on the spectra of PEO and CNC/PEO elucidated the formation of intermolecular interactions (i.e., hydrogen bonding) between C–O–C and \(–OH\) groups on CNCs.

TGA: CNC/PEO nanocomposite aerogels showed a two-step thermal decomposition process with \(T_{\text{onset}}\) at 277 and 351 °C, which are believed to assign to the pyrolysis of CNC and PEO, respectively.\[^12\] It demonstrated that CNC/PEO nanocomposite aerogels are a physical
mixture, with no chemical reactions expected between PEO and CNCs during unidirectional ice-templating and freeze-drying processes.

Figure S4. XRD patterns of VCA-U, VCA-3, VCA-5, VCA-7.
Figure S5. Fitted Raman spectra of a) VCA-U, b) VCA-3, c) VCA-5 and d) VCA-7 (Peak Fitted by Lorentz models).
Figure S6. Fitted C 1s, and O 1s core-level XPS spectra of a) VCA-3, b) VCA-5, c) VCA-7 and d) VCA-U.
Figure S7. Electrochemical properties of the VCA electrodes in SIBs. Cyclic voltammetry curves of a) VCA-5 and b) VCA-7 at a scan rate of 0.1 mV s\(^{-1}\). e) Cycling performance at a current density of 0.5 C. (1 C = 300 mA g\(^{-1}\)).
Figure S8. Electrochemical properties of the VCA electrodes in PIBs. Cyclic voltammetry curves of a) VCA-3 and b) VCA-7 at a scan rate of 0.1 mV s\(^{-1}\). c) Cycling performance at a current density of 0.5 C. (1 C = 279 mA g\(^{-1}\)).
Figure S9. CV curves at various scan rates of a) VCA-U, b) VCA-5 and c) VCA-7 from 0.1 to 5.0 mV s\(^{-1}\) in SIBs. d) Contribution ratios of the capacitive and diffusion-controlled charge at various scan rates for VCA-U.

Figure S10. Nyquist plots of a) VCA-5 and b) VCA-7 in SIBs.
Figure S11. CV curves at various scan rates of a) VCA-U, b) VCA-5 and c) VCA-7 from 0.1 to 5.0 mV s\(^{-1}\) in PIBs. d) Contribution ratios of the capacitive and diffusion-controlled charge at various scan rates for VCA-U.
Figure S12. Nyquist plots of a) VCA-3 and b) VCA-7 in PIBs.

Figure S13. Separation of the capacitive and diffusion-controlled charges at 0.5 mV s$^{-1}$ for VCA-U in a) SIBs and b) PIBs.
Figure S14. Percentage of the species in the SEI layer formed on sodiated VCA-3 and potassiated VCA-5 electrode.
Figure S15. Cycling performance at a current density of 2.0 C for a) VCA-3 electrode in half cells of SIBs and b) VCA-5 electrode in half cells of PIBs.

Figure S16. HRTEM image and inset SAED patterns of a) the pristine VCA-3 and b) the pristine VCA-5. Ex-situ HRTEM image and inset SAED patterns of c) post-cycling VCA-3 electrode in half cells of SIBs and d) post-cycling VCA-5 electrode in half cells of PIBs after 200 cycles at a current density of 2.0 C.
During the freezing process, the CNC/PEO nanoparticles concentrate in the space between the anisotropic ice crystals. When the cooling rate increases, the magnitude of supercooling ahead of the solidifying interface is increased, and hence the tip radius of the anisotropic ice crystals decreases. A finer microstructure as a negative replica of the crystals is thus obtained after the sublimation of anisotropic ice crystals by freeze-drying. Using a high cooling rate of 7 K min\(^{-1}\), we have obtained the smaller and finer vertical-aligned channels with a relatively high extent of homogenous and interconnectivity, which is also demonstrated by SEM images (see Figure S1, Supporting Information).

More importantly, it was also observed that the unidirectional freezing synchronously induced the orientation of highly crystalline and rod-shaped CNCs (Figure S2, Supporting Information); this can assist in retaining the short-range ordered structures in VCAs. This hierarchically ordered structure is thought to be instrumental in conveying the unique hierarchically-tailored properties of our materials. A similar phenomenon that the nano-alignment of reduced graphene oxide along the growth direction of ice due to the squeezing effect during the ice-templating process has also been reported by D. Li et al. Similarly, cellulose nanocrystals/polyethylene oxide (CNCs/PEO) nanomaterials are concentrated at the boundary of the anisotropic ice crystals and then aligned along the growth direction of ice due to the squeezing effect, thus ultimately causing the increased degree of ordering and the finer ordered structures of our VCAs with the increasing cooling rates from 3 to 7 K min\(^{-1}\). Accordingly, the defect density within the graphitic layers decreased and the interlayer spacing of graphitic nanodomains slightly decreased with the increasing cooling rates from 3 to 7 K min\(^{-1}\).

In terms of the oxygen contents, it could be seen from Figure S1 and Table S2 (Supporting Information) that the higher cooling rate can result in smaller and finer vertical-aligned channels of VCAs, which decreases to 19.7 µm (VCA-7) from 47.9 µm (VCA-3) (Table S2, Supplementary Information). Based on the different channel widths of VCA-3, 5, 7, we draw a schematic diagram to get a better understanding of the different oxygen content after the carbonization process, as shown in Figure S17. In the process of carbonization, some oxygen atoms stemming from PEO and CNCs would escape in the gas forms of H\(_2\)O and CO\(_2\), thus the remained oxygen functional groups refer to the oxygen-doping active sites in VCAs after the completion of carbonization. At the cooling rate of 3 K min\(^{-1}\), the CNC/PEO aerogels possess accessible hollow channels that allow the escape of oxygen gas. In contrast with
that of 7 K min\(^{-1}\), relatively more hollow channels facilitate the escape of more oxygen, resulting in the lower content of oxygen-containing functional groups for VCA-7 (8.8 wt.%) than that for VCA-5 (9.2 wt.%) and VCA-3 (13.77 wt.%).

**Figure S17.** Schematic diagram of oxygen-content comparison of VCA-3 and VCA-7 materials after the carbonization.
**Table S1.** Apparent densities of aligned CNC/PEO aerogels.

| CNC/PEO Aerogels | U       | 3       | 5       | 7       |
|------------------|---------|---------|---------|---------|
| Density (mg cm\(^{-3}\)) | 17.8 ± 0.3 | 19.9 ± 0.4 | 24.0 ± 0.5 | 28.3 ± 0.5 |

**Table S2.** Physical parameters of VCA materials.

| Samples   | Channel width (µm) | 2θ (002) (°) | \(L_D^a\) (nm) | \(D_{Avg}^b\) (nm) | \(V_t^c\) (cm\(^3\) g\(^{-1}\)) |
|-----------|---------------------|--------------|----------------|-------------------|-------------------|
| VCA-U     | 77.2 ± 13.4         | 22.24        | 1.39           | 5.47              | 0.161             |
| VCA-3     | 47.9 ± 7.8          | 22.47        | 1.46           | 7.22              | 0.083             |
| VCA-5     | 30.1 ± 6.7          | 22.76        | 1.50           | 5.52              | 0.081             |
| VCA-7     | 19.7 ± 2.6          | 22.99        | 1.56           | 6.47              | 0.109             |

\(^a\) \(L_D\): Average in-plane distance of the graphene layer

\(^b\) \(D_{Avg}\): Average pore diameter (4V/A by BET method)

\(^c\) \(V_t\): Total pore volume (NLDFT method)

**Table S3.** The charge-transfer resistance \((R_{ct})\) of VCAs for half-cells SIBs and PIBs.

| Electrodes | \(R_{ct}\) (SIBs) (Ω) | \(R_{ct}\) (PIBs) (Ω) |
|------------|------------------------|------------------------|
| VCA-U      | 100                    | 791                    |
| VCA-3      | 80                     | 508                    |
| VCA-5      | 90                     | 477                    |
| VCA-7      | 87                     | 534                    |
Table S4. The sodium storage properties for reported sodium-ion full cells.

| Full cell (Anode//Cathode) | Specific capacity (mAh g⁻¹) | Energy density (Wh kg⁻¹) | References |
|---------------------------|------------------------------|--------------------------|------------|
| VCA-3//Na₃V₂(PO₄)₃       | 295 at 30 mA g⁻¹            | 220 (0.0–3.8 V)          | This work  |
| HCT1300//Na₀.₉[Cu₀.₂₂Fe₀.₃₀Mn₀.₄₈]O₂ | 290 at 30 mA g⁻¹            | 207 (1.0–4.0 V)          | [16]       |
| Na₂Ti₃O₇//VOPO₄         | 114 at 30 mA g⁻¹            | 220 (0.8–3.0 V)          | [17]       |
| Porous carbon-Fe₃O₄//Na₂FeP₂O₇ | 93 at 30 mA g⁻¹            | 203 (1.1–4.2 V)          | [18]       |
| NOHPHC//Na₃V₂(PO₄)₃/C  | 91 at 100 mA g⁻¹            | 53 (1.0–3.9 V)           | [19]       |

Table S5. The potassium storage properties for reported potassium-ion full cells.

| Full cell (Anode//Cathode) | Specific capacity (mAh g⁻¹) | Energy density (Wh kg⁻¹) | References |
|---------------------------|------------------------------|--------------------------|------------|
| VCA-5//k₂PTCDA            | 194 at 27.9 mA g⁻¹           | 118 (0.0–3.8 V)          | This work  |
| rGO@MCSe//PTCDA@450 °C   | 125 at 27.9 mA g⁻¹           | NA (2.0–4.3 V)           | [20]       |
| Soft carbon semi-hollow microrods//K₀.₆CoO₂ | 101 at 10 mA g⁻¹            | NA (0.4–3.4 V)           | [21]       |
| NCM//KPB                  | 78 at 50 mA g⁻¹             | NA (2.0–3.8 V)           | [22]       |
| Bi//K₀.₇₂Fe[Fe(CN)₆]       | 38 at 200 mA g⁻¹            | 108 (0.8–3.3 V)          | [23]       |
| MCS-7-900//PTCDA          | 105 at 100 mA g⁻¹           | 60 (0.8–3.0 V)           | [24]       |

Specific capacity is the calculated discharge capacity based on the mass of anode.
References

[1] X. Ma, C. Yuan, X. Liu, Materials (Basel) 2013, 7, 75.
[2] C. Casiraghi, A. Hartschuh, H. Qian, S. Piscanec, C. Georgi, A. Fasoli, K. Novoselov, D. Basko, A. Ferrari, Nano Lett. 2009, 9, 1433.
[3] L. G. Cançado, A. Jorio, E. M. Ferreira, F. Stavale, C. A. Achete, R. B. Capaz, M. V. d. O. Moutinho, A. Lombardo, T. Kulmala, A. C. Ferrari, Nano Lett. 2011, 11, 3190.
[4] A. C. Ferrari, D. M. Basko, Nat. Nanotechnol. 2013, 8, 235.
[5] V. Augustyn, P. Simon, B. Dunn, Energy Environ. Sci. 2014, 7, 1597.
[6] Y. Shao, M. F. El-Kady, J. Sun, Y. Li, Q. Zhang, M. Zhu, H. Wang, B. Dunn, R. B. Kaner, Chem. Rev. 2018, 118, 9233.
[7] Z. Xu, F. Xie, J. Wang, H. Au, M. Tebyetekerwa, Z. Guo, S. Yang, Y. S. Hu, M. M. Titirici, Adv. Funct. Mater. 2019, 29, 1903895.
[8] C. Thunyaratchatanon, A. Luengnaruemitchai, J. Jitjamnong, N. Chollacoop, S.-Y. Chen, Y. Yoshimura, Energy Fuels 2018, 32, 9744.
[9] S. Huan, L. Bai, G. Liu, W. Cheng, G. Han, RSC Adv. 2015, 5, 50756.
[10] X. Xu, F. Liu, L. Jiang, J. Zhu, D. Haagenson, D. P. Wiesenborn, ACS Appl. Mater. Interfaces 2013, 5, 2999.
[11] S. Padmaja, S. Jayakumar, Mater. Today: Proc. 2018, 5, 14473.
[12] N. Inai, A. Lewandowska, O. Ghita, S. Eichhorn, Compos. Sci. Technol. 2018, 154, 128.
[13] S. Deville, E. Saiz, R. K. Nalla, A. P. Tomsia, Science 2006, 311, 515.
[14] L. Qiu, J. Z. Liu, S. L. Chang, Y. Wu, D. Li, Nat. Commun. 2012, 3, 1.
[15] S. Peng, F. Gong, L. Li, D. Yu, D. Ji, T. Zhang, Z. Hu, Z. Zhang, S. Chou, Y. Du, J. Am. Chem. Soc. 2018, 140, 13644.
[16] Y. Li, Y. S. Hu, M. M. Titirici, L. Chen, X. Huang, Adv. Energy Mater. 2016, 6, 1600659.
[17] H. Li, L. Peng, Y. Zhu, D. Chen, X. Zhang, G. Yu, Energy Environ. Sci. 2016, 9, 3399.
[18] J. Ming, H. Ming, W. Yang, W.-J. Kwak, J.-B. Park, J. Zheng, Y.-K. Sun, RSC Adv. 2015, 5, 8793.
[19] M. Huang, B. Xi, Z. Feng, J. Liu, J. Feng, Y. Qian, S. Xiong, J. Mater. Chem. A 2018, 6, 16465.
[20] Z. Sun, X.-L. Wu, J. Xu, D. Qu, B. Zhao, Z. Gu, W. Li, H. Liang, L. Gao, Y. Fan, K. Zhou, D. Han, S. Gan, Y. Zhang, L. Niu, Small 2020, 16, 1907670.
[21] X. Wang, K. Han, D. Qin, Q. Li, C. Wang, C. Niu, L. Mai, Nanoscale 2017, 9, 18216.
[22] B. Wang, F. Yuan, Q. Yu, W. Li, H. Sun, L. Zhang, D. Zhang, Q. Wang, F. Lai, W. A. Wang, Energy Storage Mater. 2021, 38, 329.
[23] K. Lei, C. Wang, L. Liu, Y. Luo, C. Mu, F. Li, J. Chen, Angew. Chem. Int. Ed. 2018, 57, 4687.
[24] J. Zheng, Y. Wu, Y. Tong, X. Liu, Y. Sun, H. Li, L. Niu, Nano-Micro Lett. 2021, 13, 1.