Supporting Information

Carbon-Encapsulated Tungsten Oxide Nanowires as Stable and High-Rate Anode for Flexible Asymmetric Supercapacitors

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Experimental Section

***Preparation of carbon encapsulated WO_{3-x} (C@WO_{3-x}) nanowires*:** All reagents used were of analytical grade and were used directly without any purification. Verical WO3 nanowires were directly prepared on carbon cloth by a seed-assisted hydrothermal method. Carbon cloth (2 cm × 3 cm) was firstly cleaned with ethanol and distilled water, followed by being immerged in a solution of containing 0.695 g $Na_2WO_4 \cdot 2H_2O$, 10 mL 3 M HCl and 2 mL H_2O_2 (30vol% aqueous solution) for 10 min. Then, the carbon cloth was annealed on a hotplate in air at 300 ^oC for 10 min to form WO_3 seed on the carbon cloth. Subsequently, 1.33 g H_2WO_4 and 0.028 g CH_3COONH_4 were dissolved in a mixed solution of 26 mL distilled water and 6 mL H_2O_2 (30vol% aqueous solution), and stirred into a pellucid solution. 20 mL of this clear solution mixture together with the carbon cloth coated with WO_3 seed was transferred to a Teflon-lined stainless steel autoclave (25 mL volume). The sealed autoclave was heated in an electric oven at 180 ^oC for 12 h, and then allows it cool down slowly at room temperature. After thoroughly

washed with DI water and dried, uniforma WO_3 film was obtained on the surface of carbon cloth. Finally, C@WO_{3-x} nanowires were obtained by a glucose-assisted hydrothermal method in a 0.1 M glucose solution at 180 ^oC for 6 h and then was annealed at 800 ^oC in N_2 for 1 h. To prepare pristine WO_3 nanowires, the as-prepared WO_3 nanowires were also was

***Preparation of TiN/MnO_2 electrode*:** TiN nanowires were firstly prepared on carbon cloth according to the previous literature. [1] Then, amorphous MnO_2 layer was electrodeposited onto the surface of the TiN nanowires by using a CHI 760D workstation. The electrodeposition was performed in an electrolyte containing a containing 0.1 M manganese acetate and 0.1 M sodium sulphate at 0.8 V for 60s at room temperature.

***Fabrication of flexible solid-state asymmetric Supercapacitors (ASCs)*:** The solid-state TiN/MnO_2//C@WO_{3-x}-ASCs were fabricated by separating TiN/MnO_2 and C@WO_{3-x} electrodes with a NKK separator (Nippon Kodoshi Corporation) and polyvinyl alcohol (PVA)/LiCl gel as the electrolyte. To optimize the charge between the electrodes, the area ratio of TiN/MnO_2 electrode to C@WO_{3-x} electrode was calculated to be about 1.03:1. The PVA/LiCl gel was prepared via a solution-casting method. Typically, 2.00 g PVA and 4.24 g LiCl were dissolved in distilled water (20 mL), then the solution was heated at 85 °C under vigorous stirring until they completely dissolved in water and formed a jelly-like solution. Two electrodes and separator were soaked in the PVA/LiCl solution, and then the gel was allowed solidify at room

temperature for 6 h. Then, they were assembled together and kept at 40 °C for 6 h to remove excess water in the electrolyte.

***Characterization*:** The morphology, microstructure and composition of the as-prepared sasmples were characterized by field-emission SEM (FE-SEM, JSM-6330F), transmission electron microscopy (TEM, FEI Tecnai G^2 F30), XPS (XPS, ESCALab250, Thermo VG) and X-ray diffractometer (XRD, D8 ADVANCE). Electrochemical measurements such as cyclic voltammetry (CV) and galvanostatic charge/discharge measurements were performed on an electrochemical workstation (CHI 760D). The electrochemical studies of the individual electrode were carried out in a conventional three-electrode cell, with a graphite electrode, a saturated calomel reference electrode (SCE) and 5 M LiCl electrolyte.

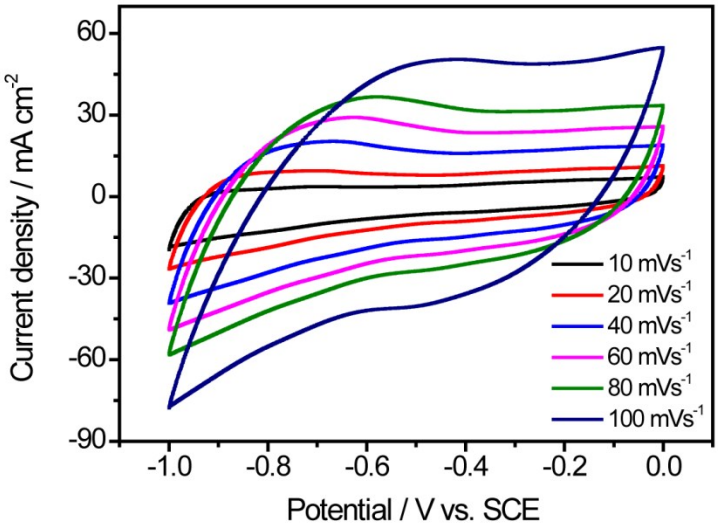

Figure S1. CV curves of the C@WO_{3-x} electrode collected at various scant rates.

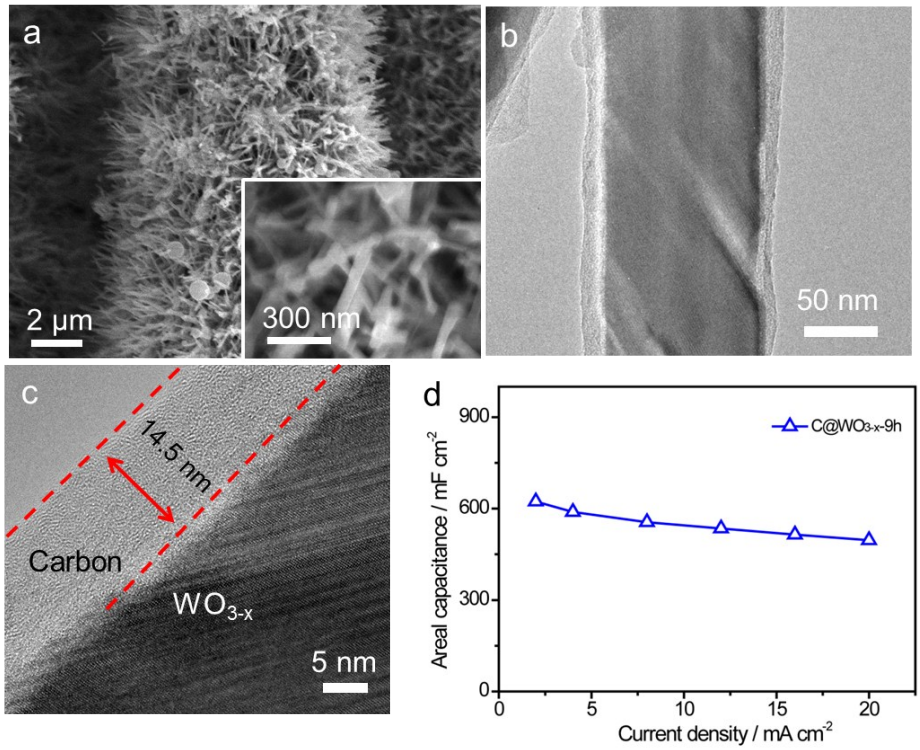

Figure S2. (a) SEM images, (b) TEM, (c) HRTEM images and (d) areal capacitances as a function of current density of the C@WO_{3-x} nanowires nanowires obtained with a hydrothermal time of 9 h.

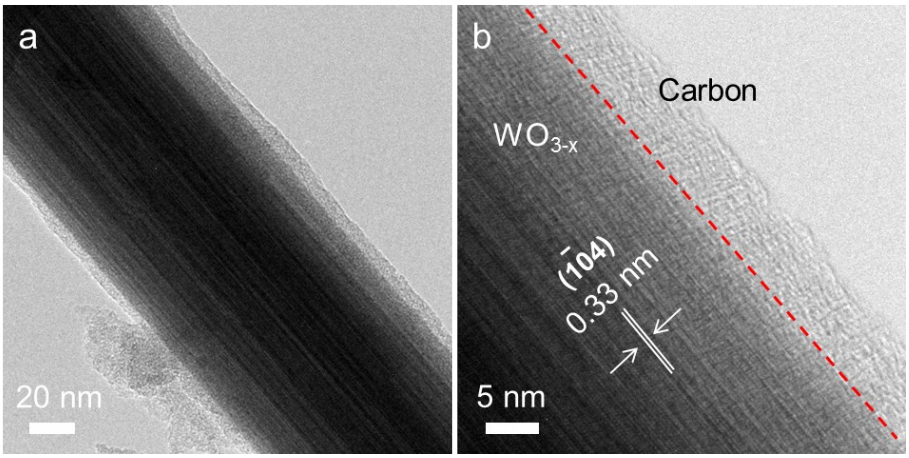

Figure S3. (a) TEM and (b) HRTEM images of t the C@WO_{3-x} electrode after 10000 cycles

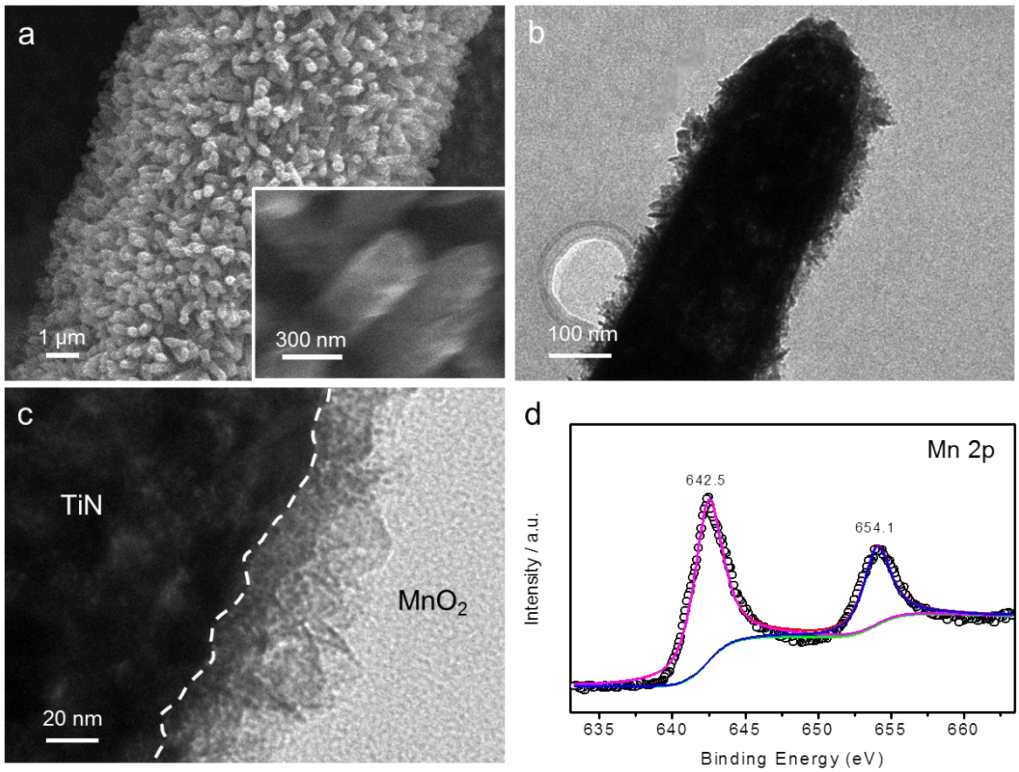

Figure S4. (a) SEM image, (b,c) TEM image, and (d) Mn 2p XPS core level spectrum of the TiN/MnO_2 nanowires.

1. X. Lu, G. Wang, T. Zhai, M. Yu, S. Xie, Y. Ling, C. Liang, Y. Tong and Y. Li, *Nano letters*, 2012, **12**, 5376-5381.

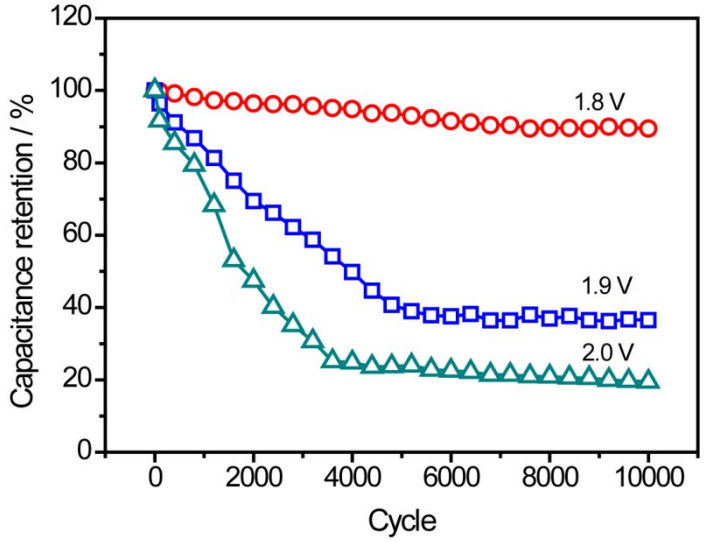

Figure S5. Cycling performance of the the TiN/MnO_2//C@WO_{3-x}-ASC device collected at 100 mV s^{-1} for 10000 cycles in the potential windows of 1.8 V, 1.9 V and 2.0 V.