Supplementary Information for

Series Asymmetric Supercapacitors Based on Free-standing Inner-Connection Electrodes for High Energy Density and High Output Voltage

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Methods

All chemicals were of analytical grade and were used without further purification.

Synthesis of MnO_2 Nanowires: MnO_2 nanowires were obtained through a hydrothermal method.[1] Briefly, 0.016 mol of $MnSO_4 \cdot H_2O$, an equal amount of $(NH_4)_2S_2O_4$ and 0.03 mol $(NH_4)_2SO_4$ were put into deionized water at room temperature to form a homogeneous solution, which was then transferred into a Teflon-lined stainless steel autoclave, then sealed and put into an oven, maintained at 140 ºC for 12 h. After the reaction was completed, the resulting precipitate was filtered, washed with deionized water and dried at 80 ºC in air.

Synthesis of MoO_3 Nanowires: For synthesis MoO_3 nanowires,[2] 2.38 mmol $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ was dissolved in 20 ml diluted HNO_3 (15%) to form solution A. 9.2 mmol l-Aspartic acid was dissolved in 20 ml diluted HNO_3 (15%) to form solution B. Solution B was add into solution A with stirring for 15 min at room temperature. Then the resulting mixture was transferred to and sealed in a Teflon-lined stainless steel autoclave, heated to 240 ºC and maintained at the temperature for 24 h. After the autoclave was cooled down, the products were filtered and washed with deionized water and enthanol for several times, followed by drying at 80 ºC in air.

Preparation of Free-Standing Films: An appropriate amount of MnO_2 nanowires, CNT (Beijing Boyu Gaoke New Material Technology Co., Ltd), and SDBS (Sinopharm Chemical Reagent Co., Ltd. The mass ratio of these materials is 7:3:6) were mixed and put into 50 ml deionized water, then probe sonicated for 30 min to

form a homogeneous suspended mixture. The as-prepared solution was filtered through a membrane (450 nm pore size). The obtained filter cake of MnO_2/CNT was dried and then peeled off. Then, a free-standing film had prepared. Other free-standing films, such as MoO_3/CNT films, inner-connection films, were obtained by a similar process with the same mass ratio.

Fabrication of the ASC and Inner-Connection ASCs: The free-standing films were cut to suitable area to fabricate the devices. An organic solution (EC/DMC/$LiPF_6$) was used as the electrolyte. The free-standing films of anode, cathode and inner-connection segment were separated by a PP separator (Celgard2400, Celgard. USA.). Then they were sealed in coin cells in a glove box.

Characterization and Electrical Measurements: The morphology and structure of the samples were investigated using scanning electron microscopy (SEM, FEI Nova Nano-SEM 450), transmission electron microscopy (TEM, FEI Titan G^2 60-300) and XRD (PANalytical B. V. X'Pert PRO). Electrochemical tests were carried out using CHI660E electrochemical station (CHI Instrument) at room temperature. The EIS experiments were carried out with a frequency ranging from 0.01 Hz to 100 KHz.

Calculation

1.The areal capacitance with respect to full cell for CV measurement is calculated by the following equation:

$$C_s = \frac{S}{2 \times \Delta U \times v \times S_{total}} \quad (1)$$

where C_s is the areal capacitance of the cell, S is the mathematical area integrated by

the CV curve, ΔU is the voltage range during the CV test, v is the scan rate, and S_{total} is the total area of the electrodes. The volumetric capacitance is derived from the same formula in which S_{total} is replaced by the total volume (V_{total}) of the electrodes.

2.The areal capacitance with respect to full cell for GCD measurement is calculated by the following equation:

$$C_s = \frac{Q_e}{\Delta U \times S_{total}} \tag{2}$$

where C_s is the areal capacitance, Q_e is the charge obtained from the discharge curve of the full cell device, ΔU is the voltage range during the discharge process, S_{total} is the total area of the electrodes. The volumetric capacitance is derived from the same formula in which S_{total} is replaced by the total volume (V_{total}) of the electrodes.

3.The energy density and average power density derived from the discharge process of the device can be calculated from the following equations:

$$E = 0.5 C_s (\Delta U)^2 \tag{3}$$

$$P = 3600\, E / \Delta t \tag{4}$$

where E is the energy density, C_s is the areal capacitance which can be obtained through equation 2, ΔU is the voltage range during the discharge process, P is the average power density and Δt is the discharge time.

Supporting figures

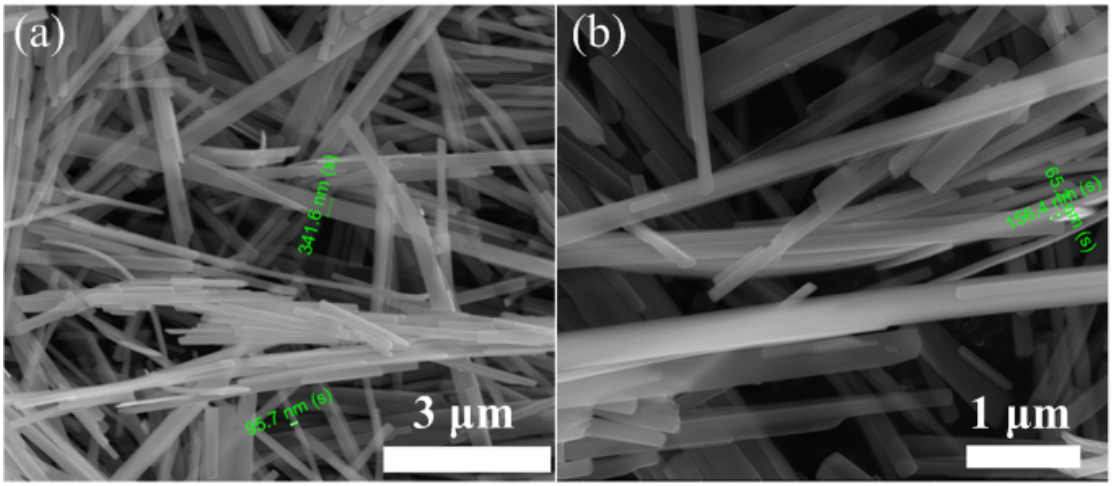


Figure S1. SEM images of MoO_3 nanobelts showed the width range (95~342 nm) and thickness (~65 nm).

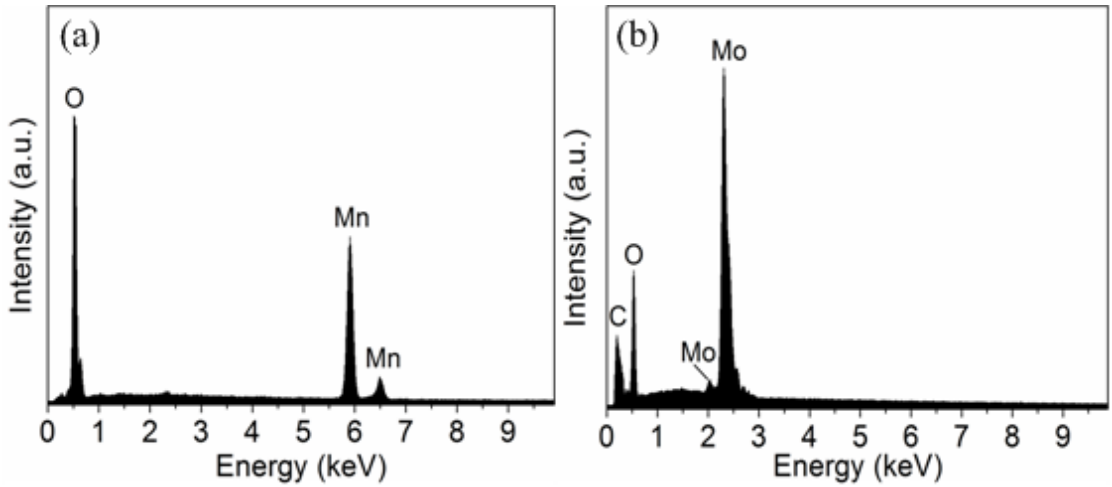


Figure S2. EDS of MnO_2 nanowires and MoO_3 nanobelts. The C signal in (b) is from the conductive tape. The results revealed the containing chemical elements of the as-prepared nano materials.

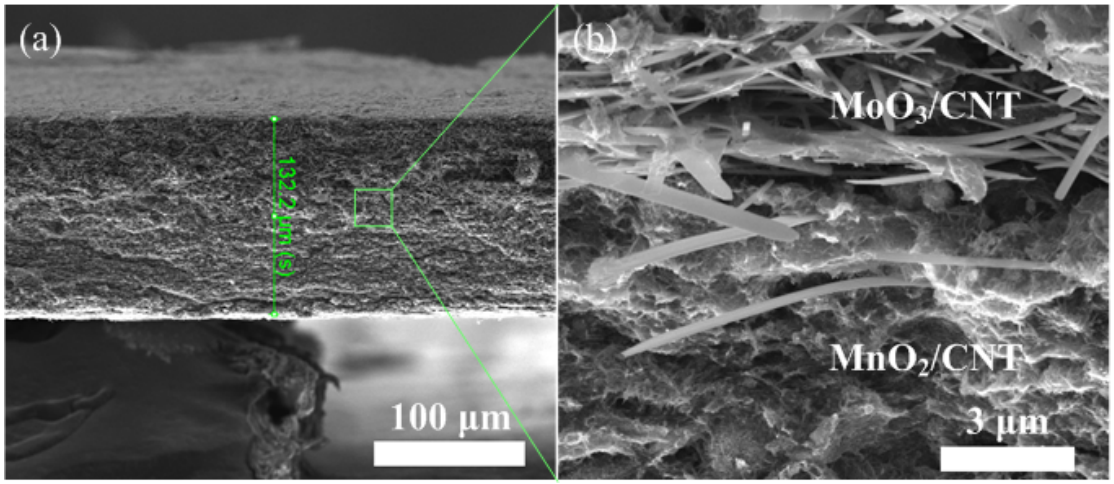


Figure S3. Side views of the middle layer with inner-connection structure: (a) the thickness of the middle layer is about 132.2 μm (the mass density is about 16 mg cm^{-2}). (b) the interface between MnO_2/CNT composite and MoO_3/CNT composite. ~~showed the thickness (~132.2 nm) and the interface of MnO_2/CNT composite and MoO_3/CNT composite, respectively.~~

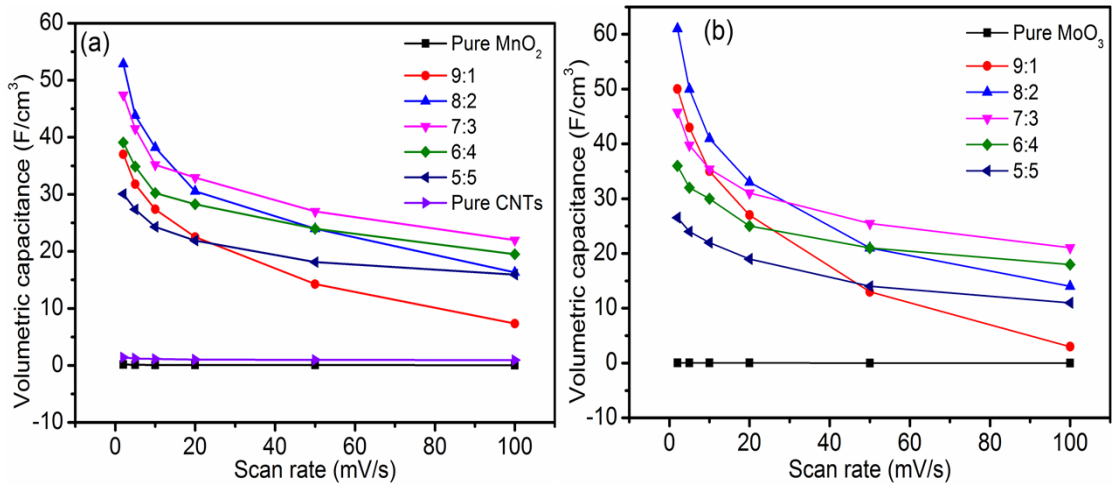


Figure S4. The optimization process of the electrodes: (a) Volumetric capacitance of SCs fabricated by symmetric electrodes with different mass ratio (MnO_2 : CNT); (b) Volumetric capacitance of SCs fabricated by symmetric electrodes with different mass ratio (MoO_3 : CNT). Considering both the volumetric capacitance and its decrement under higher scan rate, we accept the mass ratio of 7:3 for our devices.

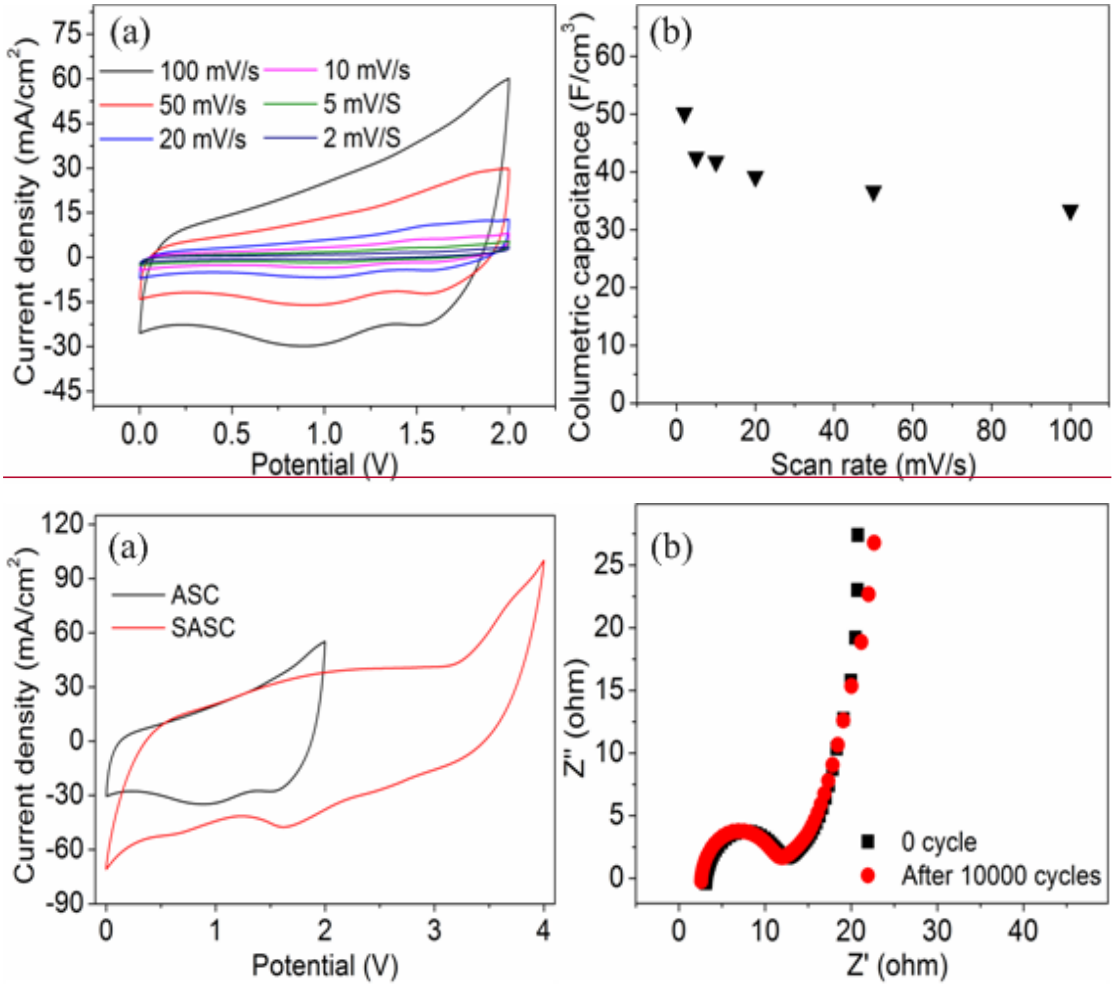


Figure ~~S4~~S5. (a) CV curves of the optimized ASC and SASC at the same scan rate of 100 mV s^{-1} within different potential windows~~CV curves of the ASC based on MnO2/CNT and MoO3/CNT composite electrodes~~; (b) ~~Volumetric capacitances of the ASC at different scan rates~~ Nyquist plots of the SASC before and after 10000 cycles.

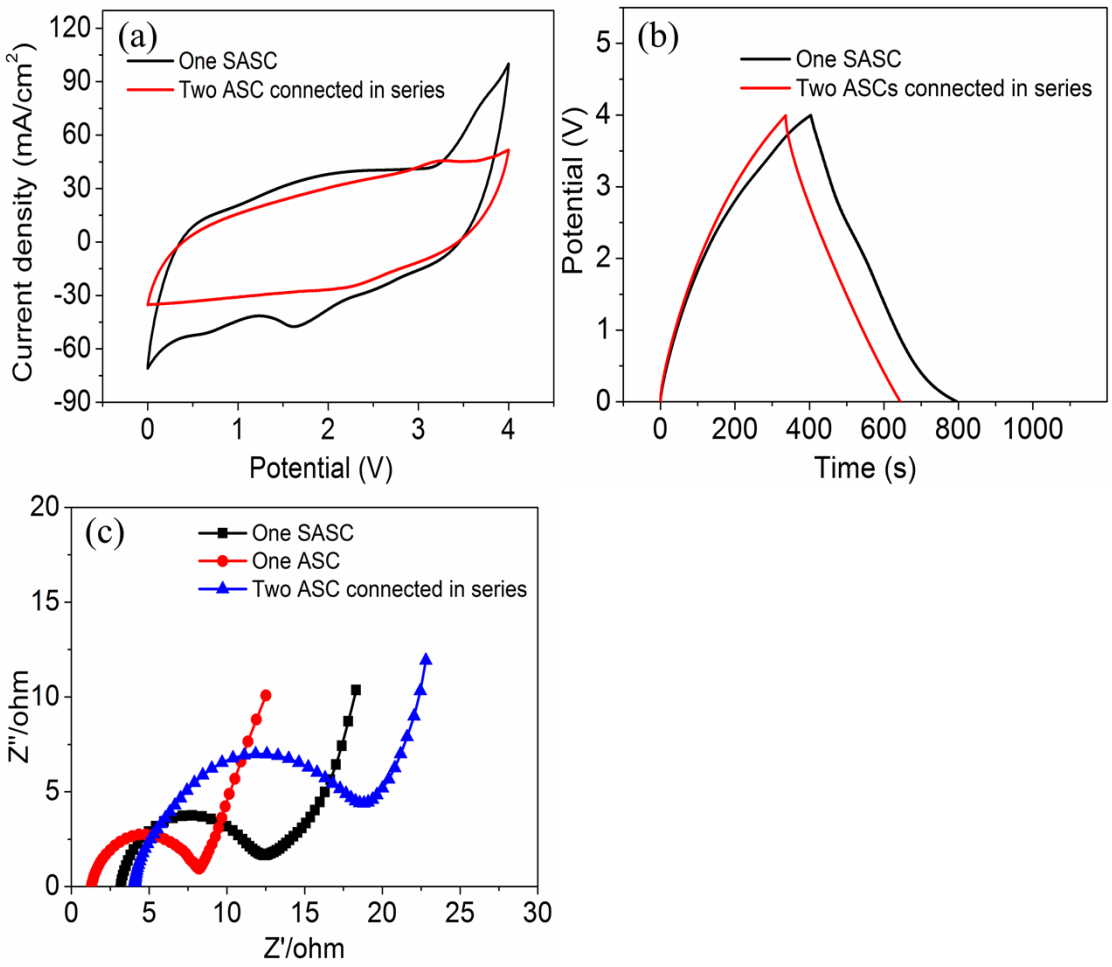
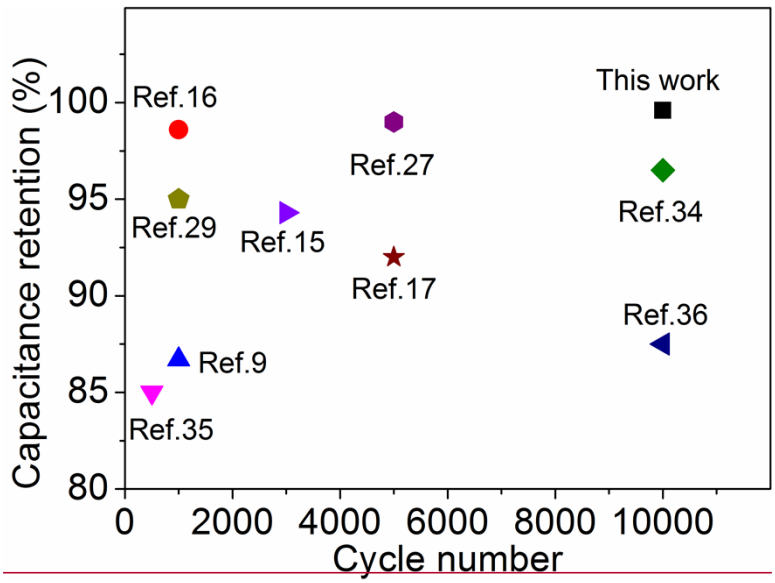


Figure S6. The comparison of electrochemical performance of different devices: (a) CV curves of a SASC and a series-wound ASC (two ASCs connected in series) at the same scan rate of 100 mV/s. (b) GCD curves of a SASC and a series-wound ASC at the same current density of 3.5 mA/cm^2. According (a) and (b), the volumetric capacitance ratios of a SASC and a series-wound ASC are of 1.33 and 1.27, respectively. (c) EIS of a ASC, a series-wound ASC and a SASC. The combined resistance (R_S, including intrinsic resistance of electrode materials, ionic resistance of electrolyte and contact resistance between electrode and current collector, is decided by the x-intercept on real axis) and the the charge transfer resistance (R_{CT}, decided by the diameter of semicircle) of the SASC is lower than that of a series-wound ASC.



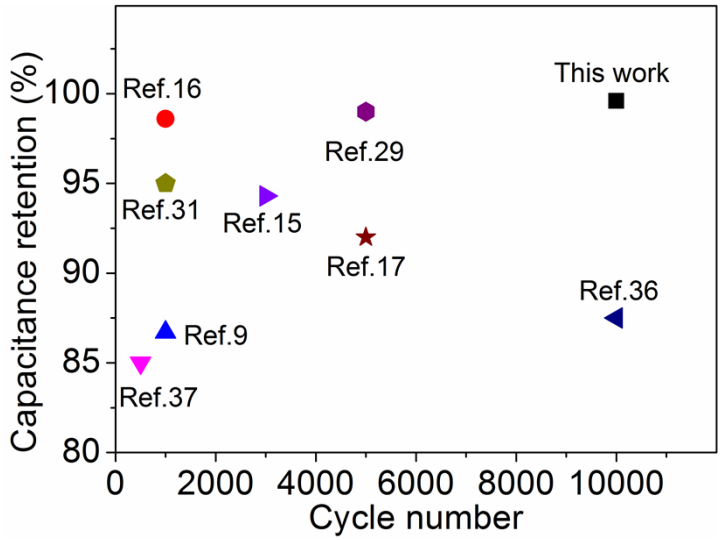


Figure S~~5~~7. Long-term cycling performance of the as-fabricated SASC and some other previous reports.

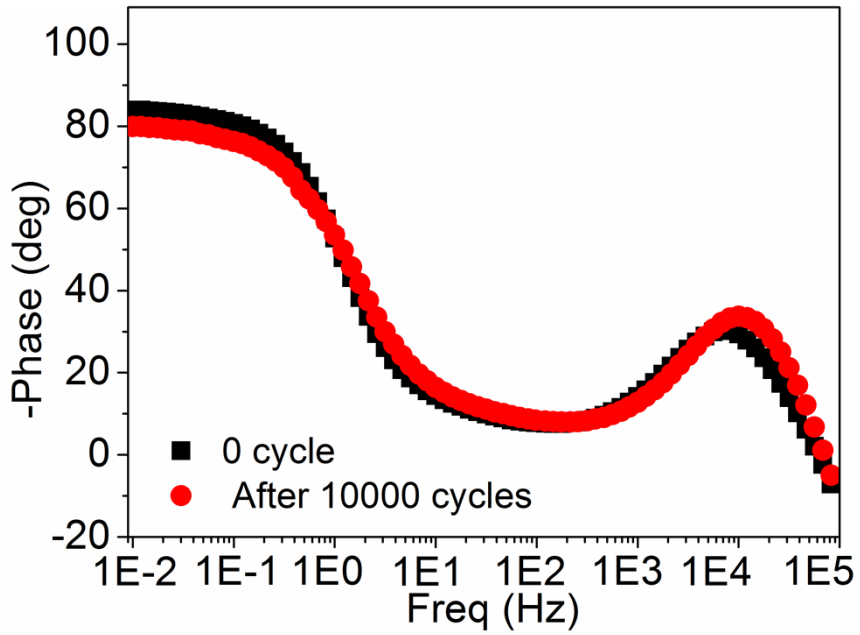


Figure S~~6~~8. Phase angle for the SASC measured before and after 10000 cycles in frequency range of 100 kHz to 0.01 Hz, respectively. The almost overlapped curves and ~ -80º of the phase angle indicated the good stability and excellent capacitor performance of the device.

References

1. X. Wang and Y. D. Li, *J. A.C.S.*, 2002, 124, 2880-2881.
2. R. L. Liang, H. Q. Cao and D. Qian, *Chem. Commun.*, 2011, 47, 10305-10307.