Supporting Information for

Achieving High Energy-High Power Density in a Flexible Quasi-Solid-State Sodium Ion Capacitor

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Experimental Section

Synthesis of urchin-like NTO.

The mixture of titanium tetraisopropoxide [Ti-(OC_3H_7)$_4$, TIP] (0.5 mL), distilled water (28 mL) and 30 wt. % hydrogen peroxide (2 mL) and was sealed in a 50 mL Teflon-lined stainless-steel autoclave at 200 ℃ for 24 h. The product was collected by centrifugation, and washed with DI water and ethanol for five times. After being dried at 60 ℃ overnight, the as-synthesized samples were calcined at 500 ℃ for 2 h in air to obtain pure urchin-like NTO.

Synthesis of PSC.

The cathode material PSC was prepared from the biomass precursor (outer peanut shell) as described previously.[1] Typically, the pretreated outer peanut shell (1.2 g), concentrated sulfuric acid (2 mL) and distilled water (40 mL) were sealed in 80 mL Teflon-lined stainless-steel autoclave and kept at 180 ℃ for 48 h before cooling down to room temperature naturally. The precipitate was collected by vacuum-filtration, washed thoroughly with distilled water, and dried at 60 ℃ overnight. The dried PSC precursor and KOH, in a mass ratio of 1:3, were thoroughly ground using an agate mortar. Then, the mixtures were calcinated at 800 ℃ for 1 h in an argon flow. The activated samples were washed thoroughly with diluted hydrochloric acid (2 M) and distilled water, and finally dried at 100 ℃ overnight.

Synthesis of sodium ion conducting gel polymer.

The preparation of the P(VDF-HFP) membrane is based on literature reported by Wu's group with minor modifications.[2] Typically, P(VDF-HFP) was dissolved into a mixture of DMF and distilled water at 80 °C with a weight ratio of P(VDF-HFP): DMF: H_2O=15:85:3. The solution was cast onto a clean glass plate, and then immersed in a water bath at 80 °C, yielding a homogeneous white membrane. Then the white membrane was dried under vacuum at 100 °C for 10 h. After that, the dried membrane was punched into circular pieces (d = 19 mm). For the flexible quasi-solid-state NIC, the membrane was cut according to the size of the flexible anode or cathode. Finally, these membranes were soaked in an organic electrolyte (1 mol L^{-1} $NaClO_4$ solution in dissolved in propylene carbonate with 2 vol% fluorinated ethylene carbonate as an electrolyte additive) over 12 h in a glove box (water content: <1 ppm) to obtain the gel polymer electrolyte.

Material Characterization.

XRD patterns were performed on a Rigaku MiniFlex 600 equipped with Cu Kα radiation. Program VESTA was used to draw the schematic illustrations of the crystal structures.[3] SEM/STEM observations were carried out on a Hitachi scanning electron microspcope (S-5500) respectively. N_2 adsorption/desorption was determined by Brunauer-Emmett-Teller (BET) measurements using an ASAP-2010 surface area analyzer.

Electrochemical Measurements.

Half cells were constructed using the CR2032 coin-type cells with Na metal as the counter and reference electrode, and sodium ion conducting gel polymer as the electrolyte. The NTO anode was prepared by a slurry-coating procedure. The slurry consisted of 80 wt% active materials, 15 wt% Super P, and 5 wt% CMC (carboxyl methyl cellulose) dissolved in DI water. This slurry was spread on copper foil, which acted as a current collector. The PSC cathode was also prepared by a slurry-coating procedure. The slurry consisted of 80 wt% active materials, 15 wt% Super P, and 5 wt% PVDF (polyvinylidenediflouride) dissolved in NMP (N-methylpyrrolidone), which was then casted on aluminum foil. Electrochemical measurements of the quasi-solid-state NIC were conducted using two-electrode cells at room temperature. The aformentioned NTO and PSC electrode was acted as the anode and cathode, respectively. The cell balance was achieved by setting the electrode mass ratio of cathode/anode to ca. 1.5. Before assembling the NIC devices, both the NTO anode and PSC cathode were galvanostatically (0.1 A g^{-1}) cycled a few times in half cells (*i.e. vs.* Na/Na^{+}), ending in a desodiated and sodiated condition, respectively. Then, the above half cells were disassembled and the electrodes were taken out and re-assembled into a full cell. Cyclic voltammetry (CV) curves were collected by Bio-logic potentiostat (VMP3) at 0.1 mV s^{-1}, Galvanostatic charge/discharge experiments were performed at different current densities on LAND battery cycler (CT2001A). The device was charged and discharged between the voltage range of 0.5-3.5 V at various current densities. The power and energy densities were calculated using the following formula:

$$E = \int_{t1}^{t2} IVdt = \frac{1}{2}C(V_{max} + V_{min})(V_{max} - V_{min}) = \Delta V \times \frac{I}{m} \times t, \qquad (1)$$

$$P = \frac{E}{t} = \Delta V \times \frac{I}{m}, \quad (2)$$

$$\Delta V = \frac{V_{max} + V_{min}}{2}. \quad (3)$$

where C is the capacitance of the device; V_{min} and V_{max} are the potential at the initial and final charge curves during galvanostatic measurements, respectively; I is charge/discharge current, and m is the total mass of the active material in both the electrodes.

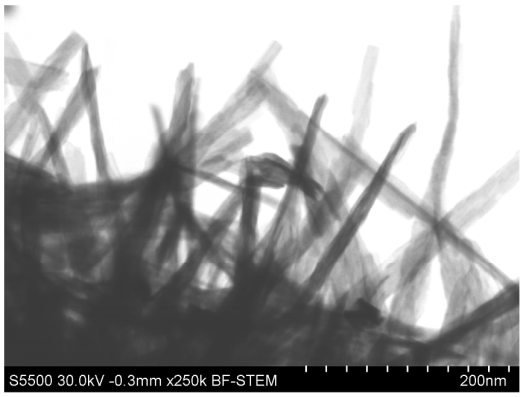

Figure S1. STEM image of the urchin-like NTO.

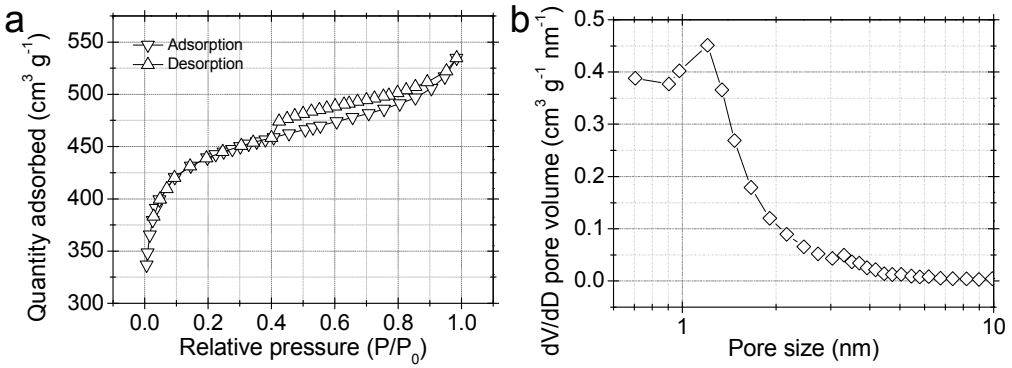

Figure S2. (a) Nitrogen adsorption-desorption isotherm and (b) pore size distribution data through the BJH method of PSC.

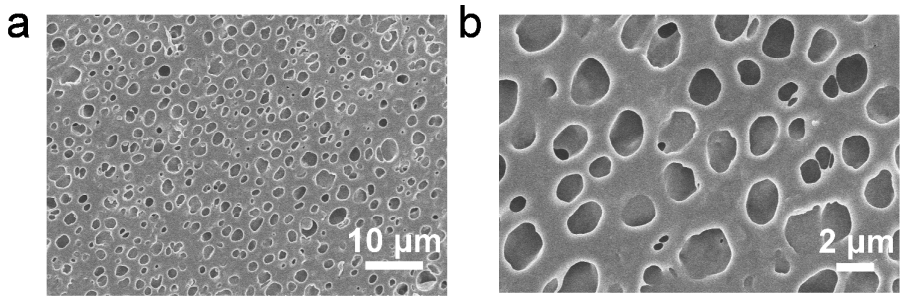

Figure S3. SEM image of the P(VDF-HFP) membrane.

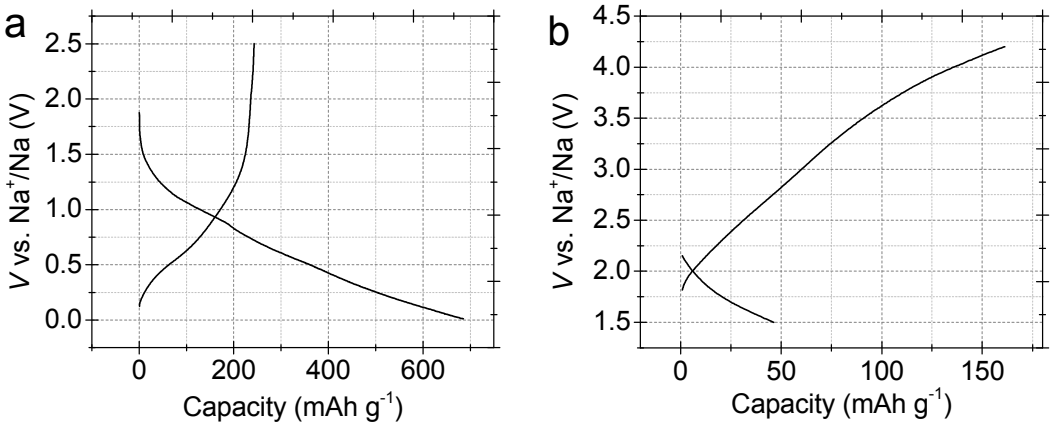

Figure S4. The first charge-discharge curves of NTO anode (a) and PSC cathode (b) at a current density of 0.1 A g^{-1}.

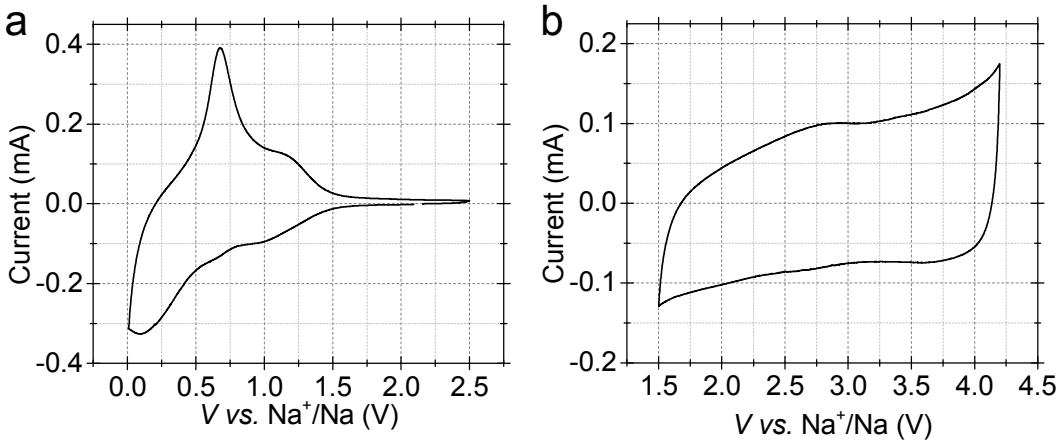

Figure S5. CV curves of the urchin-like NTO (a) and PSC (b) at a scan rate of 1 mV s^{-1}.

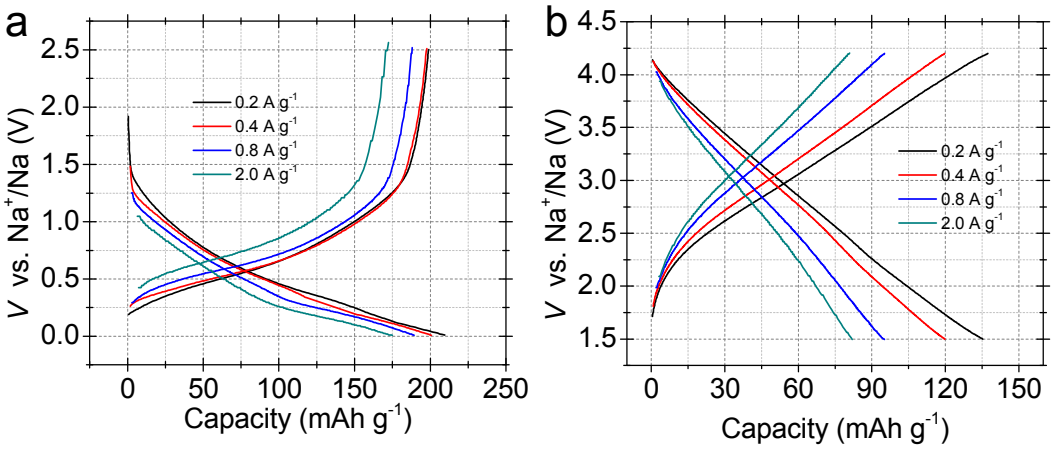

Figure S6. Charge-discharge curves of urchin-like NTO (a) and PSC (b) at different current densities.

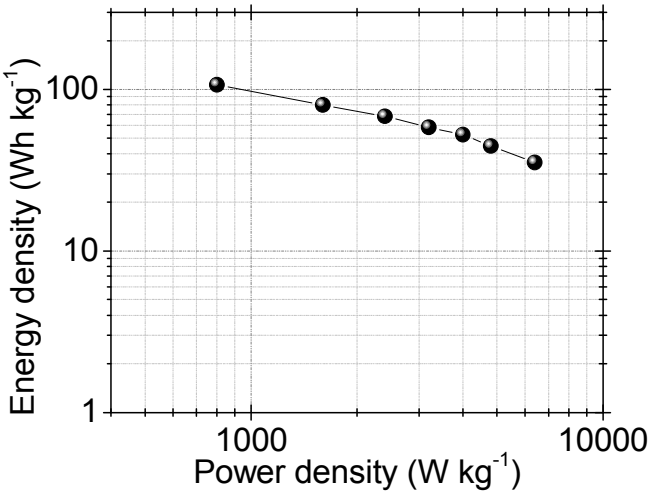

Figure S7. Ragone plot for the urchin-like NTO//PSC using the glass fiber as the separator. The energy and power densities and capacitance were calculated based on the total weight of the anode and cathode materials.

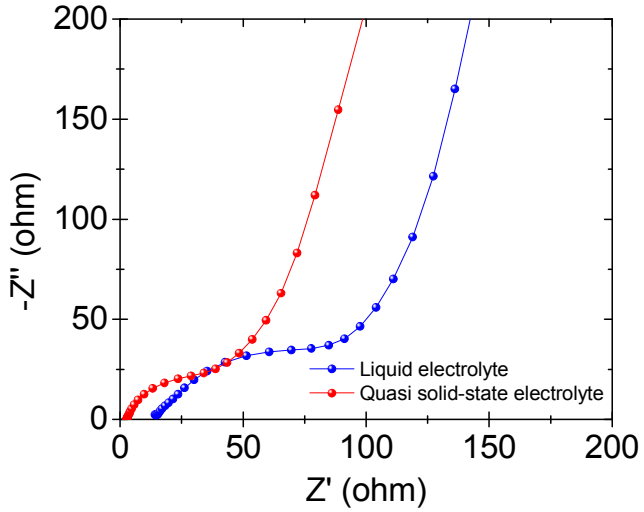

Figure S8. Impedance plots of the urchin-like NTO//PSC sodium ion capacitor using liquid electrolyte and quasi-solid-state electrolyte, respectively.

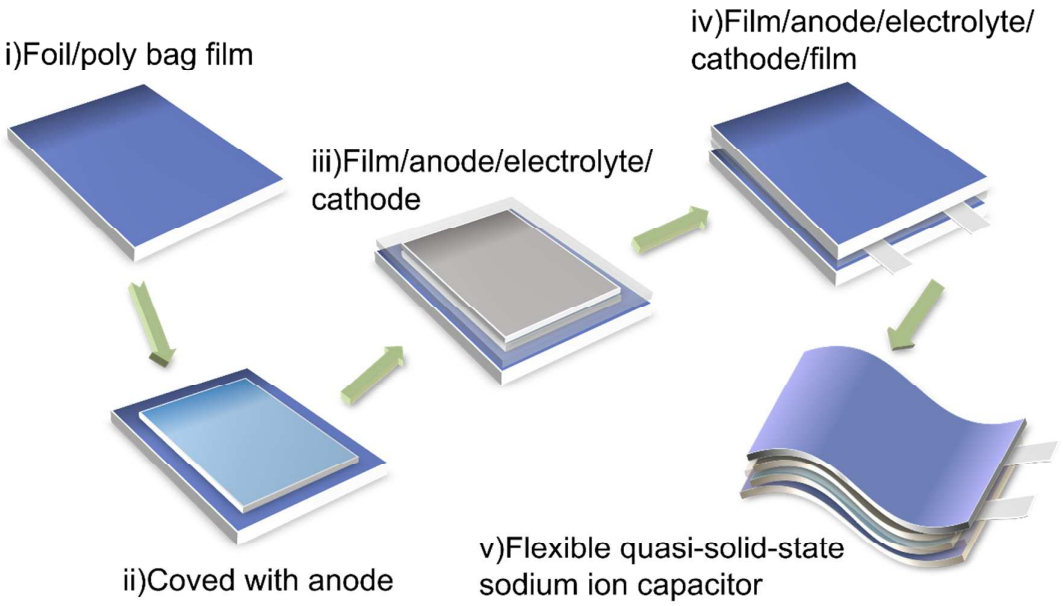

Figure S9. Schematic illustration of the sodium ion capacitor and fabrication process of the flexible quasi-solid-state sodium ion capacitor.

References

(1) Ding, J.; Wang, H.; Li, Z.; Cui, K.; Karpuzov, D.; Tan, X.; Kohandehghan, A.; Mitlin, D. *Energy Environ. Sci.* **2015**, 8, 941-955.

(2) Yang, Y.; Chang, Z.; Li, M.; Wang, X.; Wu, Y. *Solid State Ionics* **2015**, 269, 1-7.

(3) Momma, K.; Izumi, F. *J. Appl. Crystallogr.* **2008**, 41, 653-658.