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Supporting information for

Freestanding CNT-WO3 Hybrid Electrodes for Flexible Asymmetric Supercapacitors

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Experimental section

Preparation of the freestanding CNTs electrode and CNT-WO_3 electrode

Freestanding CNT film was fabricated *via* a vacuum filtration method. 0.050 g CNTs and 0.2 g sodium dodecylbenzenesulfonate were dissolved into 150 mL deionized (DI) water and ultrasonicated for 20 min, forming a CNTs ink.[1] Then the as-prepared solution vacuum filtered through a filter membrane (220 nm pore size) with DI water washed can be transferred to a freestanding film on the membrane, which then be dried and peeled off to gain the freestanding CNTs electrode. The CNT films were then vacuum evaporated using WO_3 particle powder (Aladdin, 50 nm, 15m^2 g^{-1}, 99.9%) in a physical vapor deposition system (Baoke, Shenyang) in which the working conditions were a pressure of 3.5×10^{-4} Pa in the chamber and a definite current of 100 amperes for 30min.[2]

Fabrication of the all-solid-state CNTs// CNT-WO_3 ASC device

The ASC device was assembled by CNT film as the positive electrode and CNT-WO_3 hybrid film as the negative electrode using H_2SO_4/PVA gel as a solid state electrolyte and separator (NKK TF40, 40 μm thickness, low ESR type, purchased from SCM industrial Chemical CO., LTD). The H_2SO_4/PVA gel electrolyte was prepared by mixing 6 g concentrated H_2SO_4 and 6 g PVA powder in 60 mL deionized water and being heated at 85 °C under a constant stir for 2 h. CNTs, CNT-WO_3 electrodes and the separator were dipped in the electrolyte for 5 min each and then fabricated into the ASC device. Finally the device should be retained at a room temperature to evaporate excess water overnight (about 12 h).

Characterization:

The structural properties of electrode materials were characterized by field-emission scanning electron microscopy (SEM, ZEISS ULTRA 55), transmission electron microscopy (TEM, JEOL 2100F, 200 kV) equipped with an energy dispersive X-ray spectrometer (EDS), X-ray diffraction (XRD, Rigaku, MiniFlex600, Cu Kα) and X-ray Photoelectron Spectroscope (XPS, Ulvac-Phi, PHI X-tool). Electrochemical measurements were employed using a CHI660E electrochemical workstation and a VersaSTAT 3-400 (Princeton Applied Research) . The cycle life was measured through a battery test system (Neware BTS). For a single electrode test, a piece of electrode (effective area 1 cm × 1 cm, *ca.* 1 cm^2) was dipped into the 1 M H_2SO_4 solution as a working electrode at room temperature. Ag/AgCl reference electrode and graphite rod counter electrode were used in the measurement.

Calculation methods

ASC device

The volumetric capacitance C_v was calculated from the CV curves through the following equation:

$$C_v = \frac{\int IdU}{2vVU_w} = \frac{S}{2vVU_w}$$

where v is the scan rate, V the volume of the whole device, S the area of the closed CV curve and U_w is the voltage window.

And the energy density and the average power density can be gained by employing the following equation:

$$E = \frac{C_v {U_w}^2}{2}$$

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

$$t = \frac{U_w}{v}$$

in which C_v is the volumetric capacitance calculated before.[3]

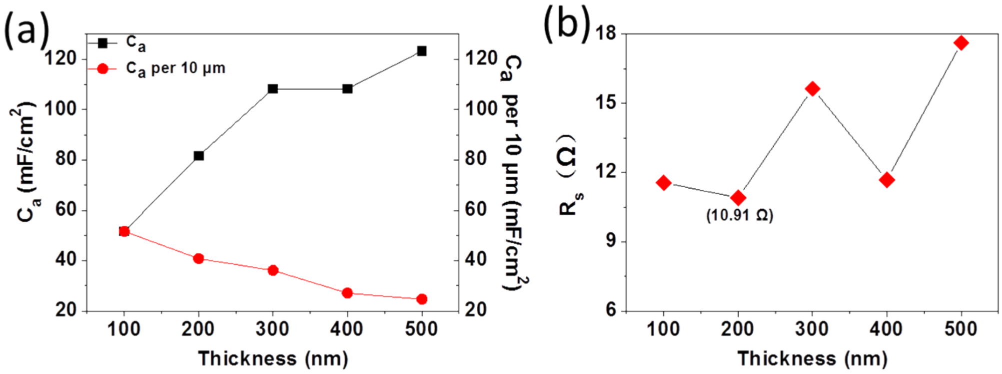

Fig.S1 (a) Areal capacitances (C_a) and Ca contribution per 10 μm of CNT-WO_3 electrodes with different thickness of WO_3 calculated from the corresponding CV curves at a scan rate of 50 mV/s. (b) Equivalent resistances (R_s) calculated from IR drops from the Galvanostatic charge-discharge curves of different WO_3 thickness at a current density of 5 mA/cm^2.

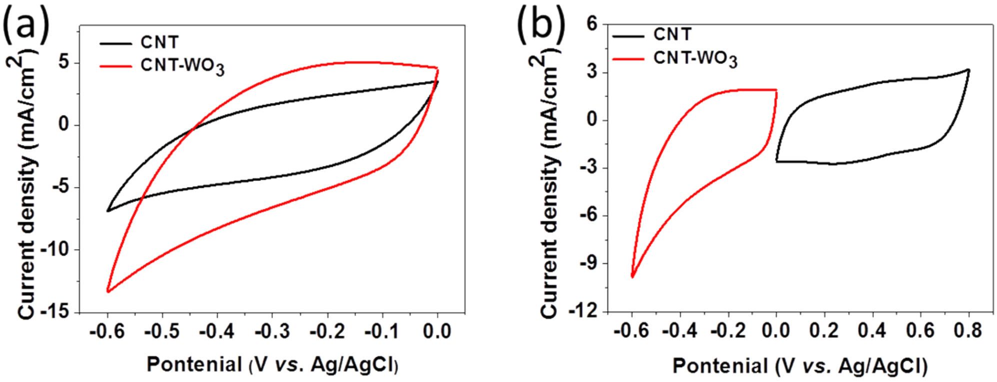

Fig.S2 CV curves of the (a) CNT-WO_3 electrode compared with the pure CNT electrode under a potential windows between -0.6 V to 0 V at a scan rate of 100 mV/s and (b) positive and negative electrodes at a scan rate of 100 mV/s, representing a proper capacitance ratio for asymmetric supercapacitor.

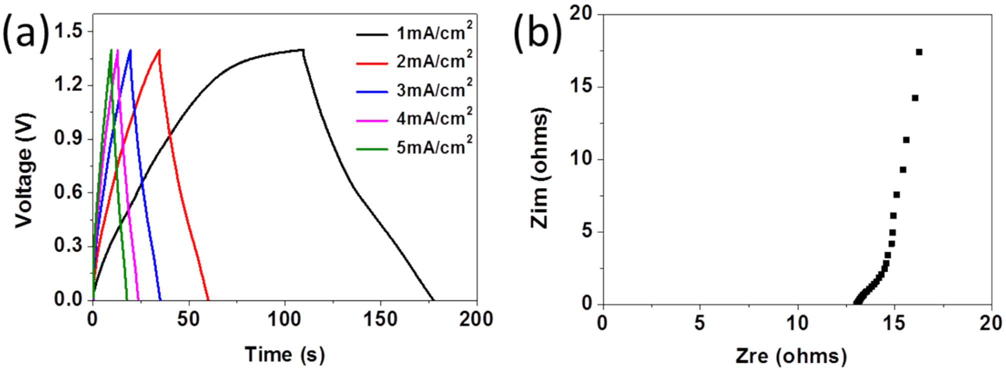

Fig.S3 (a) Galvanostatic charge-discharge curves of the ASC device collected at different current density. (b) Nyquist plots of the solid-state ASC device.

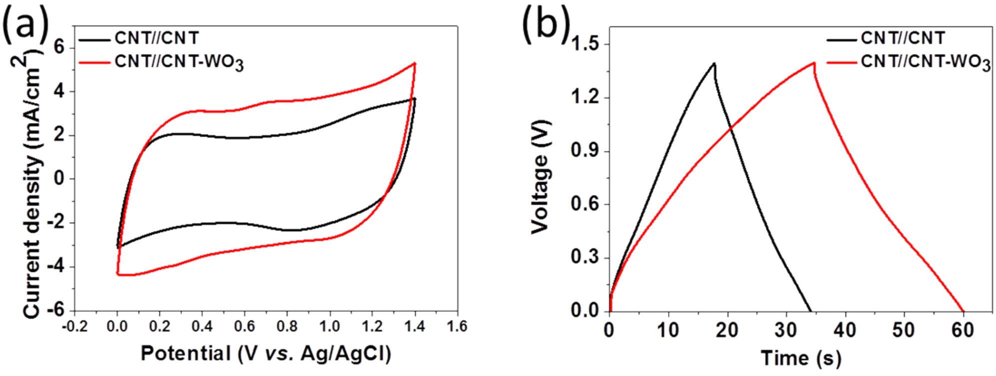

Fig.S4 Comparison of (a) CV curves at a scan rate of 100 mV/s and (b) Galvanostatic charge-discharge curves at current density of 1mA/cm^2 collected from the CNT//CNT-WO_3 ACS device and the CNT//CNT SC device.

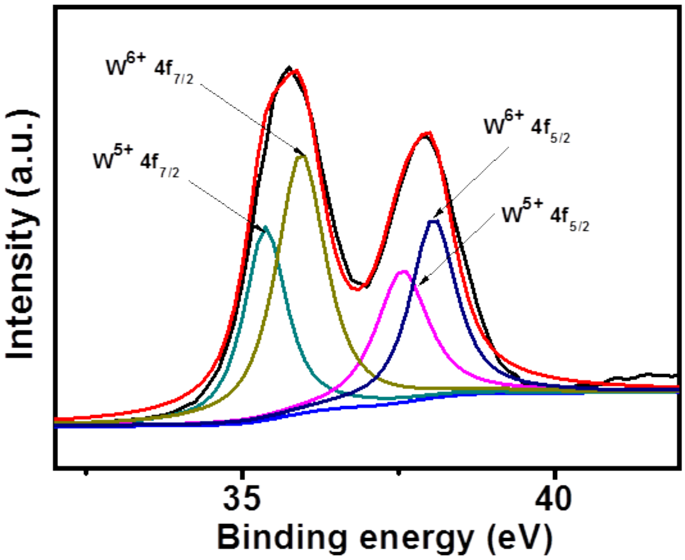

Fig.S5 XPS patterns of the CNT-WO_3 films.

Notes and references

1. L. Du, P. Yang, X. Yu, P. Liu, J. Song and W. Mai, *J. Mater. Chem. A*, 2014, **2**, 17561-17567.

2. P. Yang, P. Sun, Z. Chai, L. Huang, X. Cai, S. Tan, J. Song and W. Mai, *Angew Chem Int Ed Engl*, 2014, **53**, 11935-11939.

3. P. Yang and W. Mai, *Nano Energy*, 2014, **8**, 274-290.