Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information

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Section I. Supporting Figures

Figure S1 Raman spectroscopy of as-prepared porous carbon nanofiber (PCNF). The low ratio of *D*/*G* band intensity (~1.12) demonstrates the partial graphitization of as-prepared carbon nanofibers.

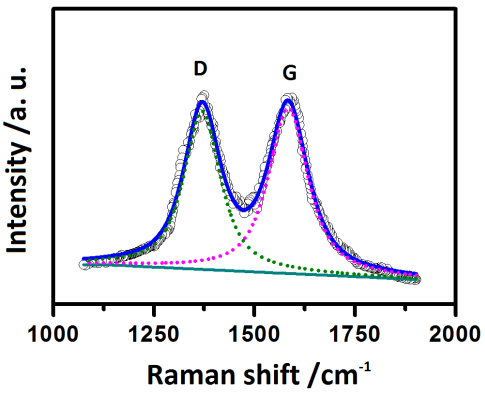


Figure S2 Pore size analysis of the as-prepared hybrid nanofiber. The multiple peaks demonstrate the hierarchical porous architecture of the hybrid nanofiber.

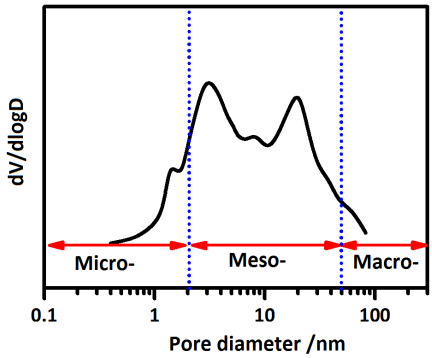


Figure S3 Schema of the crystal structure of bloedite-type hydrated sulfate (*i.e.* $Na_2Fe(SO_4)_2 \cdot 2H_2O$). It has the basic unit of $Fe(SO_4)_2(H_2O)_4$, which is constructed by one $FeO_2(OH)_4$ octahedron and two SO_4 tetrahedra. Sodium ions located at large channels are coordinated by six oxygen atoms.

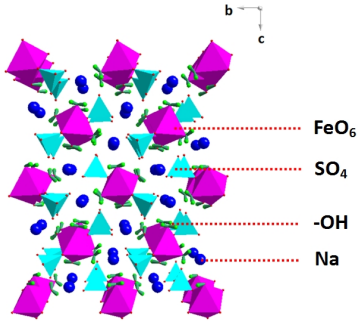


Figure S4 Morphology of the reference samples with (a,b) actived carbon, (c,d) carbon nanotube and (e,f) graphene supports. The irregular agglomeration are observed for the reference samples.

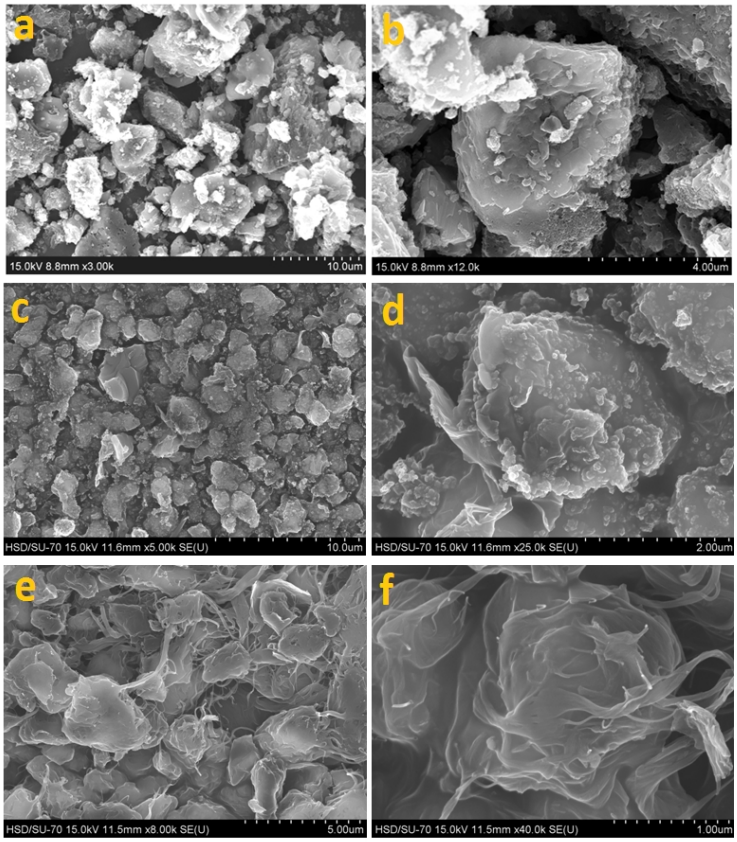
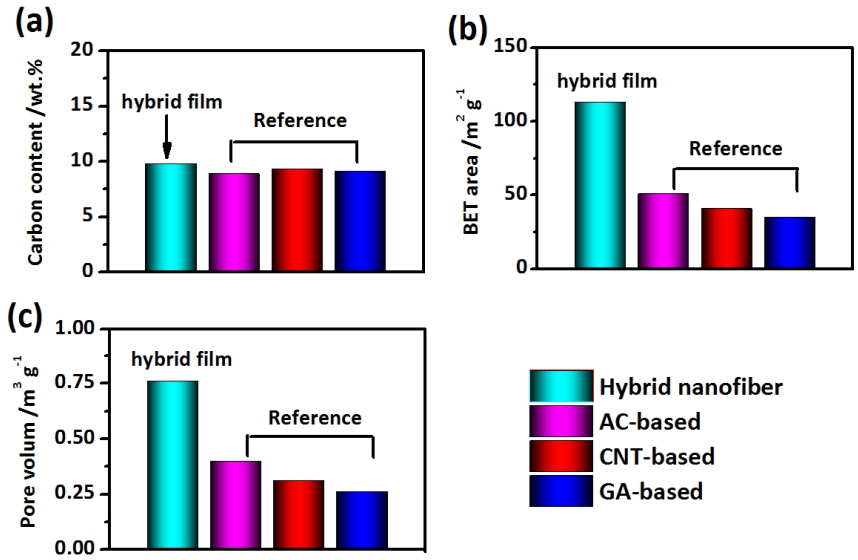


Figure S5 Physical characteristics, including carbon content (a), BET area (b) and pore volume (c) of the hybrid film and the CA-, GA- and CNT-based reference samples.



Section II. Calculation Process

Calculation process for sodium intercalation coefficients based on the GITT results

The sodium ion intercalation kinetics of the composites is investigated by GITT measurements. According to the simplified equation of Fick's second diffusion law, D_{Na} can be calculated from the following equation:[s1,s2]

$$D_{Na} = \frac{4}{p\,t}\left(\frac{m_B V_m}{M_B A}\right)^2 \left(\frac{\Delta E_S}{\Delta E_t}\right)^2 \qquad (t << L^2/D_{Na}) \qquad (1)$$

where D_{Na} (cm^2s^{-1}) is the sodium diffusion coefficient; m_B, M_B and V_m are the mass, molecular weight and molar volume of the electrode material, respectively; A is the interfacial area between electrode and electrolyte; τ is duration of the current pulse.

References:

[S1] W. Weppner, R. A. Huggins, *J. Electrochem. Soc.* **1977**, *124*, 1569.

[S2] E. Deiss, *Electrochimica Acta* **2005**, *50*, 2927.