Supporting Information

3D-Printed Hierarchical Porous Frameworks for Sodium Storage

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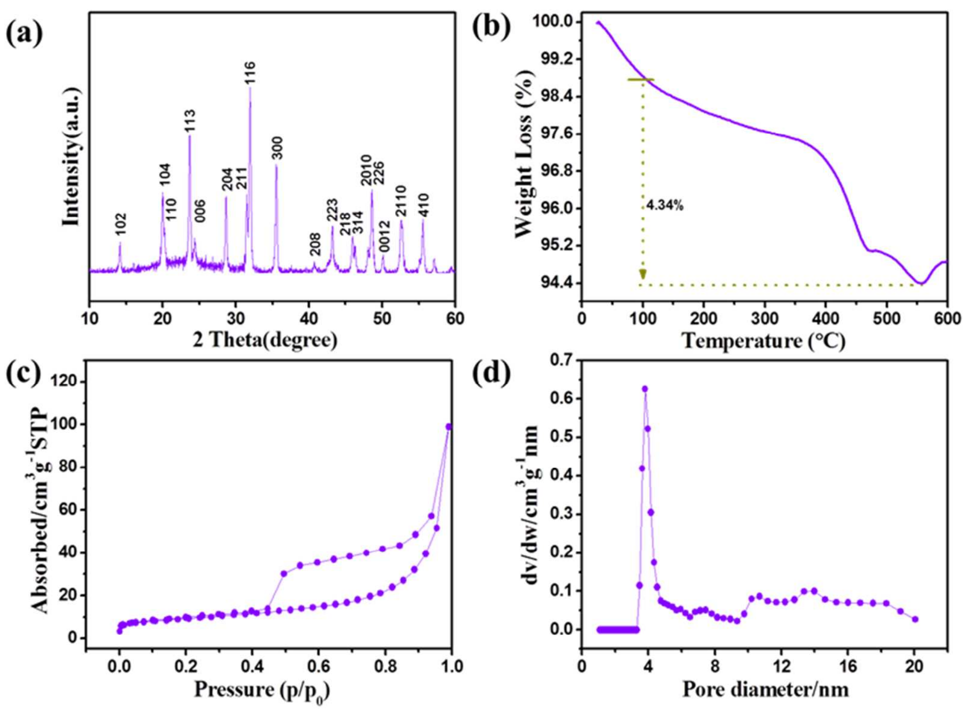

Figure S1. (a) XRD pattern, b) TGA curve, (c) Nitrogen adsorption-desorption isotherm, and (d) pore size distribution curve of NVP.

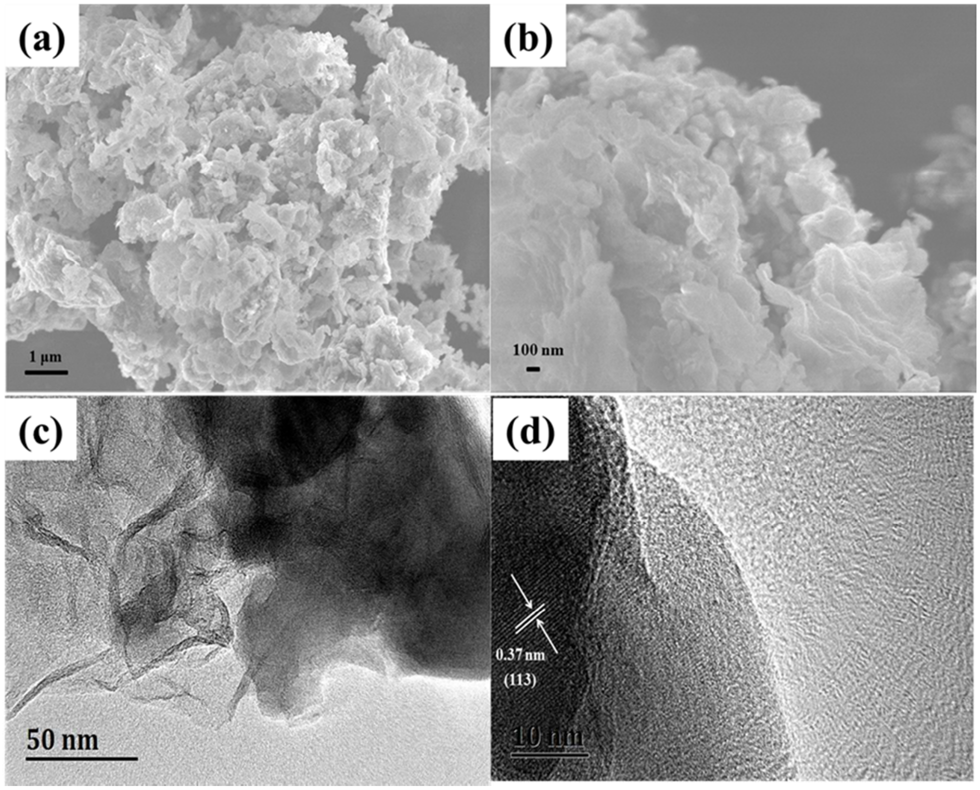

Figure S2. (a, b) SEM images with different magnifications, (c) TEM image, and (d) HRTEM image of NVP, showing a significant portion of NVP are encapsulated within rGO nanosheets.

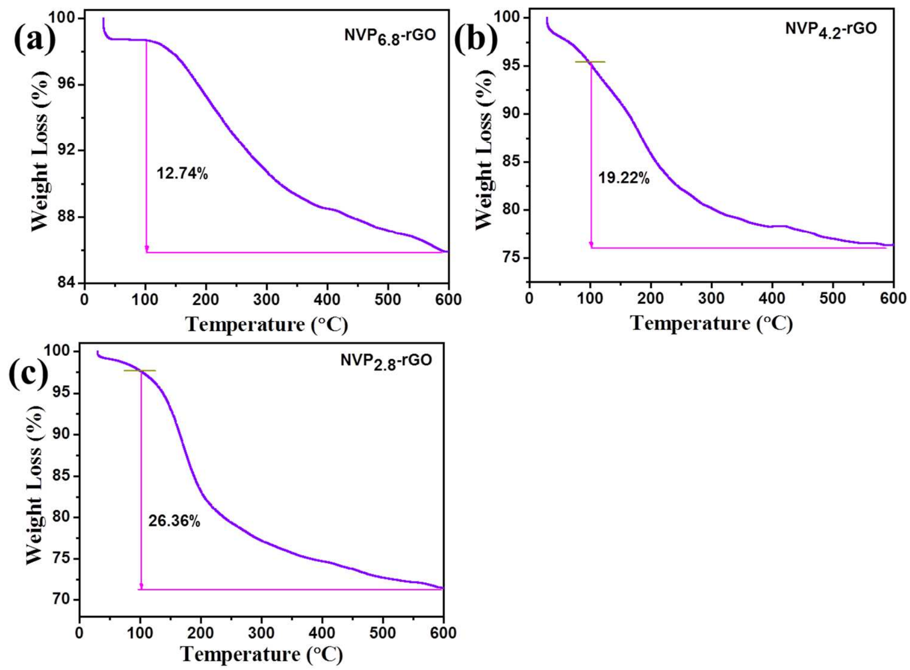

Figure S3. (a-c) TGA curves of different hierarchical porous frameworks, showing different rGO contents.

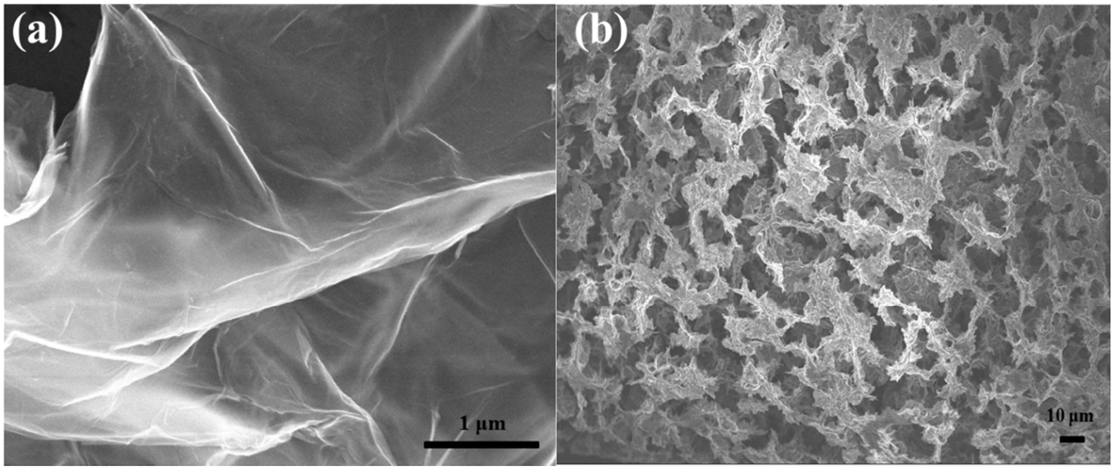

Figure S4. SEM images of GO sheet (a) and GO-NVP sheets of 3D-printed hierarchical porous frameworks without thermal annealing (b). Showing the adopted GO sheets with the average size of ～20 μm.

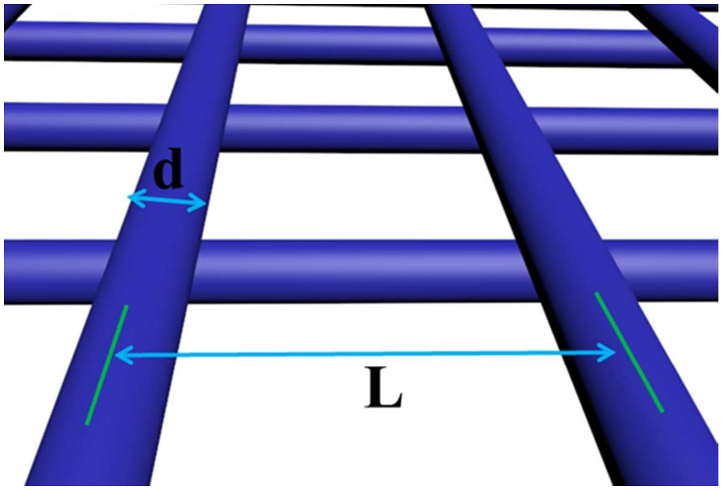

Figure S5. Schematic illustration of the 3D-printed frameworks with a spacing-to-diameter ratio of ～4. The in-plane center-to-center rod spacing is defined as *L*, and the filament diameter is defined as *d*.

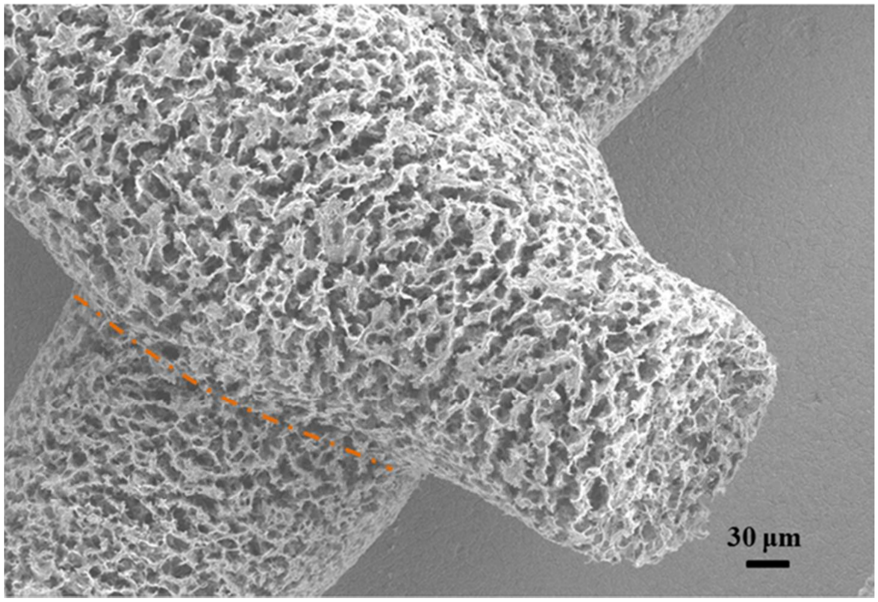

Figure S6. Cross-sectional SEM image of 3D printed frameworks, showing continuous filaments and hierarchical porous structure.

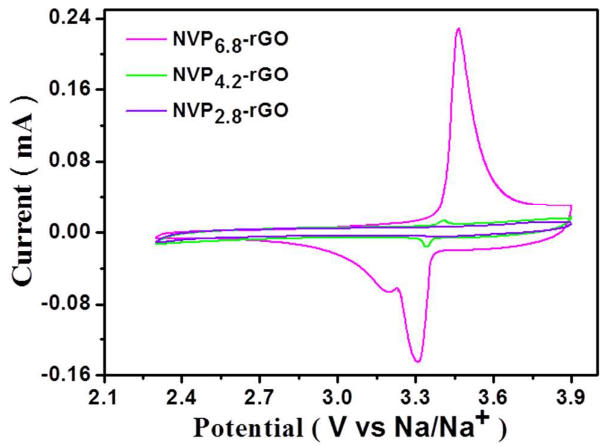

Figure S7. The CV profiles of 3D printed NVP-rGO frameworks.

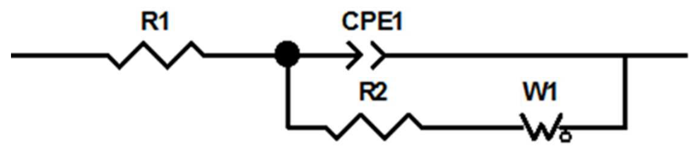

Figure S8. Randles equivalent circuit for 3D printed NVP-rGO frameworks electrode/electrolyte interface. *R1* is the bulk resistance, *R2* is the charge transfer resistance, *CPE1* is the constant phase element, and *W1* is the Warburg impedance related to the diffusion of sodium ions into the bulk electrodes.

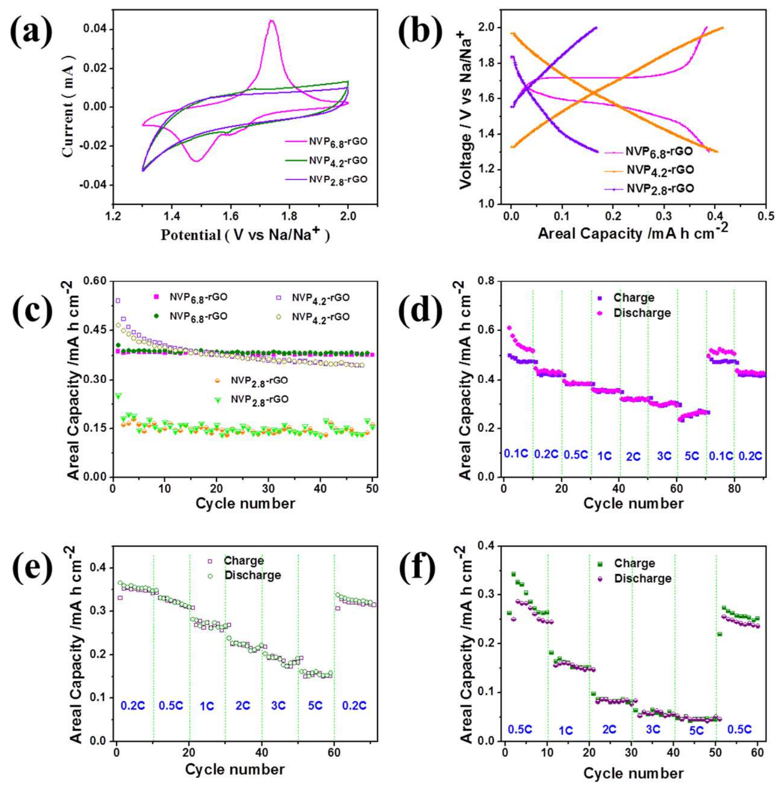

Figure S9. The electrochemical performances of 3D printed NVP-rGO frameworks. (a) CV profiles. (b) Selected 10th charge and discharge profiles at 1C. (c) Cycle performance at 1C. Cycling and discharge rate performance of (d) $NVP_{6.8}$-rGO, (e) $NVP_{4.2}$-rGO, and (f) $NVP_{2.8}$-rGO.

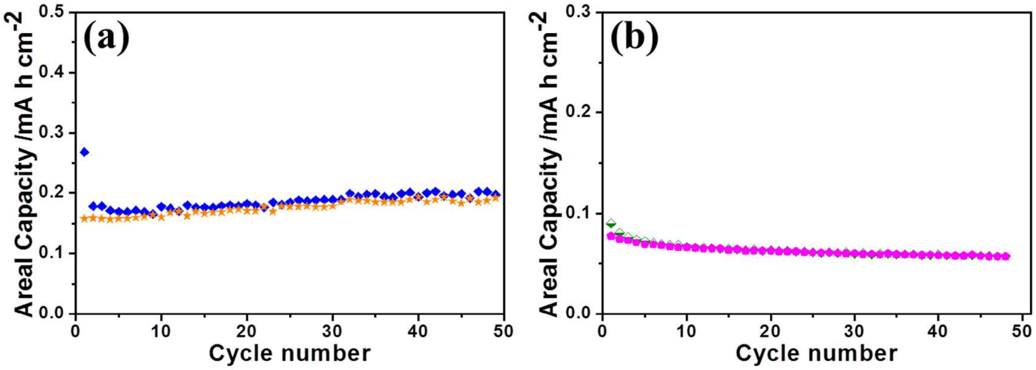

Figure S10. The electrochemical performances of 3D printed $NVP_{6.8}$-rGO frameworks without freeze-drying process. (a) Cycle performance at 2C as the cathode material. (b) Cycle performance at 1C as the anode material.

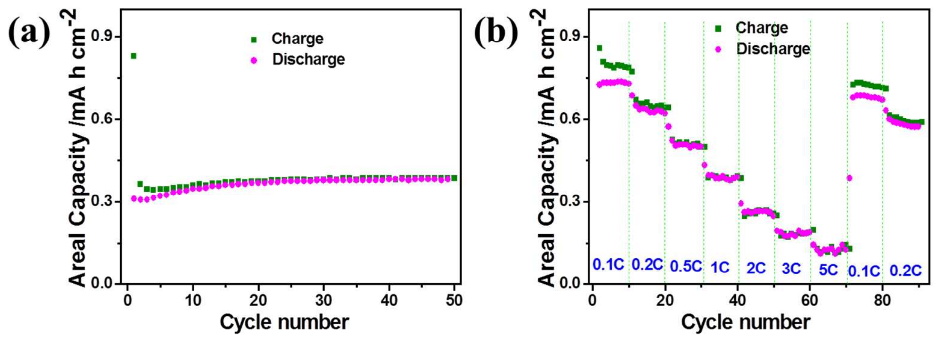

Figure S11. The electrochemical performances of 3D printed $NVP_{6.8}$-rGO frameworks symmetric full-cell. (a) Cycle performance at 1C. (b) Rate profiles.

Table S1. Comparison of the electrochemical performances of 3D printed electrodes with reported sodium ion batteries.

Electrode materials	Specific capacity (mAh/cm^2@mA/cm^2)	Rate performance (mAh/cm^2@mA/cm^2)	References
SnS_2@rGO	1.49@0.23	0.78@30	1
SnS-G	1.04@0.03	0.31@7.3	2
Sb@TiO_{2-x} Nanotubes	1@0.2	0.73@20	3
Ge nanowire	0.05@0.02	0.01@0.44	4
TiO_2@G nanocomposites	0.66@0.13	0.23@30	5
Expanded graphite	0.14@0.01	0.09@0.05	6
$NVP_{6.8}$-rGO frameworks	1.26@0.42 cathode 0.43@0.42 anode	0.65@42 0.32@4.2	This work

Table S2. Kinetic parameters of 3D printed NVP-rGO frameworks.

Samples	R_1 (Ω)	R_2 (Ω)	σ_w (S^{-1} $s^{-1/2}$)	D_{Na+} (cm^2 s^{-1})
$NVP_{6.8}$-rGO	5.8	157	13.59	6.12×10^{-13}
$NVP_{4.2}$-rGO	18.3	417	69.84	2.32×10^{-14}
$NVP_{2.8}$-rGO	12.3	802	98.27	1.17×10^{-14}

References

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(6) Wen, Y.; He, K.; Zhu, Y.; Han, F.; Xu, Y.; Matsuda, I.; Ishii, Y.; Cumings, J.; Wang, C. Expanded Graphite as Superior Anode for Sodium-Ion Batteries. *Nat. Commun.* **2014**, 5, 4033.