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Supporting Information

Facile Synthesis of Hierarchical Porous Manganese Nickel Cobalt Sulfide Nanotube Arrays with Enhanced Electrochemical Performance for Ultrahigh Energy Density Fiber-Shaped Asymmetric Supercapacitor

Xiaona Wang[a,b#], Qichong Zhang[a#], Juan Sun[a], Zhenyu Zhou[a], Qiulong Li[a], Bing He[a], Jingxin Zhao[a], Weibang Lu[a], Ching-ping Wong[b], Yagang Yao[a*]

a. Division of Advanced Nanomaterials, Key Laboratory of Nanodevices and Applications, Joint Key Laboratory of Functional Nanomaterials and Devices, CAS Center for Excellence in Nanoscience, Suzhou Institute of Nano-tech and Nano-bionics, Chinese Academy of Sciences, Suzhou 215123, China

b. School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332, United States

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

[#] These authors contributed equally to this work.

Synthesis of $NiCo_2O_4$ nanowire arrays on carbon nanotube fibers (CNTFs)

Cobalt nitrate hexahydrate (1.746 g), nickel nitrate hexahydrate (0.872 g), ammonium fluoride (0.111 g), and urea (0.54 g) were dissolved in distilled water (80 mL) to form a pink homogeneous solution. The solution was transferred into Teflon lined stainless steel autoclave liners (100 mL). Then, the CNTFs were immersed in the reaction solution. The stainless steel autoclave was then held at 130 ^oC for 5 h. After cooling to room temperature naturally, the as-obtained CNTFs were taken off and washed repeatedly with ethanol and distilled water and dried for 12 h at 60 °C. The samples were then annealed at 300 °C in air for 4 h to obtain $NiCo_2O_4$ NWAs grown on CNTFs.

Balance the charge of two electrodes in FASC device

The negative and positive electrodes need to obtain the balance when assemble fiber-shaped asymmetric device. For an asymmetric supercapacitor, the charges between the two electrodes should be balanced according to $Q^+ = Q^-$ and $Q = C \times X \times V$, where C is the specific capacitance, X is the area (2πrL) or volume (πr^2L) of the electrode, and V is the potential range. To achieve $Q^+ = Q^-$ (current density at 1 mA/cm^2), the matching length ratio for our FASC device should be:

L (VN /CNTF) / L (MNCS/CNTF) ≈ 2.7,

C (MNCS/CNTF) = 7030 mF/cm^2, V(MNCS/CNTF) = 0.4V

C (MNCS/CNTF) = 1009 mF/cm^2, V(MNCS/CNTF) = 1V

The areal capacitance was calculated using the following equation:

$$C_a = \frac{i \times t}{a \times \Delta V} \qquad S1$$

where C_a is the areal capacitance of the active material supported on the CNTFs, i is the discharge current during the charge and discharge process, t is the discharge time from high to low potential, a is the area of the electrode (one CNTF coated by active material for a single electrode or two CNTFs by active material for the whole device), and ΔV is the gap between high and low potential windows.

The volumetric capacitance was calculated using the following equation:

$$C_v = \frac{i \times t}{v \times \Delta V} \qquad S2$$

where v is the volume of the electrode (), and the other parameters are consistent with *S1*

The energy density (E) and power density (P) were obtained based on Eq. *S3* and Eq. *S4*, respectively:

$$E = \frac{C_s \times \Delta V^2}{2} \qquad S3$$

where ΔV is the gap between high and low potential windows, and Cs is specific capacitance (C_a or C_v).

$$P = \frac{E}{t} \qquad S4$$

where E is the energy density and, t is the time of discharge.

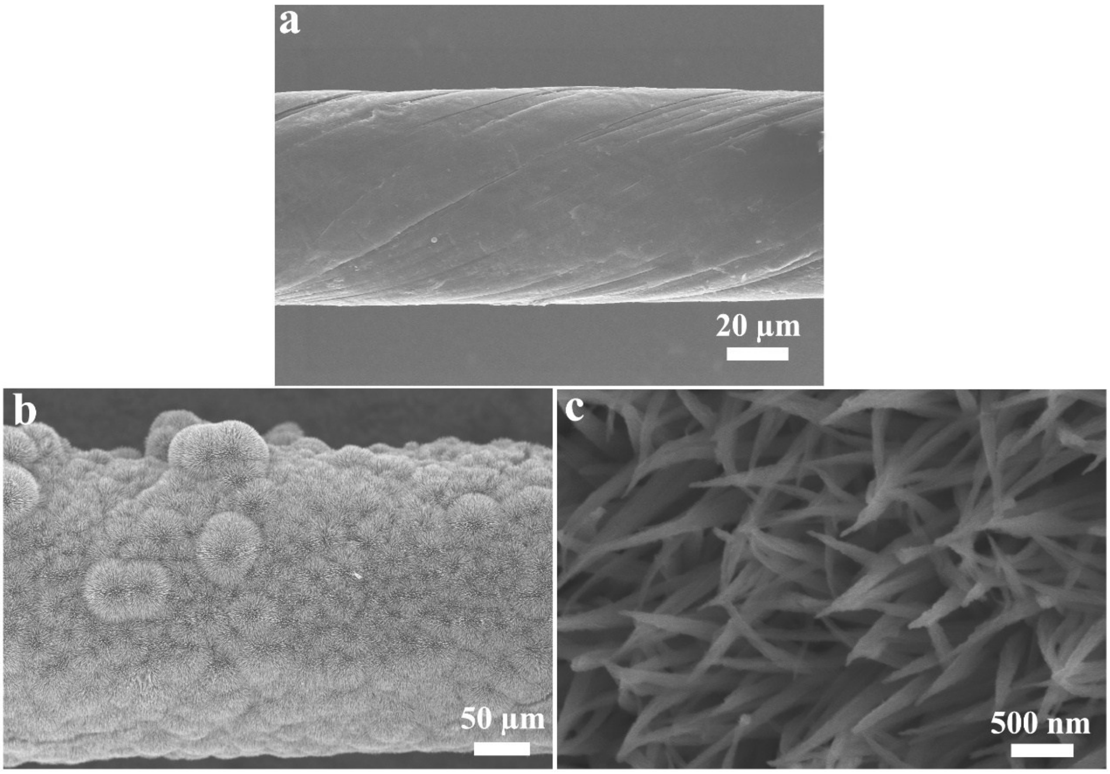

Fig. S1. (a) SEM image of CNTFs. (b-c) SEM images of Mn-Ni-Co precursor nanowire arrays grown on the CNTF at different magnification.

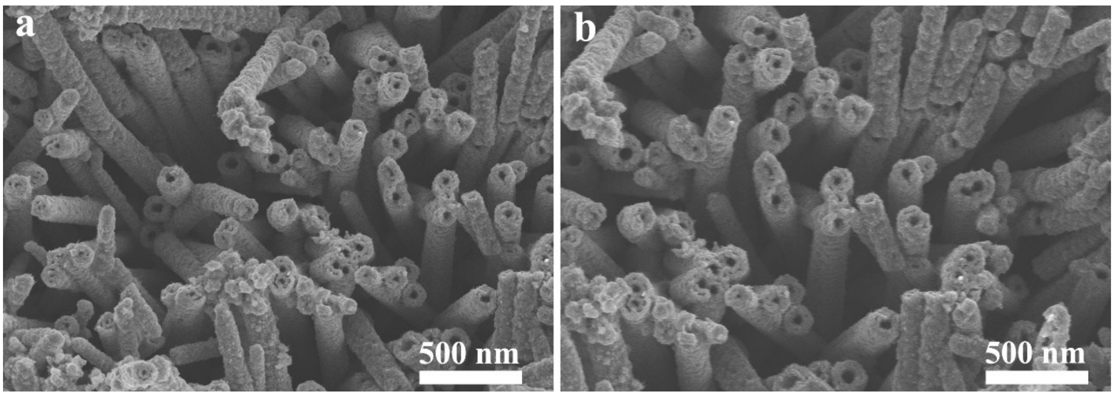

Fig. S2. (a-b) SEM images of the broken tips of MNCS NTAs revealing their hollow structure.

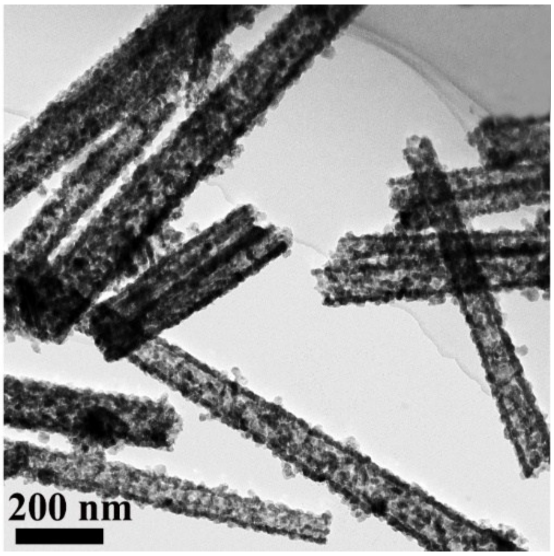

Fig. S3. TEM image of several MNCS nanotubes array structures.

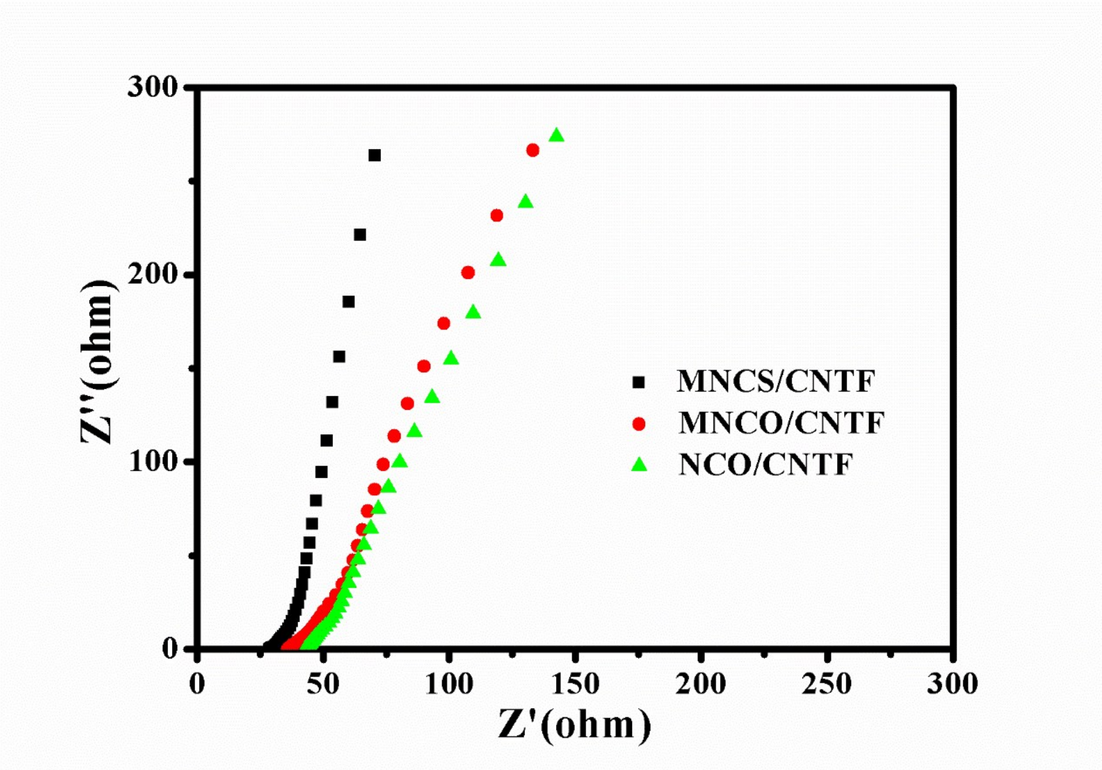

Fig. S4. EIS curves of MNCS NTA/CNTF, MNCO NWA/CNTF, and NCO/CNTF electrodes.

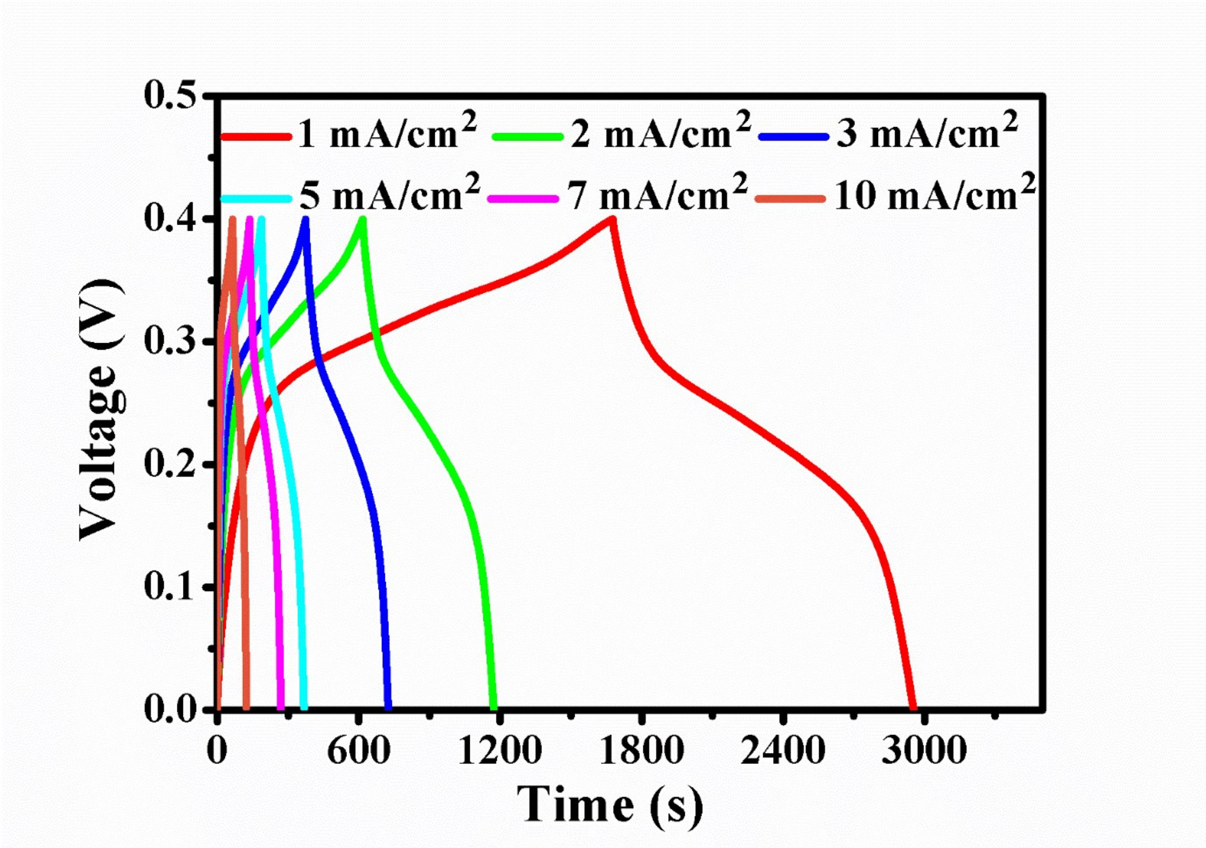

Fig. S5. GCD curves at different current densities of the MNCS NTAs/CNTF electrode measured in 1 M of KOH.

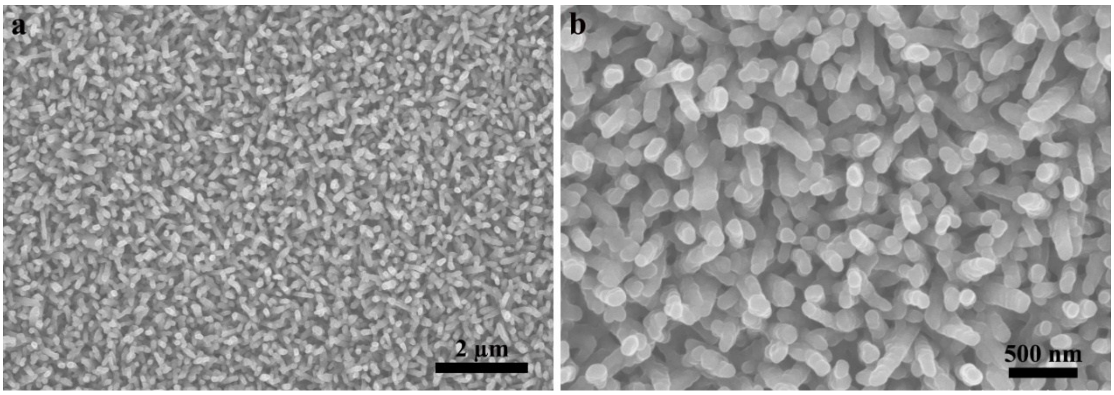

Fig. S6. (a) Low-magnification SEM image of the VN NWs. (b) High-magnification SEM image of the VN NWs.

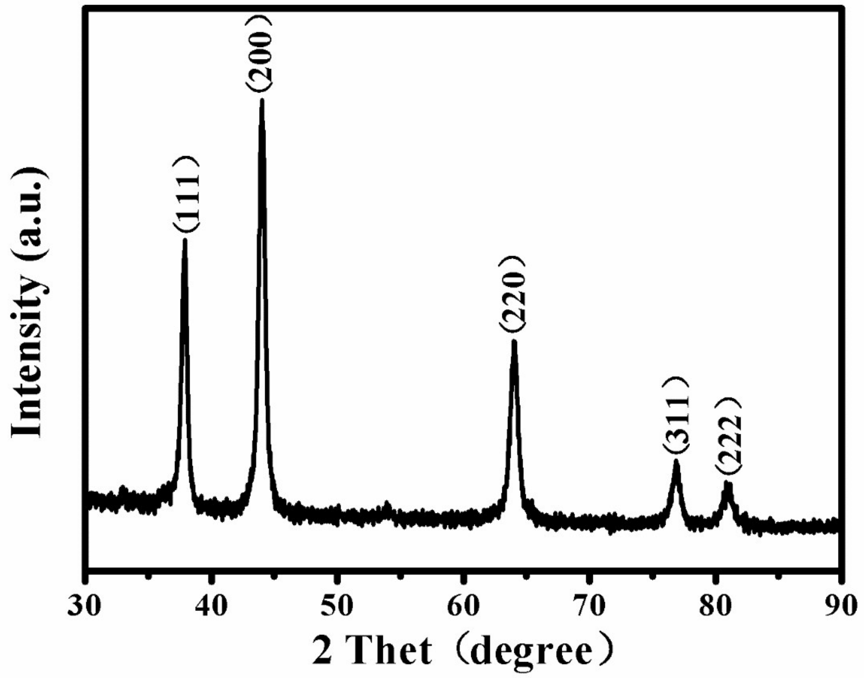

Fig. S7. XRD spectrum of the VN NWs.

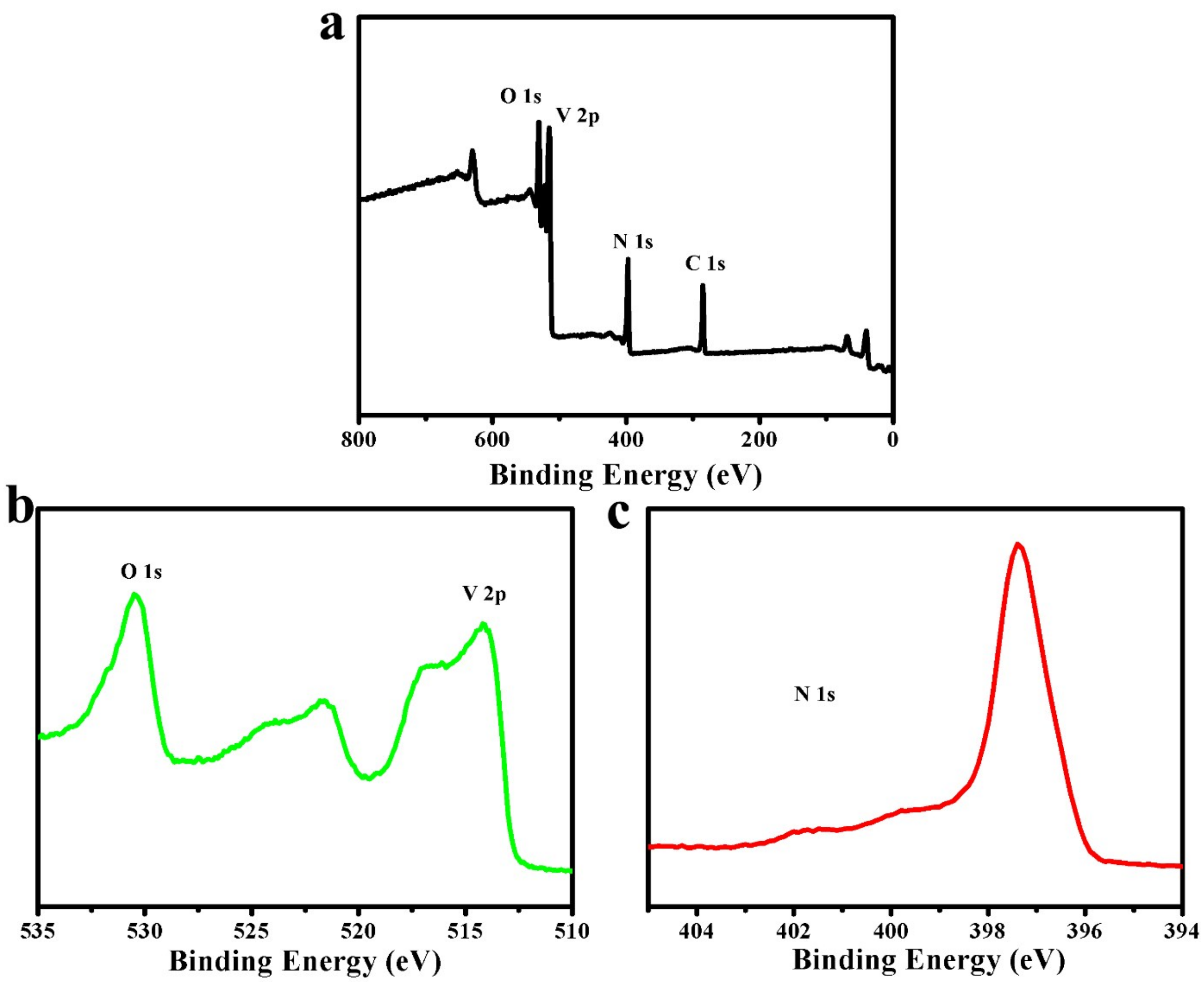

Fig. S8. (a) XPS spectrum of the as-synthesized VN NWs. (b-c) XPS survey scans of theV 2p and N 1s regions, respectively.

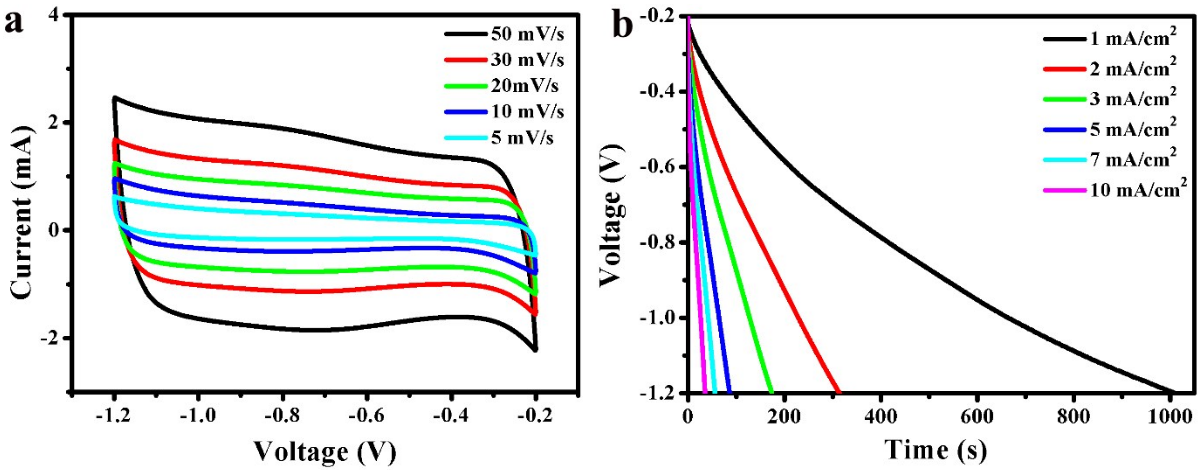

Fig. S9. (a) CV curves at different scan rates. (b) GCD curves at different current densities for the as-synthesis VN NWs.

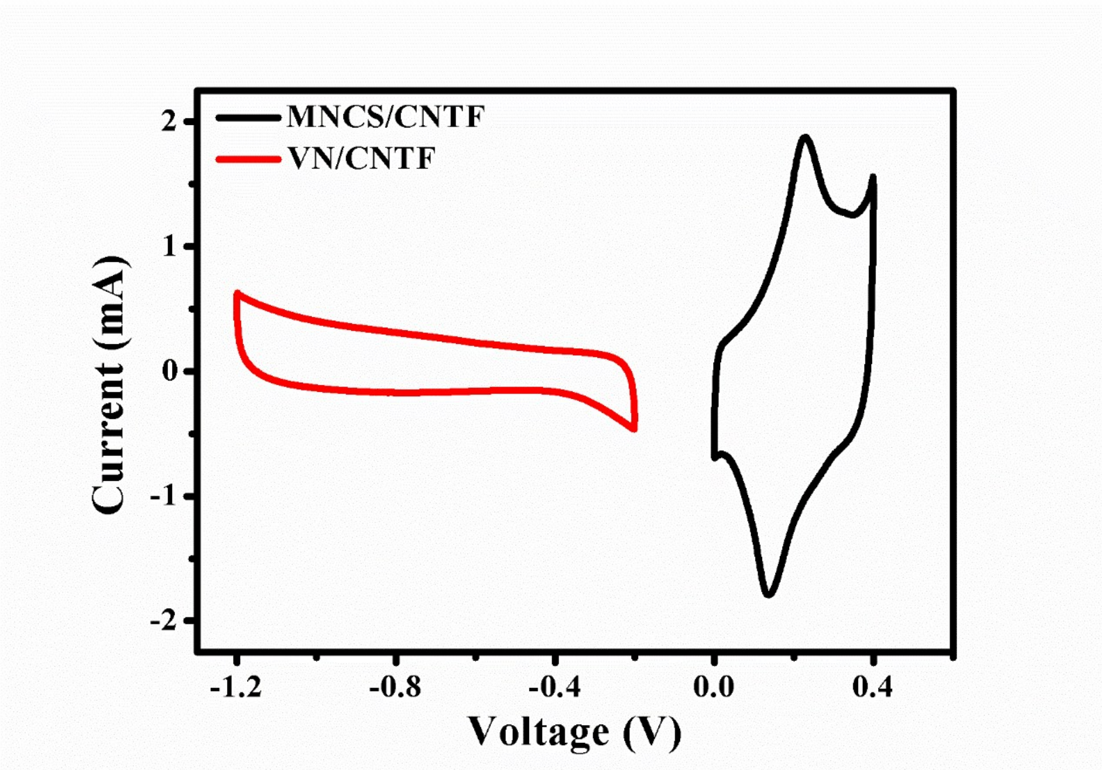

Fig. S10. Comparative CV curves obtained for the VN NWAs/CNTFs and MNCS NTAs/CNTFs in a three-electrode system.

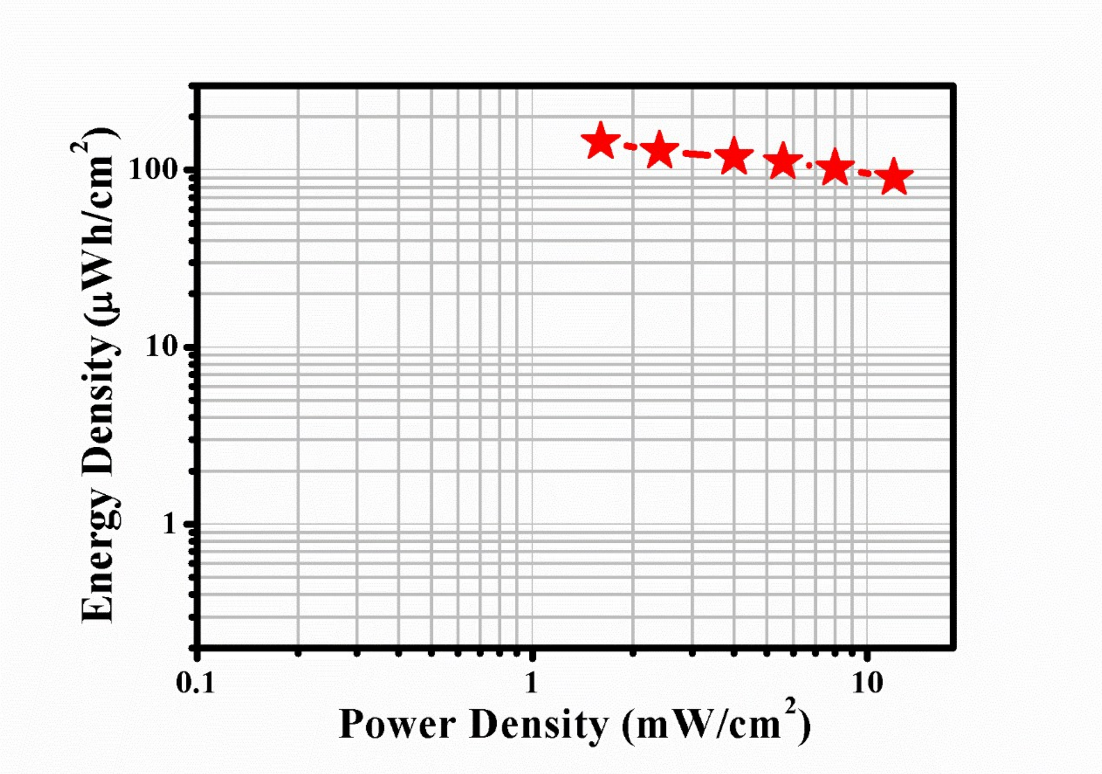

Fig. S11. Areal energy and power densities of our FASC device.

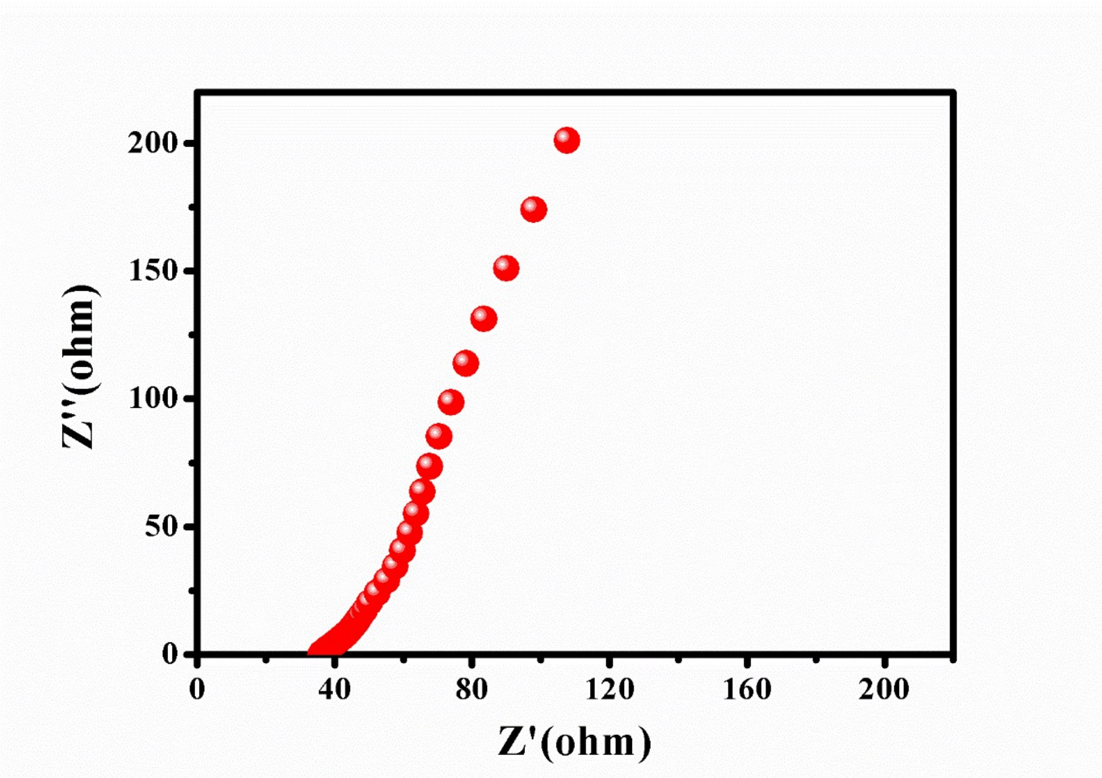

Fig. S12. Nyquist plot of the as-assembled FASC at frequencies ranging from 10^{-2} to 10^{5} Hz with a voltage amplitude of 5 mV at open-circuit potential.

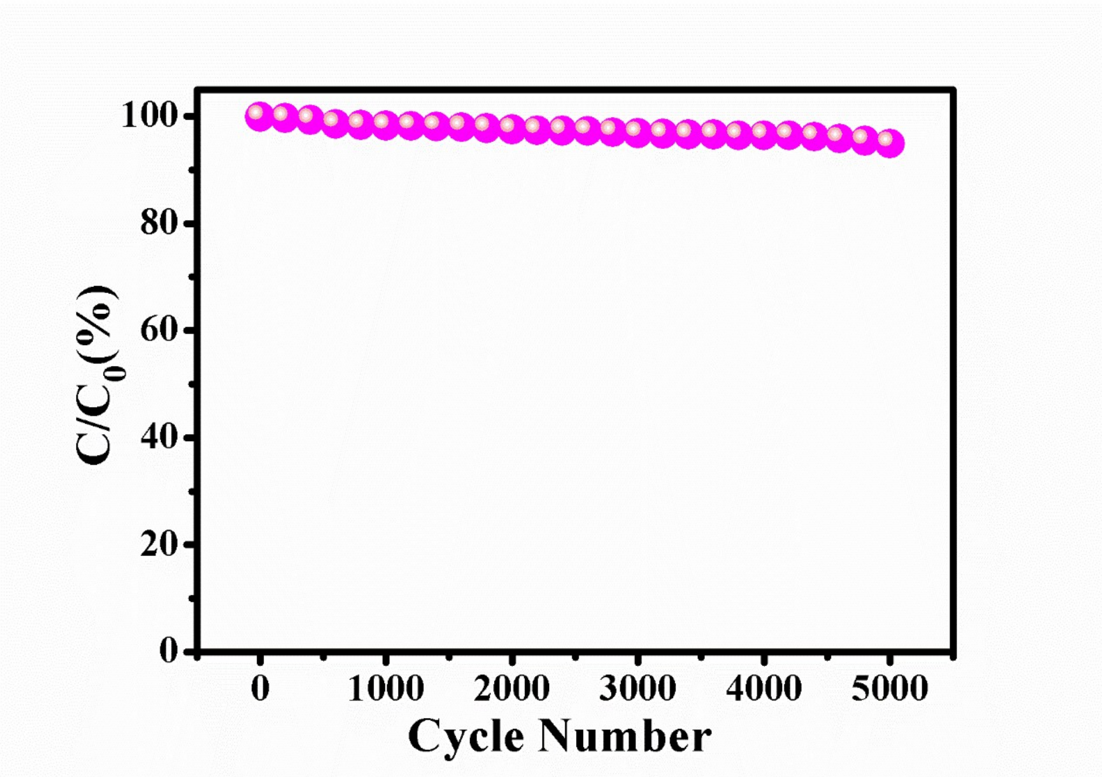

Fig. S13. Cycling performance of the as-fabricated FASC device at 5 mA cm^{-2}.