# Fabrication of three-dimensional $WO_3$ nanotube bundles on carbon cloth as binder-free electrode for high-performance supercapacitor

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**Experimental Section**

All chemicals were analytical grade and were used as received without further purification. Prior to the synthesis, a piece of carbon cloth with a size of 5 cm × 4 cm was cleaned with a 3 M HCl solution, ethanol and deionized water for 30 minutes, respectively. Typically, $Na_2WO_4$ (0.34 g) and $NaHSO_3$ (0.2 g) were dissolved in the mixture solution of deionized water (30 mL) and $H_2O_2$ (5 mL) under vigorous magnetic stirring. The above solution and the pretreated carbon cloth were then transferred into a 50 mL Teflon lined stainless autoclave and maintained at 180 ℃ for 24 h. After cooling to room temperature, the carbon cloth coated with $WO_3$ was taken out and washed with ethanol and deionized water several times, and dried. The loading weight on the carbon cloth was about 2.8 mg $cm^{-2}$. Furthermore, the $WO_3$ powders also were synthesized without carbon cloth at the same experimental condition.

**Materials Characterizations**

The energy dispersive X-ray (EDX) mapping and morphologies were investigated by field emission scanning electron microscopy (FESEM, ZEISS-Merlin) and transmission electron microscopy (TEM, JEOL, JEM-2100F). X-ray diffraction (XRD) measurements were characterized on a Bruker D8 advance setup. X-ray photoelectron spectroscopy (XPS) measurements were tested on a Perkin-Elmer Model PHI 5600 XPS system with a resolution of 0.3–0.5 eV from a monochromatic aluminum anode X-ray source. Raman spectroscopy (Jobin Yvon, T64000 spectrometer with a 514.5 nm argon ion laser) was used to characterize the products.

**Electrochemical Measurement**

Electrochemical measurements were carried out in a standard three-electrode system with an electrochemical workstation CHI 660e in 0.5 M $H_2SO_4$ solution at room temperature. A saturated calomel electrode (SCE), graphite rod, and the as-prepared samples were served as reference electrode, counter electrode, and working electrode, respectively. The cyclic voltammetry (CV) curves were conducted between 0.1 and -0.7 V. The galvanostatic charge-discharge (GCD) curves were measured at different current densities (0.5-10 A $g^{-1}$). Electrochemical impedance spectroscopy (EIS) was carried out at open circuit potential in the frequencies from 0.01 Hz to 100 kHz and the amplitude of the potential perturbation was 5 mV. The specific capacitance ($C_{sp}$) of electrodes was calculated from charge–discharge curves using the following equation: $C_{sp} = (I \times \Delta t)/(m \times \Delta V)$, where I is the discharge current, m is the mass of the electroactive material in the electrode, $\Delta V$ is the potential window, and $\Delta t$ is the discharge time. During the galvanostatic charge/discharge of supercapacitors, the energy density (E) and power density (P) were calculated by the following equations: $E = C_{sp} \times \Delta V^2/7.2$ (Wh $Kg^{-1}$), $P = E \times 3600/\Delta t$ (W $Kg^{-1}$). For comparison, 80 mg of $WO_3$ nanotube bundles was weighed by an electronic balance. Subsequently, the active material, polyvinylidene fluoride, and carbon black (8:1:1 weight ratio) were mixed in isopropyl alcohol to form homogeneous slurry. Then the slurry was painted onto CC (denoted as WNB). Finally, the electrode was dried in air at 80 ℃ for 12 h. Electrode area was 1.0 $cm^2$, and the mass of active material was about 2.8 mg.

Two pieces of $WO_3$ nanotube bundles electrode (area of 0.64 $cm^2$) were put into a button cell, with a separator between them (NKK, TF4840) and 0.5 M $H_2SO_4$ aqueous solution as the electrolyte. After that, the unsealed button cell was transferred to a hydraulic crimping machine and sustained under a pressure of 9 MPa for 15 s, ensuring its good encapsulation.

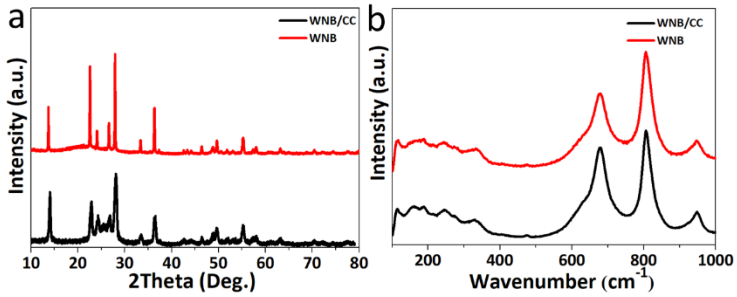


**Fig. S1** The images of XRD and Raman for WNB and WNB/CC.

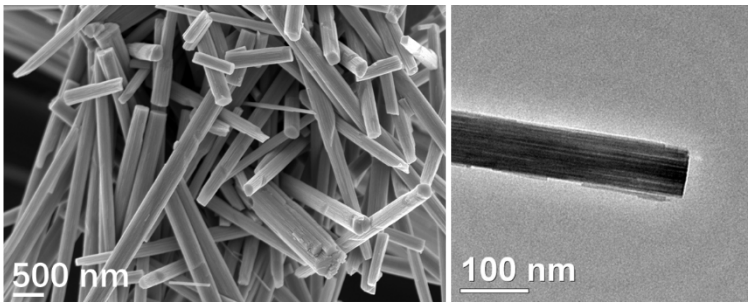


**Fig. S2** FESEM and TEM images of WNB.

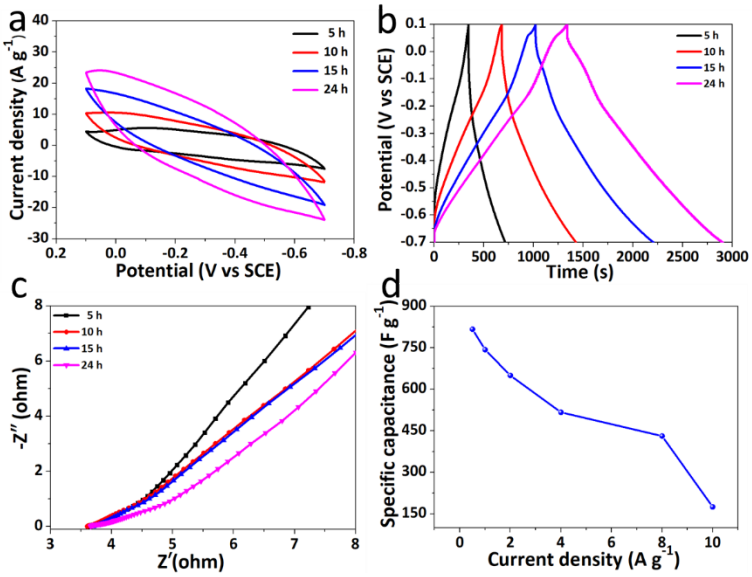


**Fig. S3** (a-c) Comparison of CV, GCD, and EIS curves for the as-synthesized $WO_3$ sample with different time at the same test condition. (d) Specific capacitance of the WNB/CC products at different current densities.

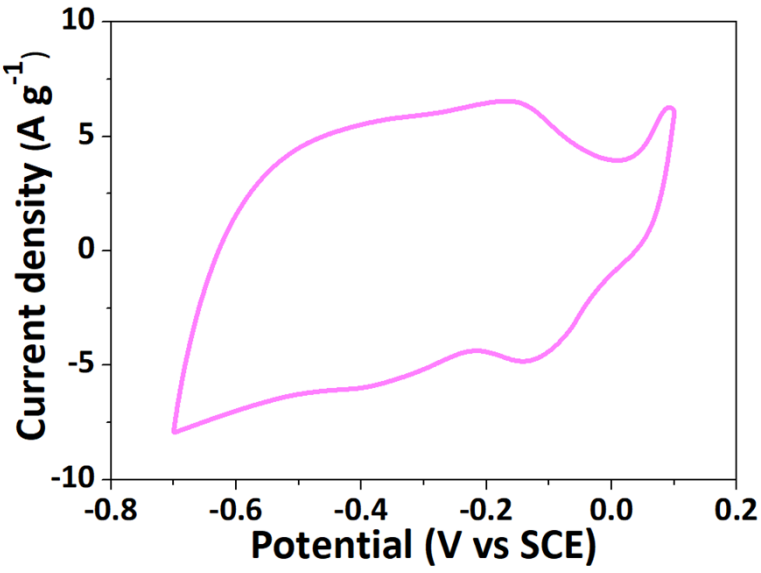

**Fig. S4** CV curve of WNB/CC electrodes at 2mV $s^{-1}$.
**Fig. S5** CV curves of CC, WNB and WNB/CC electrodes at 20 mV $s^{-1}$.
**Fig. S6** Cycling performance of WNB/CC electrode.

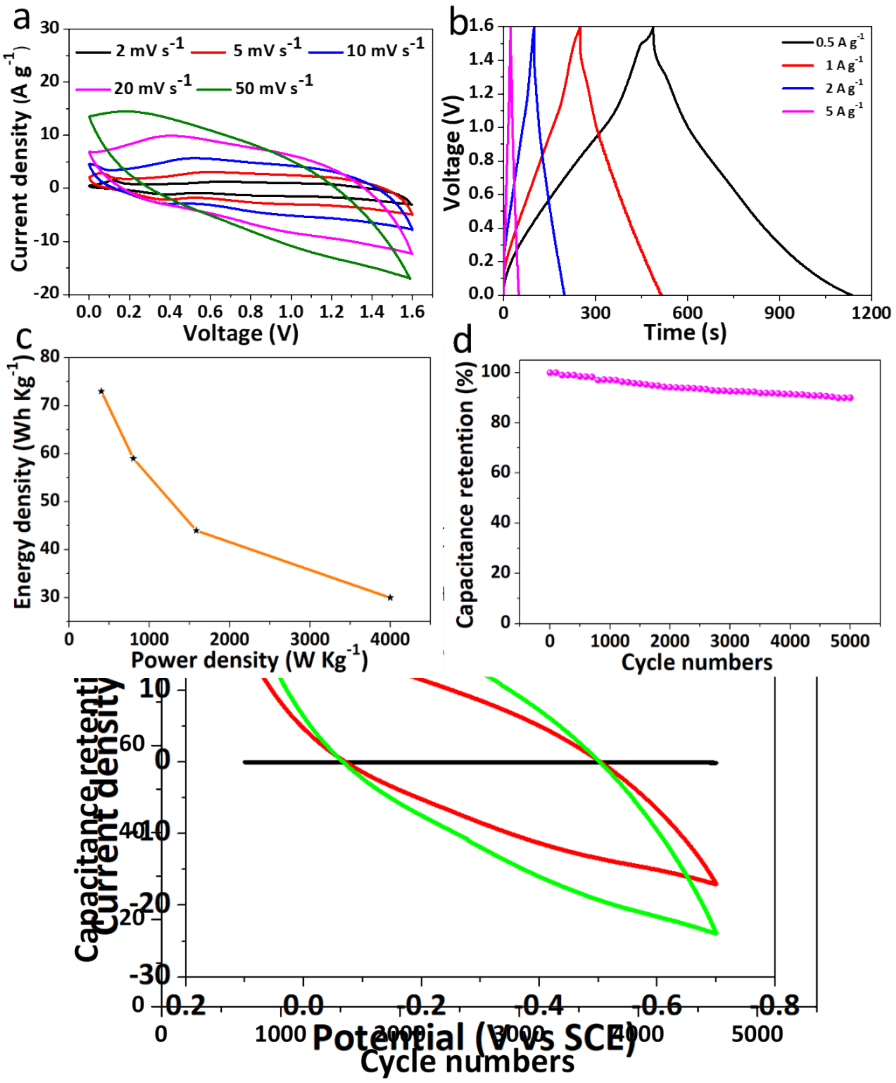


**Fig. S7** (a) CV curves of symmetric supercapacitors device at different scan rates. (b) GCD curves of the symmetric supercapacitors device at different current densities. (c) Ragone plot of the symmetric supercapacitors device. (d) Cycling performance of the symmetric supercapacitors device.