Electronic Supplementary Material (ESI) for Chemical Science.

This version of the ESI published 20/08/2020 replaces the previous version published 07/10/2015. Figure S5f is replaced with a corrected version.

Supporting Information

Asymmetric Supercapacitors with High Energy Density Based on Helical Hierarchical Porous Na_xMnO_2 and MoO_2

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Calculations:

1. **Single Electrode**:

The specific capacitance (C_{sp}, mFcm^{-2}) was calculated from the CVs and discharging curves according to the following equations:

$$C_{sp} = \frac{1}{s \times v \times \Delta V} \int I(V)dV \qquad (1)$$

$$C_{sp} = \frac{I \times \Delta t}{s \times \Delta V} \qquad (2)$$

Where I (A), ΔV(V), v(Vs^{-1}), and S(cm^2) were the current, the potential window in the CV curves, the scan rate and nominal areal, respectively.

2. ASC Devices:

The active area of electrode materials to fabricate an asymmetric device are determined taking the concept of charge neutrality into consideration, according to the following concept: Charge storage by the negative electrode = charge stored by the positive electrode.

Active area of negative electrode (S^-)×Areal capacitance (C_{sp}^-)×Voltage window (dV^-) = Active area of positive electrode (S^+)×Area capacitance (C_{sp}^+)×Voltage window (dV^+). So $S^-/S^+ = C_{sp}^+ \times dV^+/C_{sp}^- \times dV^-$. In this study S^-/S^+ is about 1.7/1.

The cell (device) capacitance (C_{cell}) and volumetric capacitance of the ASC devices were calculated from their CVs according to the following equations:

$$C_{cell} = \frac{Q}{\Delta V} \quad (3)$$

$$C_v = \frac{C_{cell}}{V} = \frac{Q}{\Delta V \times V} \quad (4)$$

Where Q (C) is the average charge during the charging and discharging process is the applied current, V is the volume (cm^3) of the whole device (The areal and thickness of our ASC devices are about 0.35 cm^2 and 0.08 cm. Hence, the whole volume of our device is about 0.03cm^3), ΔV (V) is the voltage window. It is worth mentioning that the volumetric capacitance were calculated taking into account the volume of the device stack, which includes the active material, the flexible substrate and the separator with electrolyte.

Alternatively, the cell capacitance (C_{cell}) and volumetric capacitance of the electrode (C_V) was estimated from the slope of the discharge curve using the following equations:

$$C_{cell} = \frac{I \times \Delta t}{\Delta V} \quad (5)$$

$$C_v = \frac{C_{cell}}{V} = \frac{I \times \Delta t}{\Delta V \times V} \quad (6)$$

Where I(A) is the applied current, V(cm^3) is the volumeof the whole device, Δt(s) is the discharging time, ΔV (V) is the voltage window.

Volumetric energy density(E, Wh cm^{-3}), equivalent series resistance and power density (P, Wcm^{-3}) of the devices were obtained according to the following equations:

$$E = \frac{1}{2 \times 3600} C_V \times \Delta V^2 \quad (7)$$

$$ESR = \frac{iR_{drop}}{2I} \quad (8)$$

$$P = \frac{\Delta V^2}{4 \times ESR \times V} \quad (8)$$

Where E (Whcm^{-3}) is the energy density, C_V (F cm^{-3}) is the volumetric capacitance obtained from equation (6), V (cm^3) is the volumeof the whole deviceand ΔV (V) is the voltage window. ESR (Ω) is the internal resistance of the device. P (W cm^{-3}) is the power density.

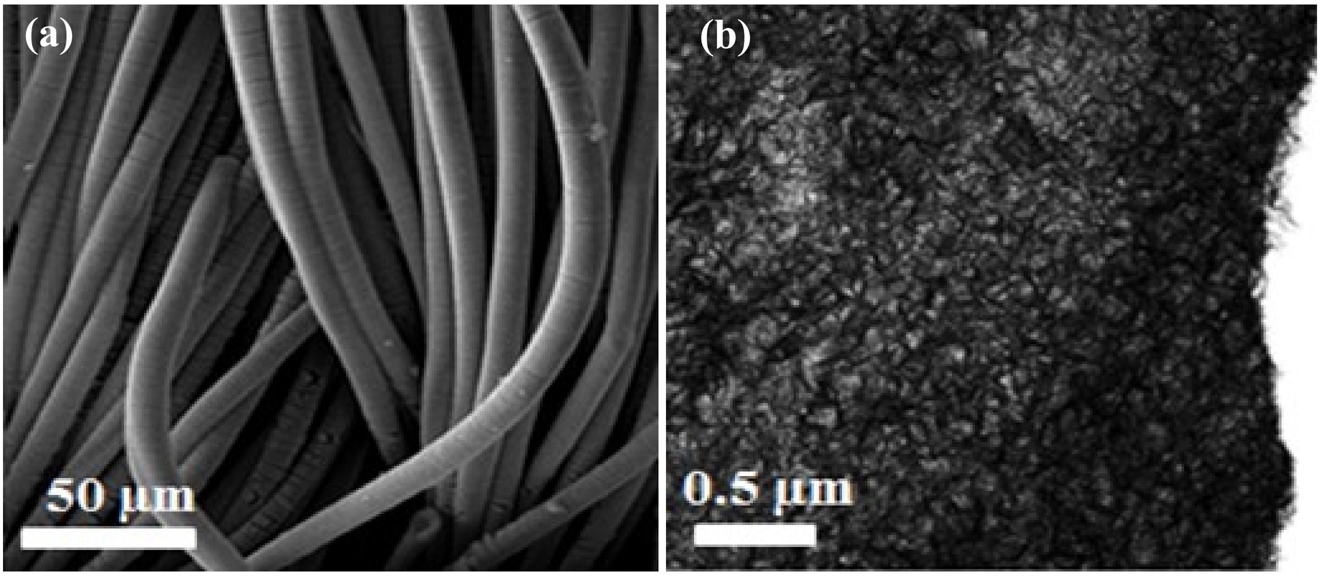

Figure S1. Low magnification (a) SEM and (b) TEM images of helical Na_xMnO_2/CC.

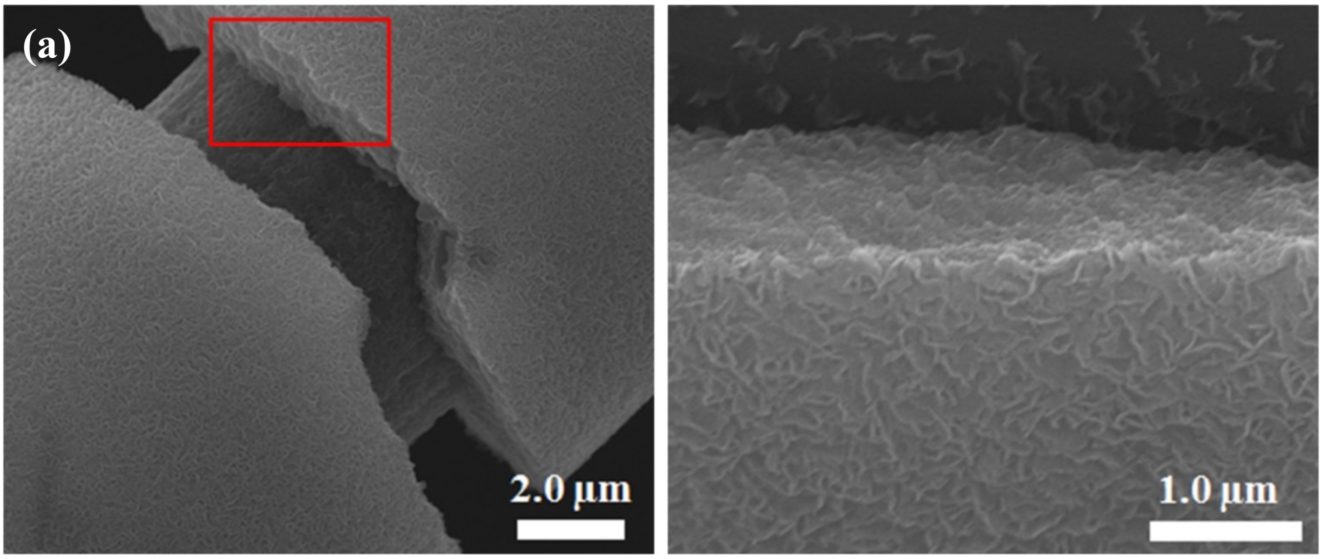

Figure S2. (a) Cross-section SEM image of helical Na_xMnO_2/CC and (b) the magnified SEM image of the red box in (a).

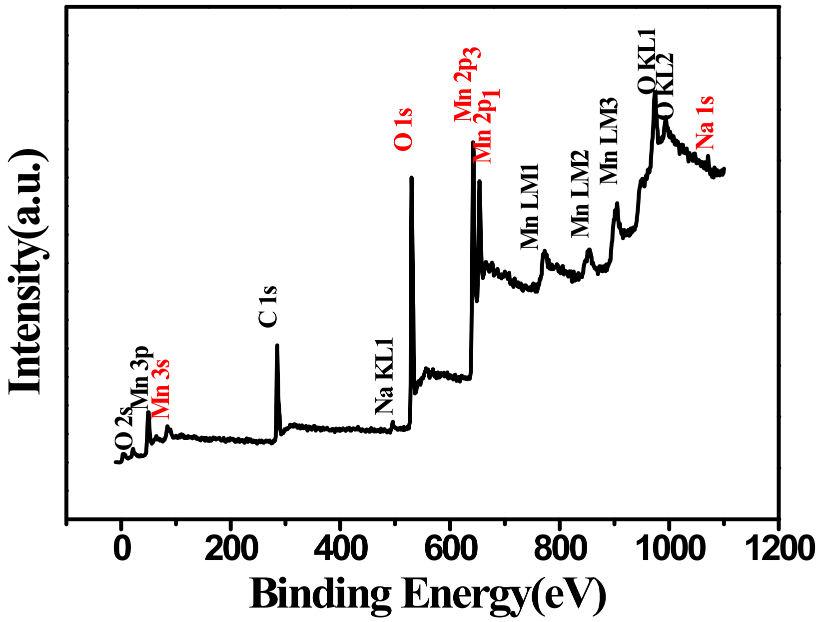

Figure S3. XPS survey spectrum of helical Na_xMnO_2/CC.

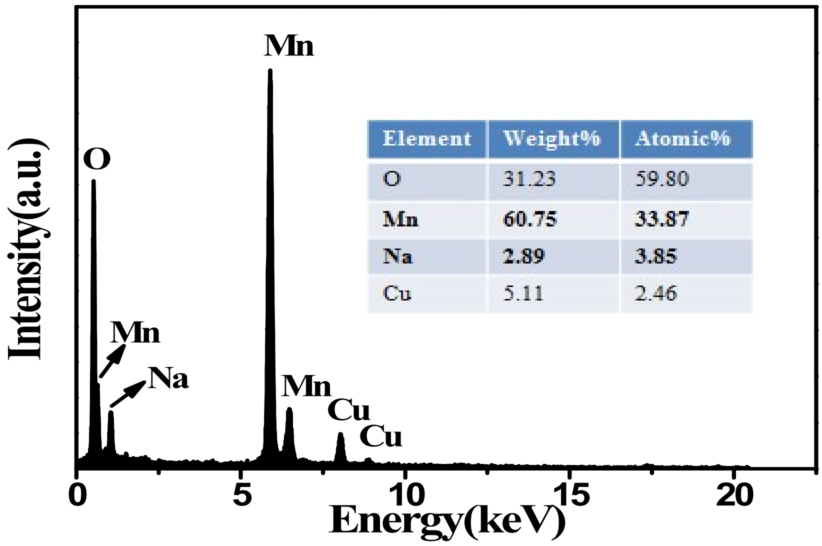

Figure S4. A typical EDX spectrum and the element compositions of helical Na_xMnO_2.

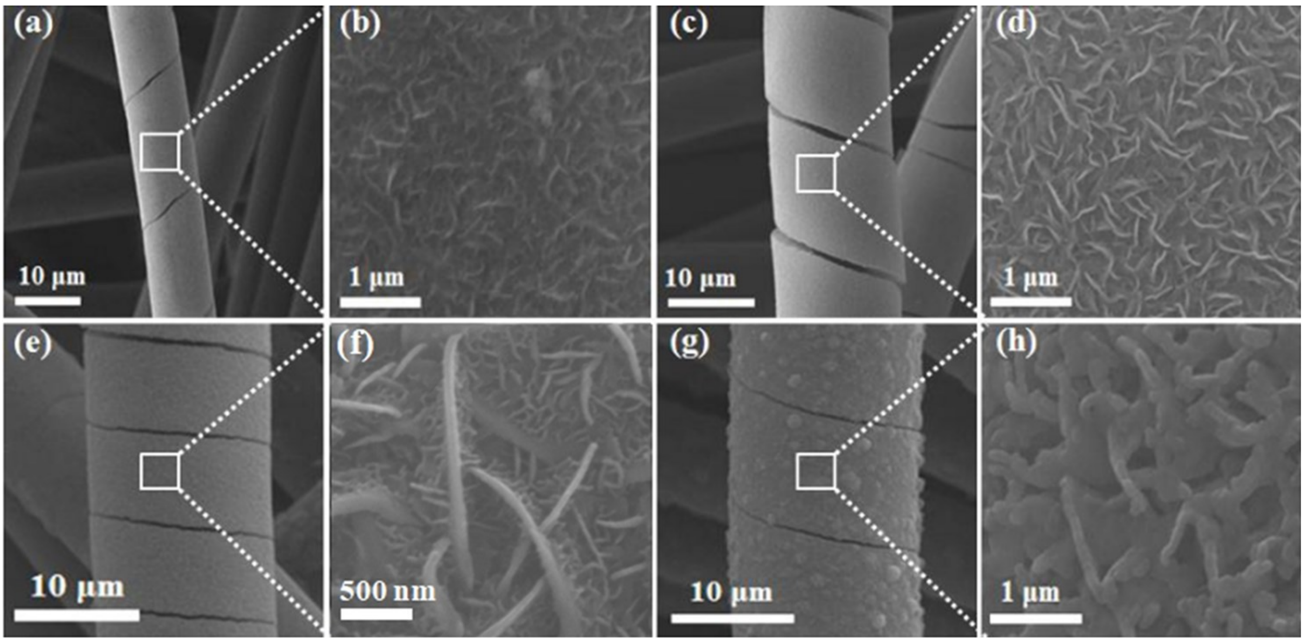

Figure S5. SEM images of helical Na_xMnO_2 with different deposition time: (a-b) 2 min, (c-d) 5 min, (e-f) 10 min, and (g-h) 15 min.

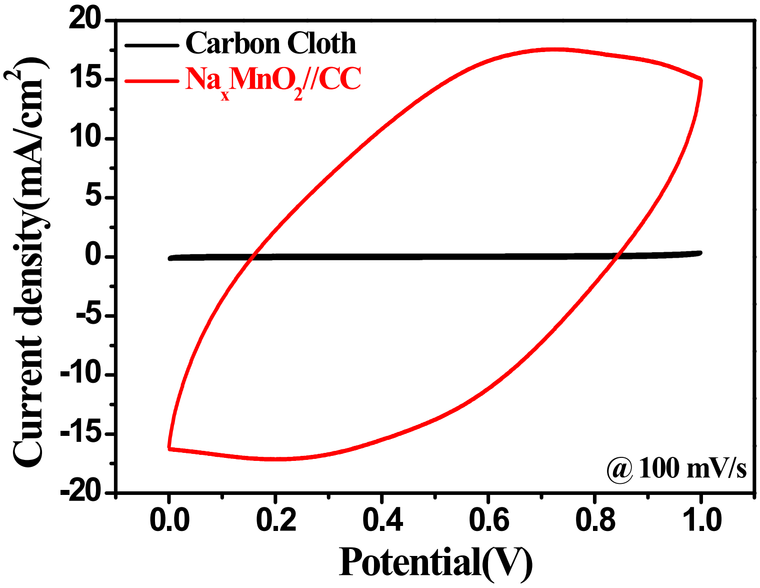

Figure S6. (a) CVs of carbon cloth (CC) and Na_xMnO_2/CC at 100 mV/s.

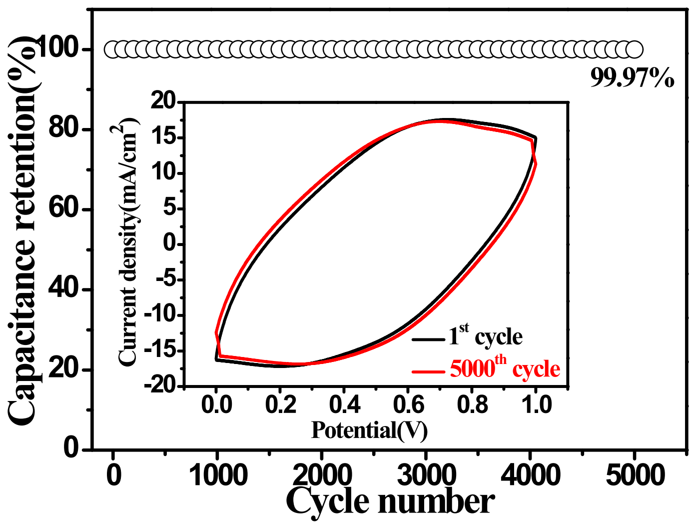

Figure S7. Cycling stability of helical Na_xMnO_2/CC collected from CVs at 100 mVs^{-1} for 5000 cycles (inset is the CVs before and after 5000 cycles).

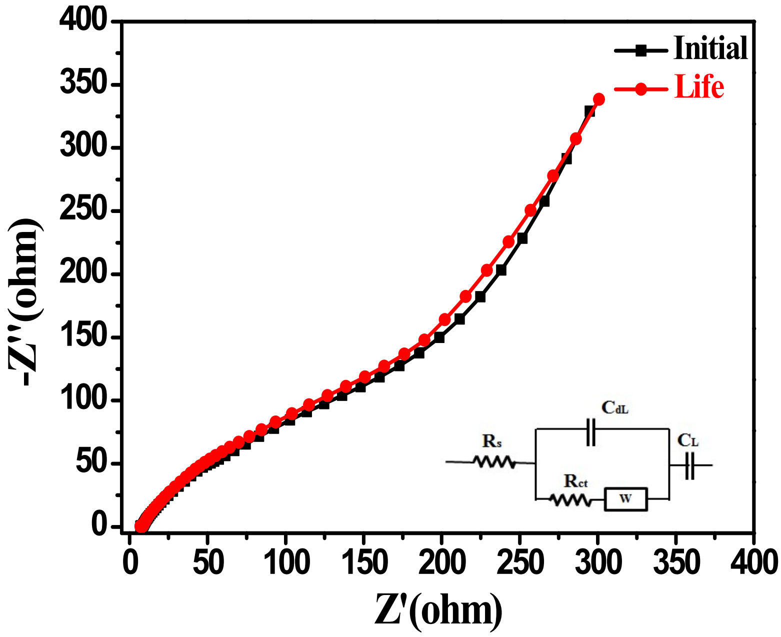

Figure S8. EIS spectrum of the Na_xMnO_2/CC before and after 5000 cycles (inset is the simulated model for Nyquist plots).

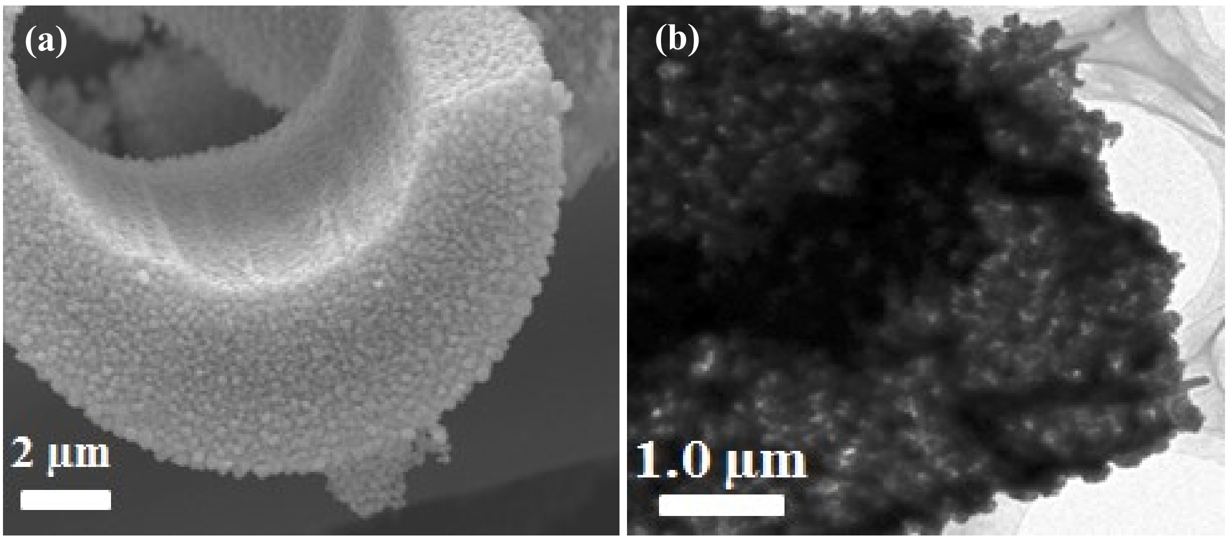

Figure S9. (a) cross-section SEM image of helical MoO_2; (b) TEM image of helical MoO_2.

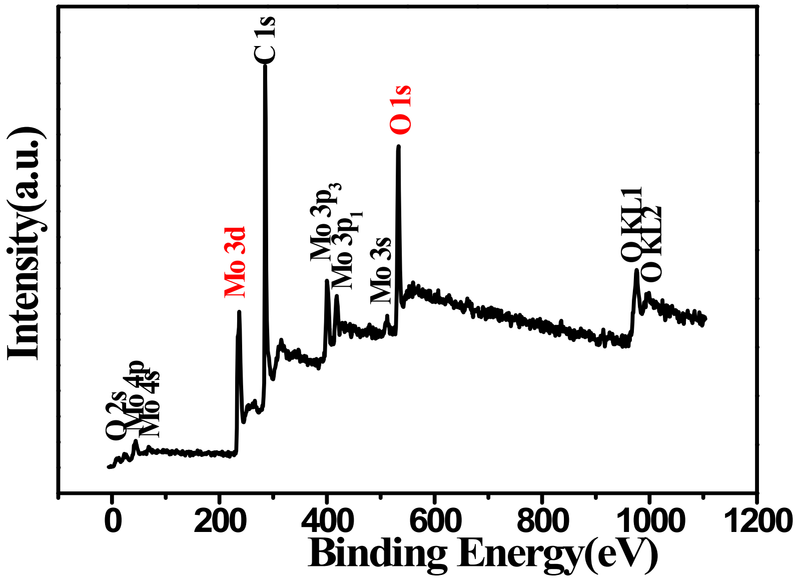

Figure S10. XPS survey spectrum of helical MoO_2/CC.

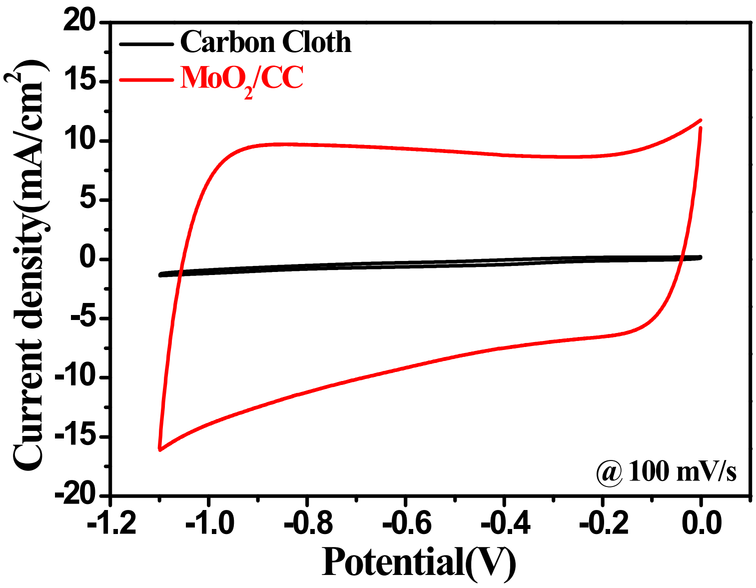

Figure S11. CVs of carbon cloth (CC) and MoO_2/CC at 100 mV/s.

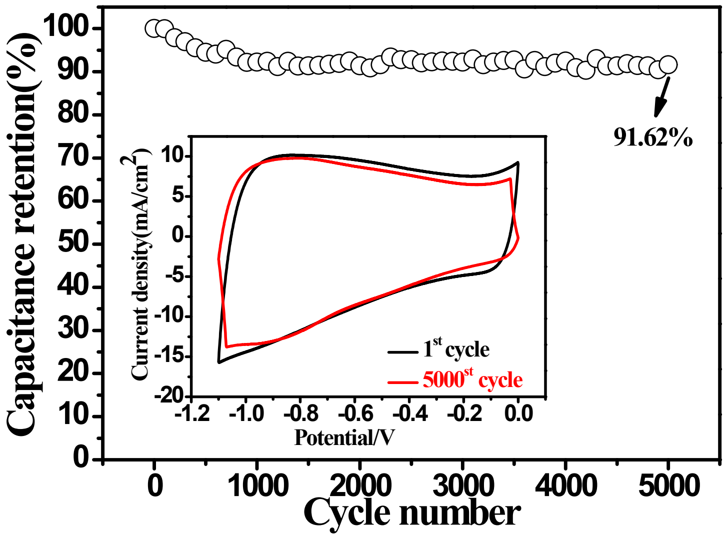

Figure S12. Cycling stability of helical MoO_2/CC collected from CVs at 100 mVs^{-1} for 5000 cycles (inset is the CVs before and after 5000 cycles).

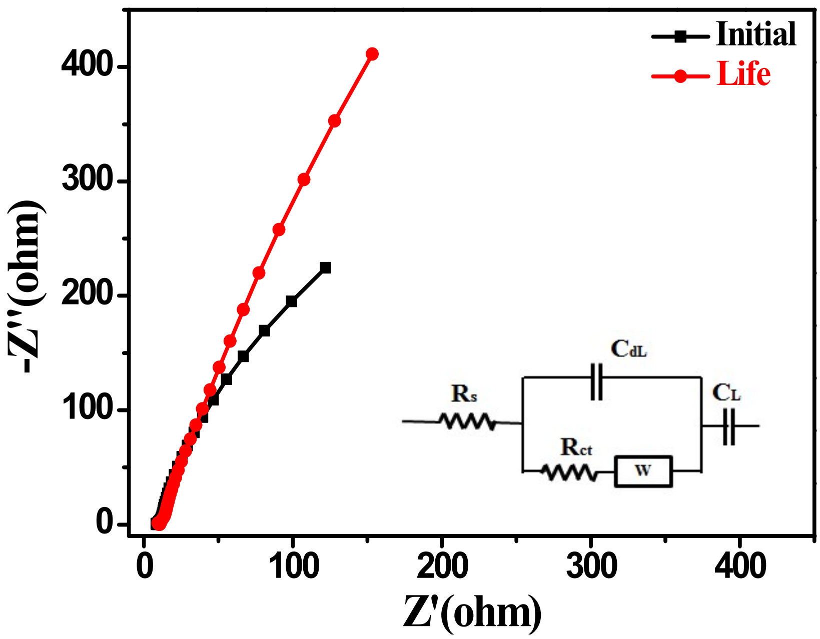

Figure S13. EIS spectrum of the helix MoO_2 before and after 5000 cycles (inset is the simulated model for Nyquist plots).

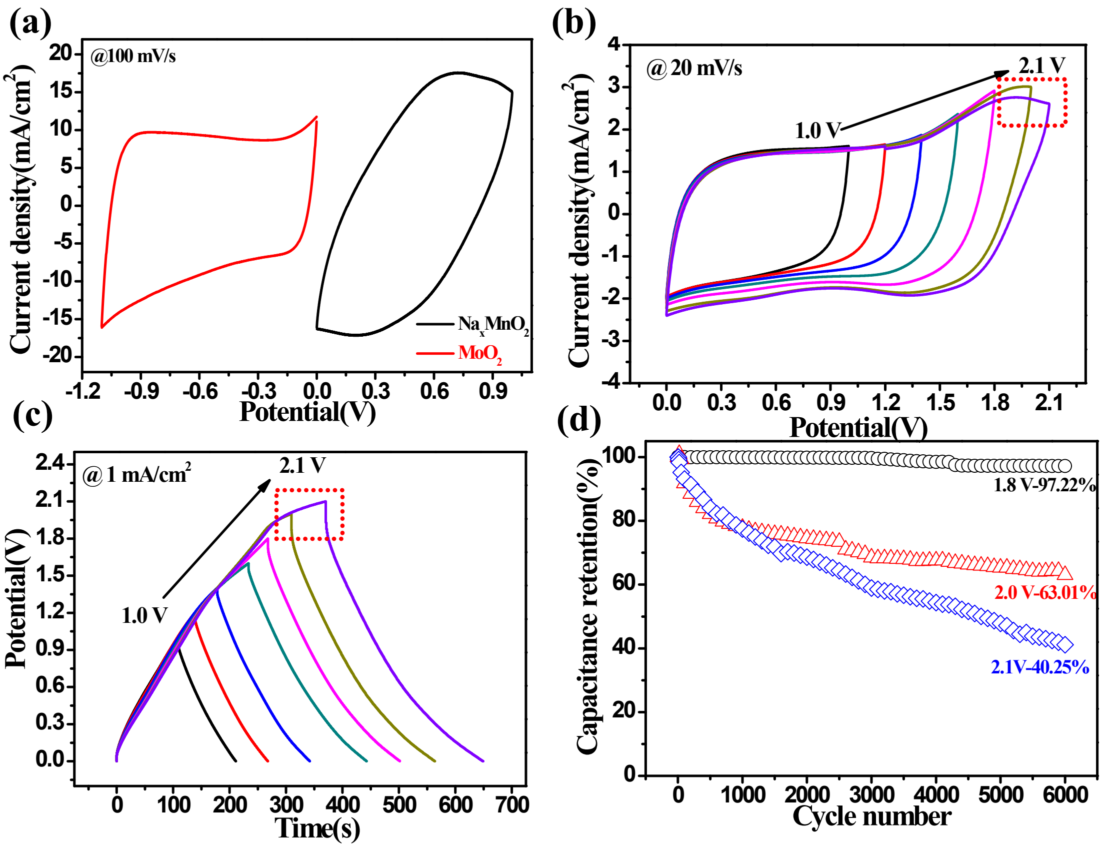

Figure S14. (a) CVs of helix Na_xMnO_2/CC and MoO_2/CC electrodes at 100 mV/s in a three-electrode system; (b) CVs of ASCs based on Na_xMnO_2/CC and MoO_2/CC electrodes with different windows at 100 mV/s; (c) GCD curves of the ASCs at 1.0 mA/cm^2 with different windows; (d) the cycling stability performance of the ASCs with a potential window of 1.8 V, 2.0 V and 2.1 V, respectively.

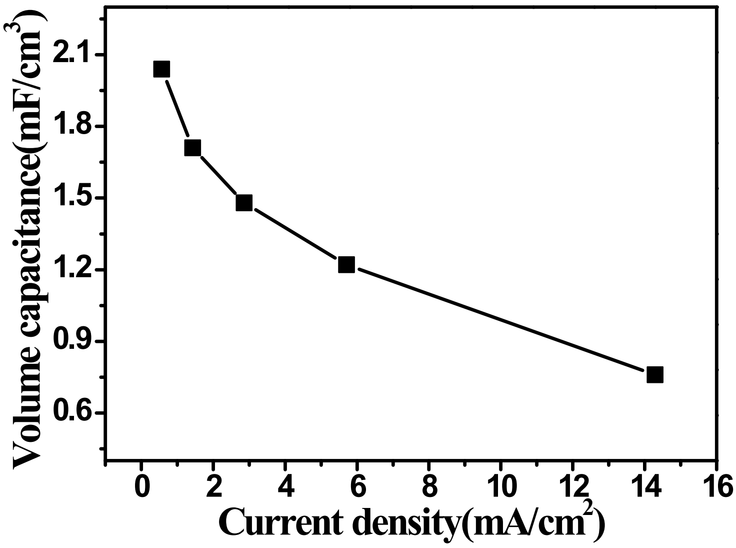

Figure S15. Volumetric capacitanceof the Na_xMnO_2/CC//MoO_2/CC ASC as a function of the current densities.

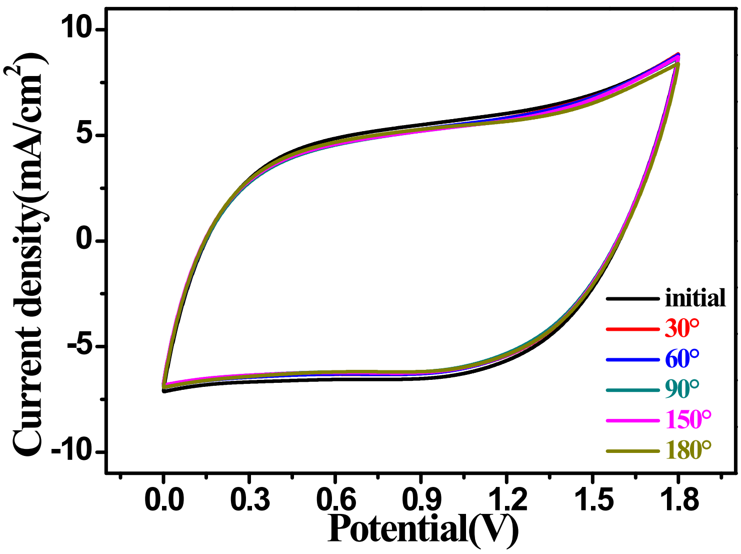

Figure S16. CVs of the Na_xMnO_2/CC//MoO_2/CC ASCs collected under different bending angles.