Supporting Information

Constructing Hierarchical Dandelion-like Molybdenum-Nickel-Cobalt Ternary Oxide Nanowire Arrays on Carbon Nanotube Fiber for High-Performance Wearable Fiber-shaped Asymmetric Supercapacitors

Juan Sun, Qichong Zhang, Xiaona Wang, Jingxin Zhao, Jiabin Guo, Jun Zhang, Zhenyu Zhou, Ping Man, Jing Sun, Qingwen Li*, and Yagang Yao*

[*] Email: ygyao2013@sinano.ac.cn

qwli2007@sinano.ac.cn

Materials

Ammonium molybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, 99%), cobalt nitrate hexahydrate ($Co(NO_3)_2\cdot 6H_2O$, 98.5%), nickel nitrate hexahydrate ($Ni(NO_3)_2\cdot 6H_2O$, 98%), ammonium fluoride (NH_4F, 98%), potassium hydroxide (KOH, 85%), ethanedioic acid dihydrate ($H_2C_4O_4\cdot 2H_2O$, 99.8%) and hydrogen peroxide (H_2O_2, 35 wt%) were purchased from Sinopharm Chemical Reagent, China. Urea ($CO(NH_2)_2$, 99%) and PVA ($[CH_2CH\ (OH)]_n$, n = 1799) were obtained from Aladdin. Vanadium pentoxide (V_2O_5, 99.2%) was offered by Alfa Aesar. All of these chemicals were utlized directly without any further purification. Carbon nanotube fibers (CNTFs) were twisting from CNT thin films which were prepared via a floating catalyst chemical vapor deposition method followed by shrinking with ethanol.

Preparation of VN@C/CNTF electrode

Vanadium nitride (VN) nanowire arrays (NWAs) were prepared by a facile two-step method. First of all, carbon nanotube fibers (CNTFs) were treated in O_2 plasma for 5 min at 150 W. In a typical progress, 2.4 g V_2O_5 powders and 5 g $H_2C_4O_4\cdot 2H_2O$ were dissolved in 80 ml deionized (DI) water with continuous stirring at 80 ^oC for 5 h to form a transparent blue solution (VOC_2O_4). A 10-ml portion of the resulting solution was transferred to a 100 ml beaker, followed by adding 2 ml H_2O_2 (35 wt%) dropwise to the breaker under vigorous stirring. 10 min later, 30 ml alcohol was added to the solution and the solution was stirred for another 5 min. Then the obtained solution and the pre-treated CNTFs were transferred to a 50 ml Teflon-lined stainless steel autoclave. After that, the autoclave was sealed and maintained at 180 ^oC for 24 h. When the autoclave cooled to room temperature, the CNTFs covered with VO_x NWAs (VO_x/CNTFs) were taken out and rinsed with ethanol and DI water several times and dried at 60 ^oC under vacuum for 12 hours. Thereafter, VO_x/CNTFs were annealed under the atmosphere of 100 sccm NH_3 and 100 sccm Ar at 600 ^oC for 2h with a heating rate of 5 ^oC/min, resulting in the formation of crystal VN/CNTFs. Moreover, VN/CNTFs were modified with a thin layer of carbon (VN@C/CNTF) via a

typical method. In detail, VN/CNTFs were immersed into 0.04 M aqueous glucose solution for 24 h and followed by carbonization at 450 °C in Ar for 2 h with a heating rate of 5 ^{o}C/min.

Electrochemical Performance Measurements

All related electrochemical profiles including cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS) curves were measured utilizing an electrochemical workstation (CHI 760E, Chenhua). The behaviors of the as-fabricated electrodes were tested by three-electrode system in 3 M KOH aqueous electrolyte. The electrode materials were directly utilized as working electrodes, the Pt wire and Ag/AgCl were selected as counter and reference electrodes, respectively. The EIS measurements were performed from 100 kHz to 0.01 Hz with a voltage amplitude of 5 mV at open-circuit potential. The performance of all-solid fiber-shaped asymmetric supercapacitor (FASC) device was carried out in a two-electrode system. The areal specific capacitance (C, mF/cm^2), energy density (E, μWh/cm^2) and power density (P, μW/cm^2) were calculated according to the following equations:

$$C = \frac{I\Delta t}{A\Delta V} \quad (1)$$

$$E = \frac{1}{7.2} C(\Delta V)^2 \quad (2)$$

$$P = 3600\frac{E}{\Delta t} \quad (3)$$

Where I is the discharge current (mA), Δt is the discharge time, ΔV is the potential window (V), and A is the total area of the fiber electrode (cm^2).The volumetric specific capacitance (C, F/cm^3), energy density (E, mWh/cm^3) and power density (P, mW/cm^3) were calculated according to the following equations:

$$C = \frac{I\Delta t}{V\Delta V} \quad (1)$$

$$E = \frac{1}{2} C(\Delta V)^2 \quad (2)$$

$$P = \frac{E}{\Delta t} \qquad (3)$$

Where I is the discharge current (mA), Δt is the discharge time, V represents the total volume (cm^3) of the two electrodes, and ΔV is the potential window (V). The cycle life was tested by GCD measurements with a constant current density of 2 mA/cm^2 for 3,000 cycles.

Procedure of twisting MNCO/CNTF and VN@C/CNTF fiber electrodes

First of all, both MNCO/CNTF and VN@C/CNTF electrodes were fixed to polytetrafluoroethylene (PTFE) frameworks using high-temperature adhesive tape and then immersed into KOH/PVA gel electrolyte for 10 min and subsequently dried at 60 ^oC for 2 h. After repeating for three times, the hybrid fibers were peeled off from the framework and then their two ends were fixed on a motor and attached to a stable stage, respectively. The motors were steadily rotated so that the MNCO/CNTF and VN@C/CNTF electrodes twisted together. Finally, the untwisted ends of the device were attached to two conductive copper sheets and covered with conductive silver adhesives for its electrochemical measurement.

Balance the charge of electrodes in VN@C/CNTF// MNCO/CNTF FASC device

For an asymmetric supercapacitor, the charges between the two electrodes should be balanced according to $Q^+ = Q^-$ and $Q = C \times A \times V$, where C is the specific capacitance, V is the potential range, and A is the area of the electrode. To achieve $Q^+ = Q^-$ at 1 mV/s, the matching area ratio should be A(VN@C/CNTF)/A(MNCO/CNTF) ≈ 0.76 for our FASC device.

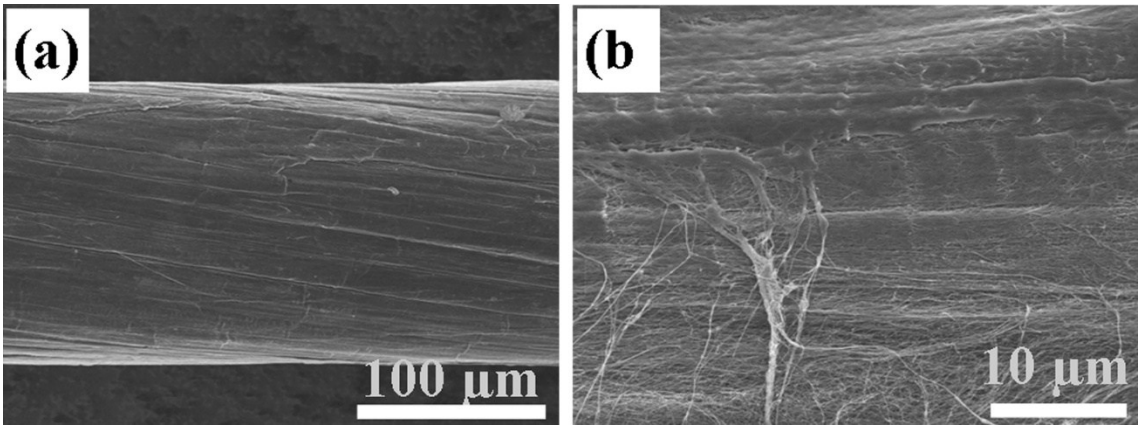

Figure S1. SEM images of pristine carbon nanotube fiber (CNTF).

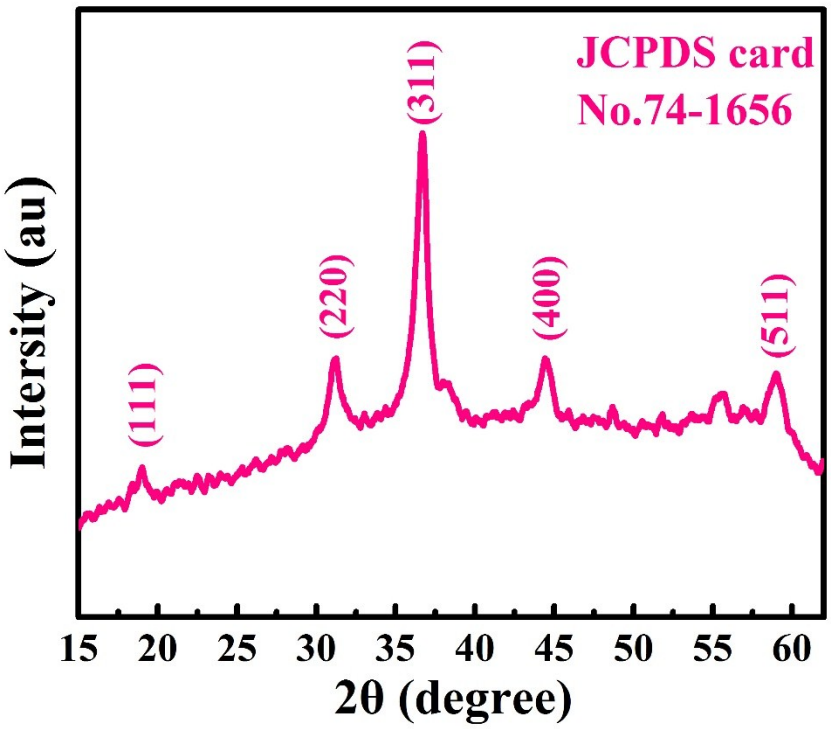

Figure S2. XRD pattern of the hierarchical dandelion-like MNCO electrode materials.

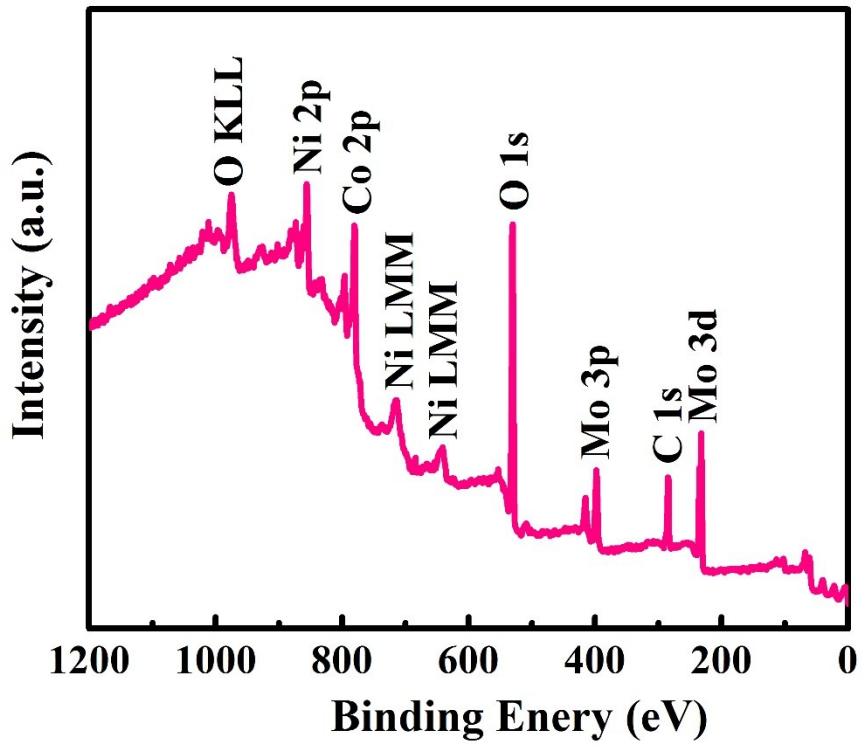

Figure S3. XPS spectra of the dandelion-like MNCO electrode materials.

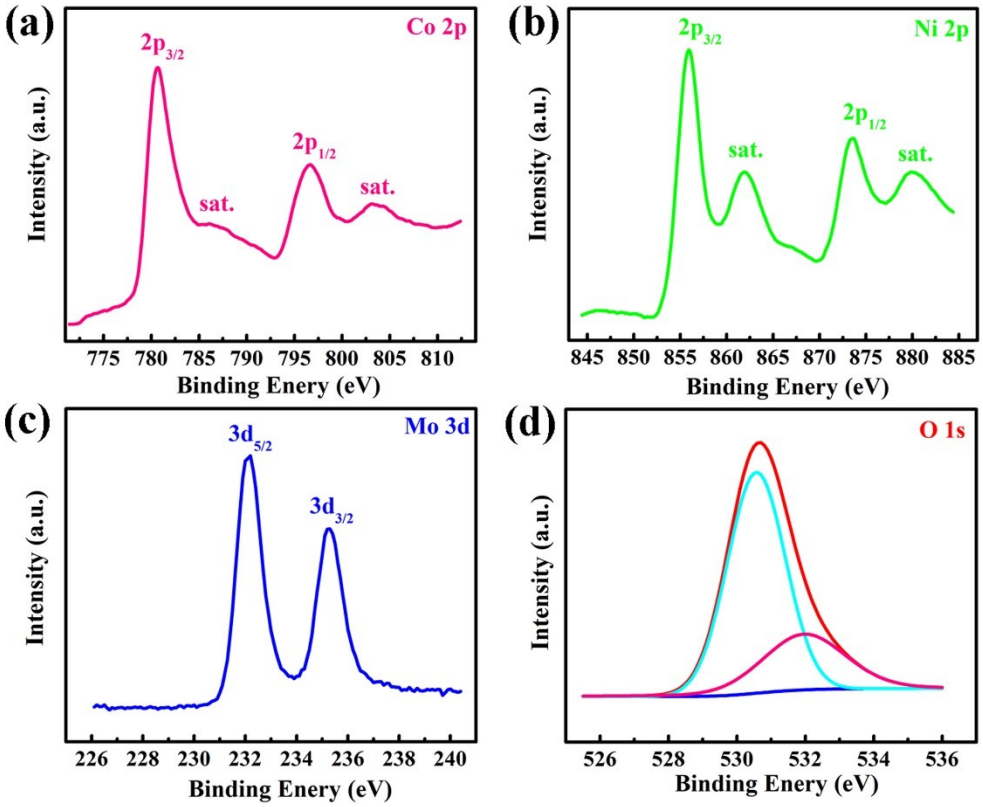

Figure S4. High-resolution XPS survey spectra of the as-prepared dandelion-like MNCO electrode materials. (a) Co 2p, (b) Ni 2p, (c) Mo 3d, (d) O 1s. XPS spectrum of Co 2p is fitted with two little shakeup satellites (indicated as "sat") and two spin-out doublets at 780.7 eV and 796.8 eV ascribing to Co $2p_{3/2}$ and Co $2p_{1/2}$. Ni 2p spectrum possesses two obvious shakeup satellites (marked as "sat") close to two spin-orbit doublets at 855.9 eV and 873.5 eV, which can be identified as Ni $2p_{3/2}$ and Ni $2p_{1/2}$. Mo 3d spectrum reveals two major peaks with the binding energy at 232.1 eV and 235.2 eV, corresponding to Mo $3d_{5/2}$ and Mo $3d_{3/2}$ spin-orbit peaks, respectively. In the O 1s spectrum, the peaks centered at 530.6 eV and 531.9 eV are assigned to –OH and O^{2-}.

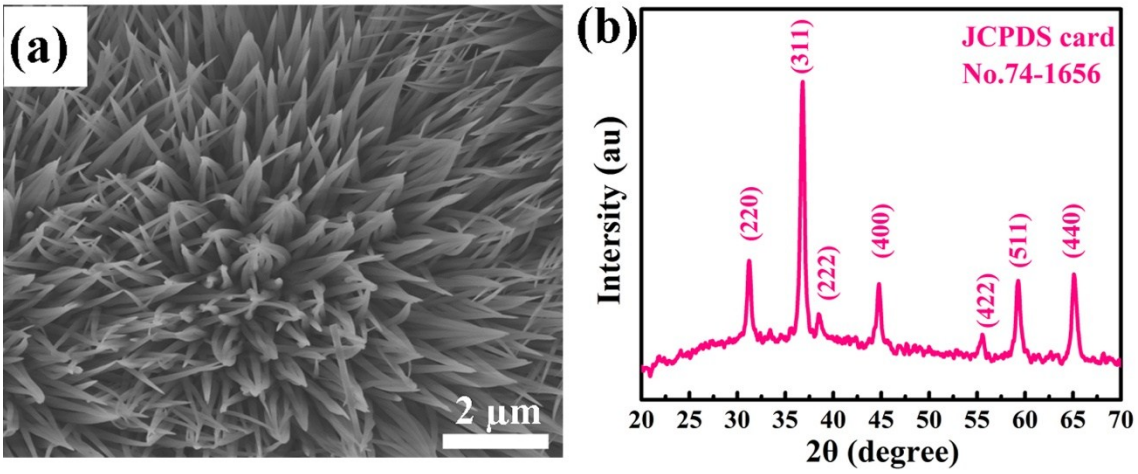

Figure S5. (a) SEM images of the as-prepared Co_3O_4 NWAs on CNTF. (b) XRD pattern of Co_3O_4 NWAs.

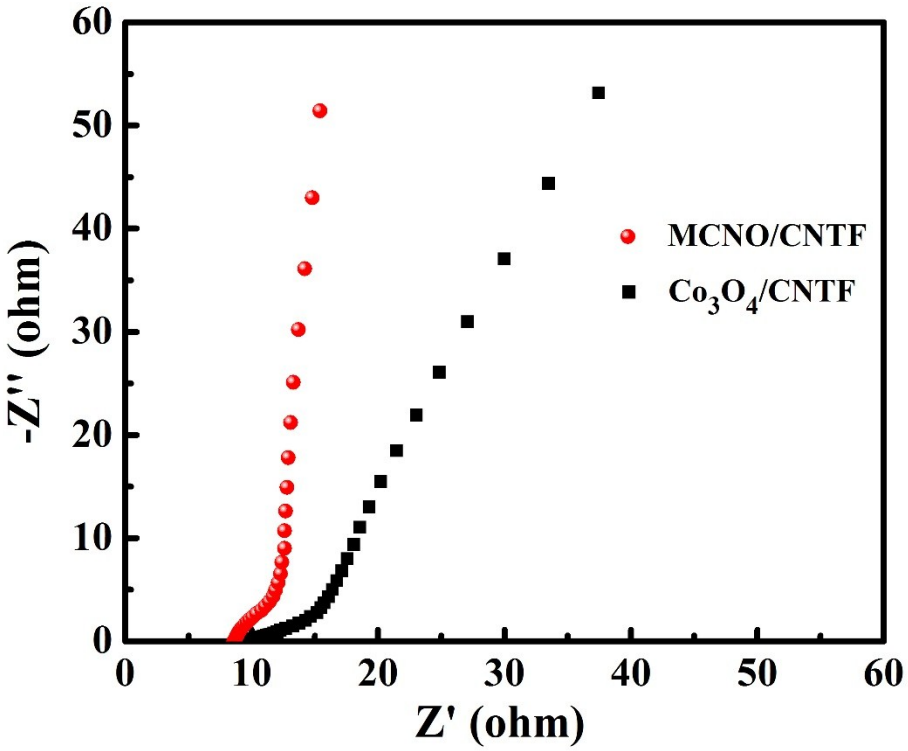

Figure S6. ESI spectra of the as-prepared Co_3O_4/CNTF and MNCO/CNTF electrodes at frequencies ranging from 10^{-2} to 10^5 Hz with a voltage amplitude of 5 mV at open-circuit potential.

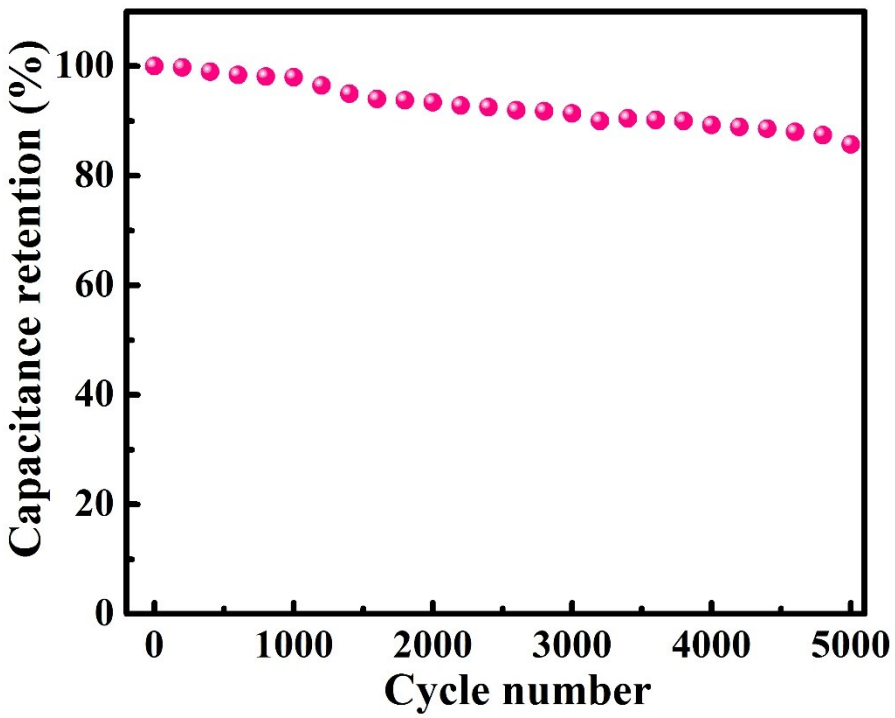

Figure S7. Cycling performance of the as-fabricated MNCO/CNTF fiber electrodes at 2 mA/cm^2.

The long-term cycling performance of MNCO/CNTF fiber electrodes was investigated by GCD at a current density of 2 mA/cm^2. The electrode demonstrates 85.7% of the initial capacitance after 5,000 cycles, indicating outstanding cycling stability.

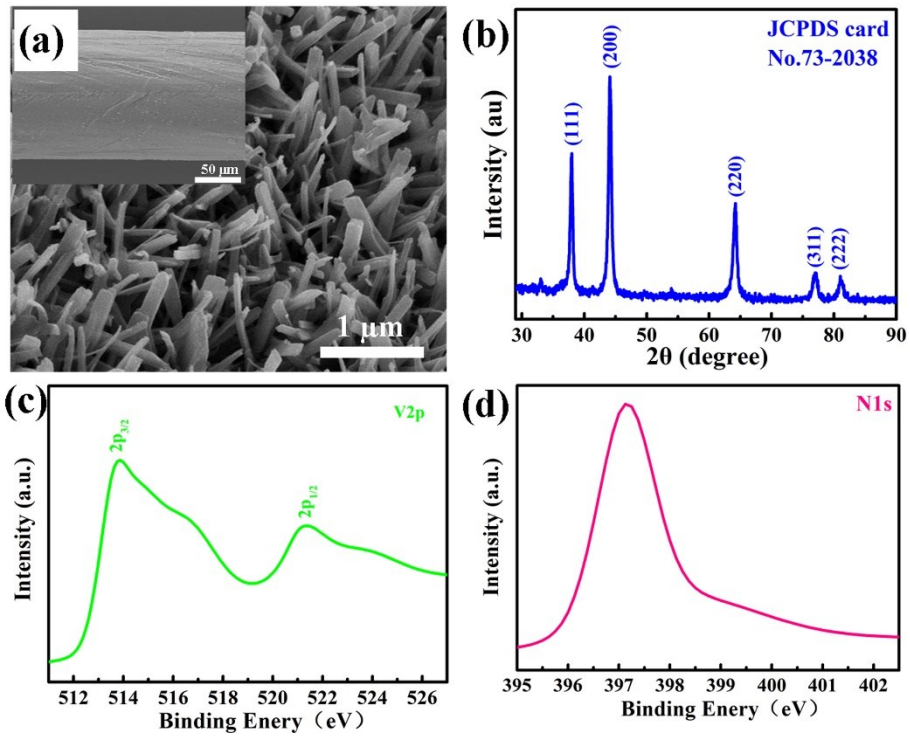

Figure S8. (a) SEM images of the as-prepared VN NWAs on CNTF with different magnifications. (b) XRD pattern of VN. XPS survey spectra for (c) V 2p and (d) N 1s of VN.

The V 2p spectrum possesses two peaks at 513.8 and 521.4 eV, corresponding to V $2p_{3/2}$ and V $2p_{1/2}$. In the N 1s spectrum, the peak centered at 397.2 eV is assigned to N from VN.

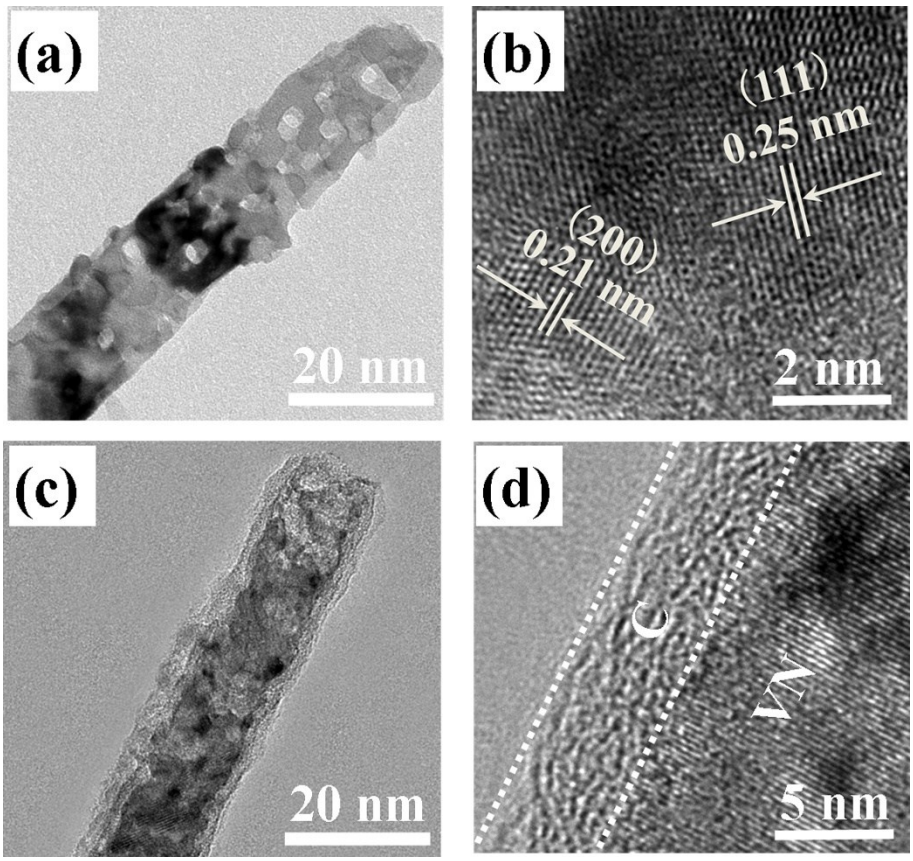

Figure S9. (a-b) TEM images of the as-prepared VN NWAs. (c-d) TEM images of the as-prepared VN@C core-shell structure.

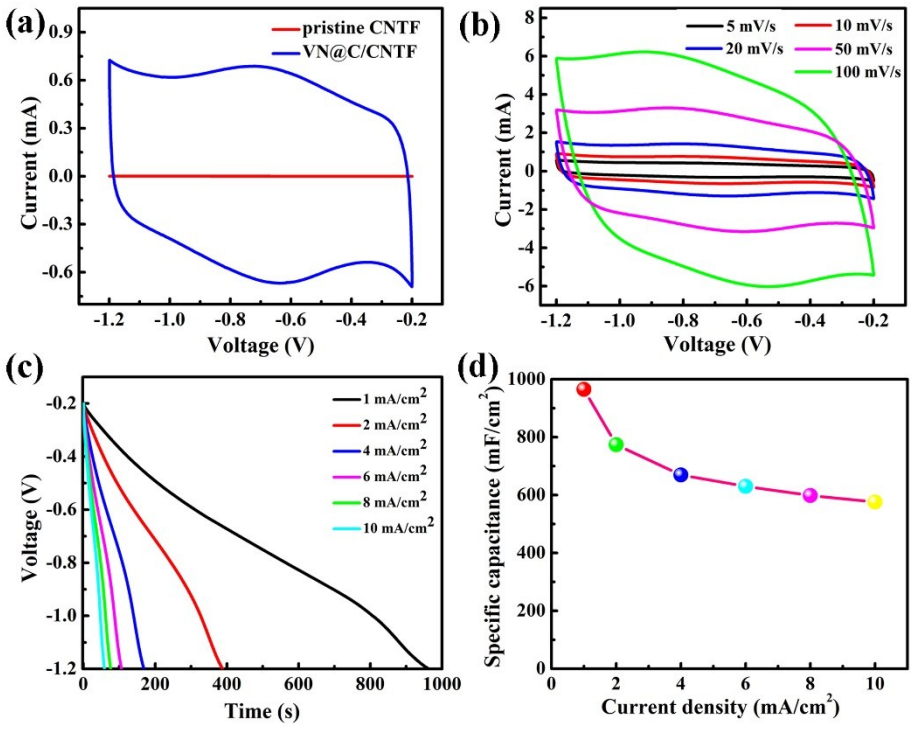

Figure S10. (a) Comparisons of CV curves of pristine CNTF and VN@C/CNTF with a scan rate of 10 mV/s. (b) CV curves of the VN@C/CNTF electrode at various scan rates. (c) Discharging curves of VN@C/CNTF electrode at different current densities. (d) Areal specific capacitance of the VN@C/CNTF electrode based on GCD curves from (c).

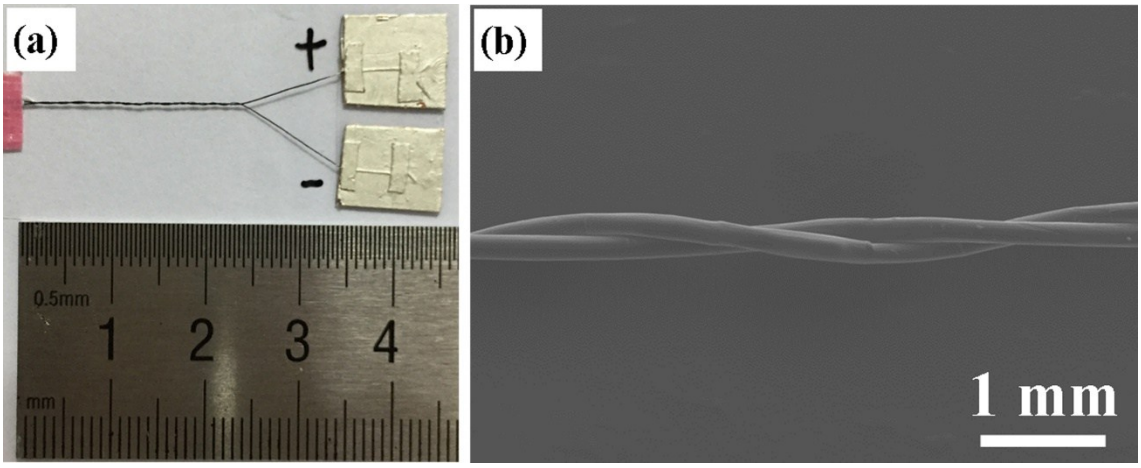

Figure S11. (a) The digital image and (b) low-magnification SEM image of the as-assembled FASC device.

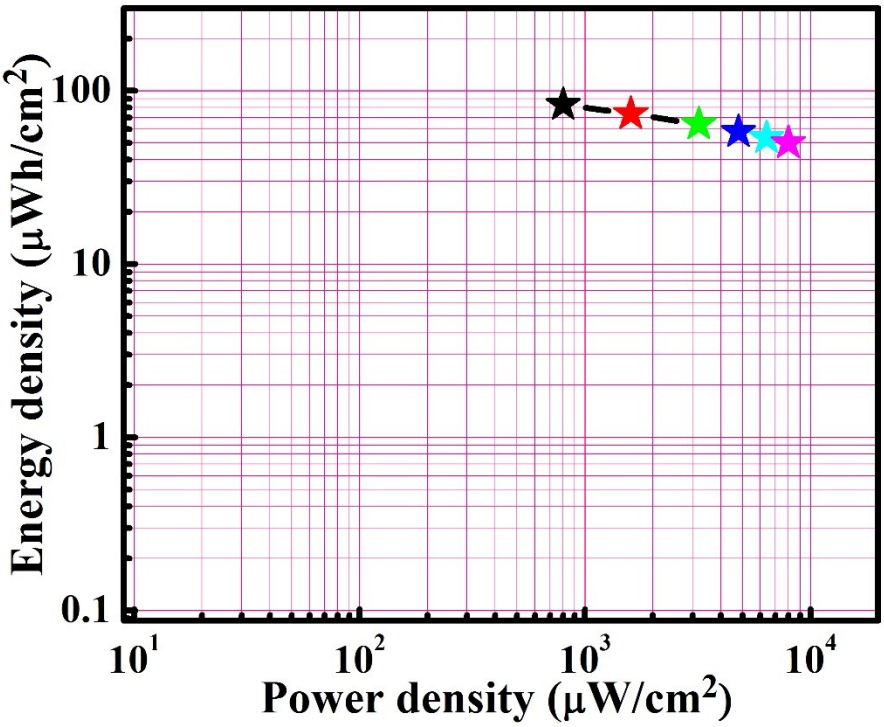

Figure S12. Areal energy and power densities of our FASC device.

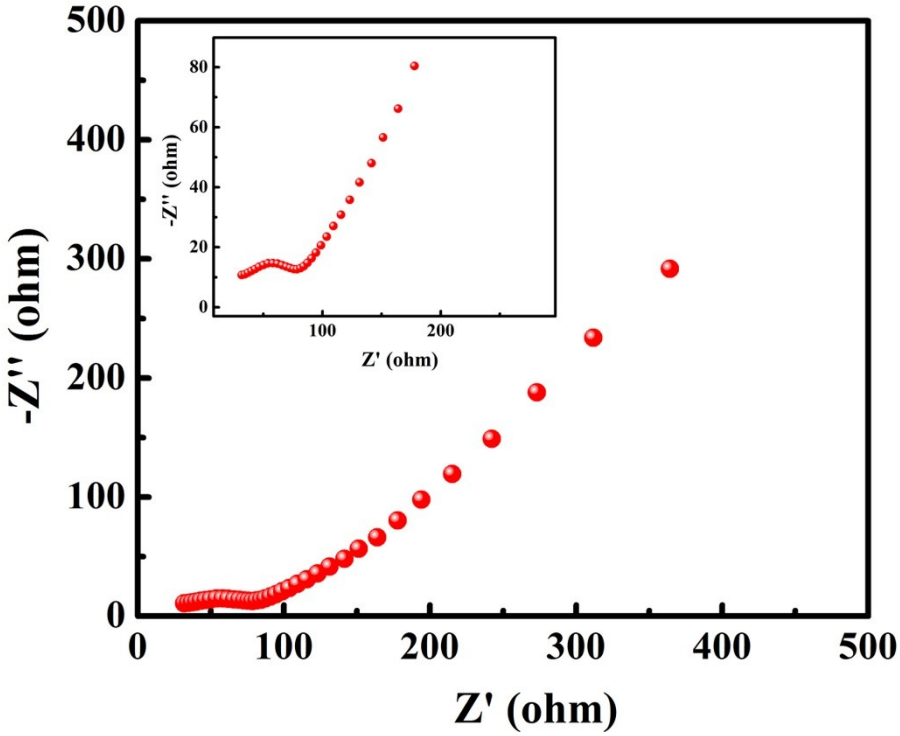

Figure S13. Nyquist plot of the as-assembled FASC at frequencies ranging from 10^{-2} to 10^{5} Hz (inset: enlarged EIS in high-frequency range) with a voltage amplitude of 5 mV at open-circuit potential.

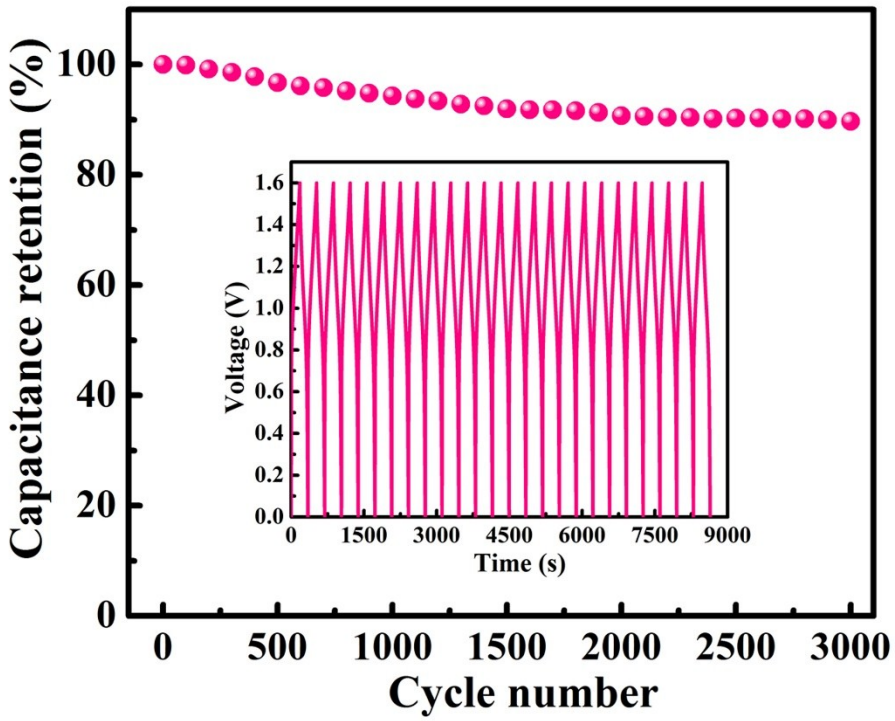

Figure S14. Cycling performance of the as-assembled FASC at 2 mA/cm^2 (inserted, charge-discharge profiles).