Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Binder-free WS_2 Nanosheets with Enhanced Crystallinity as Stable Negative Electrode for Flexible Asymmetric Supercapacitors

Si Liu,[1,3] Yinxiang Zeng,[3] Min Zhang,[1] Shilei Xie,[1] Yexiang Tong,[3] Faliang Cheng[1,*] and Xihong Lu [2,3*]

[1]*Guangdong Engineering and Technology Research Center for Advanced Nanomaterials, Dongguan University of Technology, Guangdong 523808, PR ChinaE-mail: chengfl@dgut.edu.cn (F. Cheng)*

[2]*School of Applied Physics and Materials, Wuyi University, Jiangmen, Guangdong 529020, People's Republic of China *E-mail: luxh6@mail.sysu.edu.cn (X. Lu)*

[3]*MOE of the Key Laboratory of Bioinorganic and Synthetic Chemistry, KLGHEI of Environment and Energy Chemistry, School of Chemistry, Sun Yat-Sen University, Guangzhou 510275, PR China*

**E-mail: luxh6@mail.sysu.edu.cn (X. Lu)*

Calculations:

1. Single Electrode:

Areal capacitances of single electrodes were measured by galvanostatic charge/discharge method according to the following equation:

$$C_v = \frac{I \times \Delta t}{\Delta V \cdot S} \qquad (1)$$

where C_v (F/cm^2) is the areal capacitance, I (A) is the constant discharging current, Δt is the discharging time, ΔV (V) is the potential window, and S (cm^2) is the surface area of electrode..

2. MnO_2@Tin//A-WS_2-ASCs:

The cell (device) capacitance (C_{cell}, F) and volumetric capacitance of the MnO_2@TiN//A-WS_2-ASC devices were calculated from their CVs according to the following equation:

$$C_{cell} = \frac{Q}{\Delta V} \qquad (2)$$

$$C_V = \frac{C_{cell}}{V} = \frac{Q}{V \times \Delta V} \qquad (3)$$

where Q (C) is the average charge during the discharging process in the applied current, V is the volume (cm^3) of the whole device (The area and thickness of our MnO_2@TiN//A-WS_2-ASCs is about 0.5 cm^2 and 0.1 cm. Hence, the whole volume of our MnO_2@TiN//A-WS_2-ASCs is about 0.05 cm^3), Δt (s) is the discharging time, ΔV (V) is the voltage window. It is worth mentioning that the volumetric capacitances were calculated based on the volume of the whole device stack, that includes the electrode and the separator with electrolyte.

Alternatively, the cell (device) capacitance (C_{cell}) and volumetric capacitance (C_v, F/cm^3) was estimated from the galvanostatic charge/discharge information using the following equations:

$$C_{cell} = \frac{I \times \Delta t}{\Delta V} \qquad (4)$$

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

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

Volumetric energy density, equivalent series resistance and power density of the devices were obtained from the following equations:

$$E = \frac{1}{2 \times 3600} C_V \Delta V^2 \quad (6)$$

$$\mathrm{ESR} = \frac{iR_{drop}}{2 \times I} \quad (7)$$

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

where E (Wh/cm^3) is the energy density, C_V is the volumetric capacitance obtained from Equation (4) and ΔV (V) is the voltage window. ESR (Ω) is the internal resistance of the device. P (W/cm^3) is the power density.

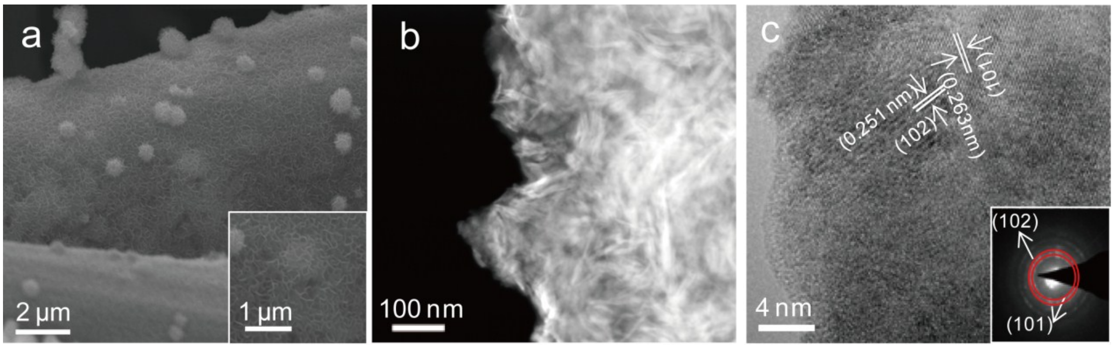

Figure S1. (a) SEM image of WS_2, (b) HAADF-STEM images of WS_2, and (c) HRTEM image of WS_2. The inset in Figure S1c is its corresponding SAED pattern.

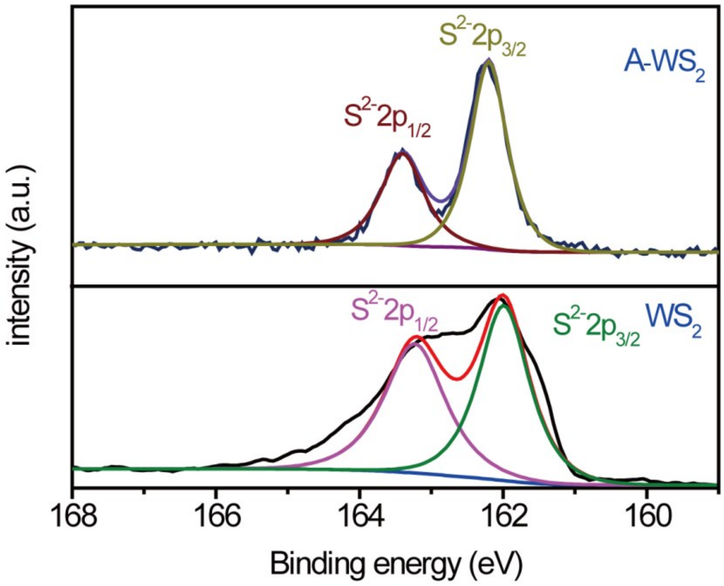

Figure S2. Core-level S 2p XPS spectra of the prepared WS_2 and A-WS_2 samples.

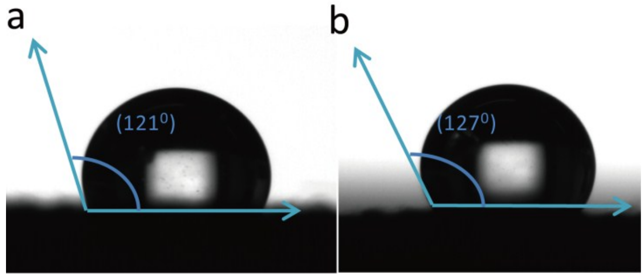

Figure S3. the contact angle images of (a) A-WS_2 and (b) WS_2

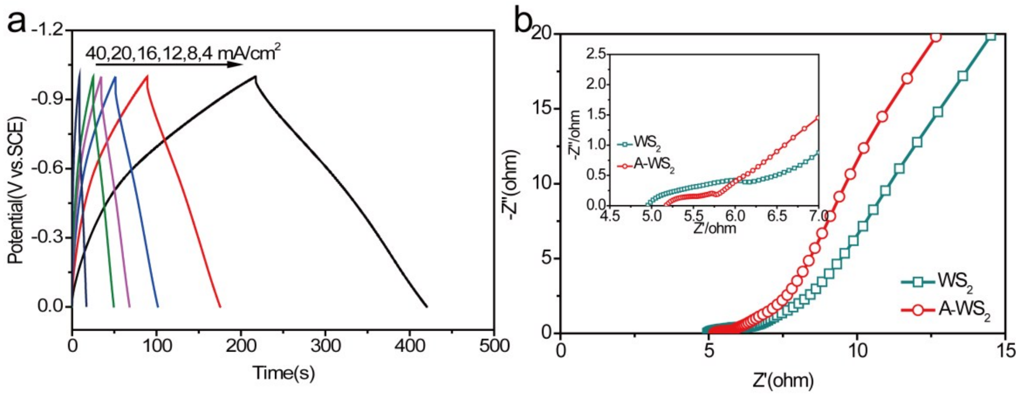

Figure S4. (a) GCD curves of A-WS_2 at various current densities and (b) Nyquist plots collected for WS_2 and A-WS_2 electrodes

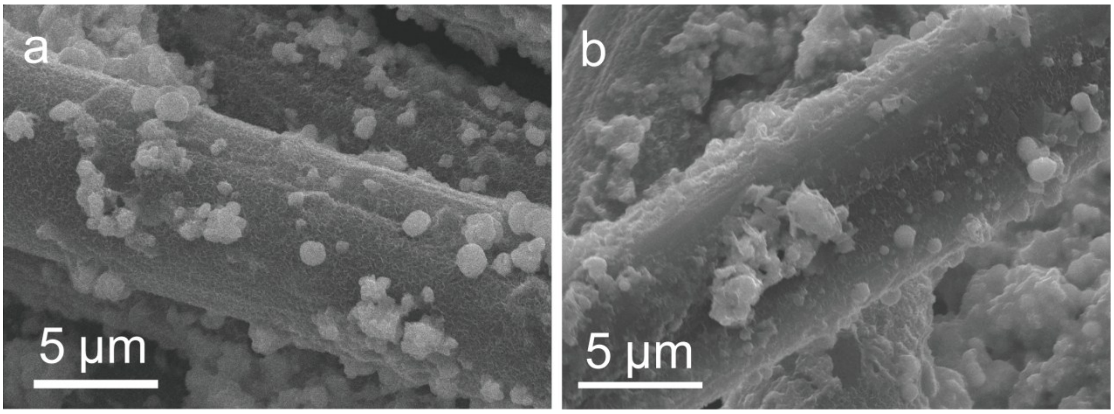

Figure S5. (a) SEM images of the A-WS_2 and (b) WS_2 electrodes after 10000 cycles

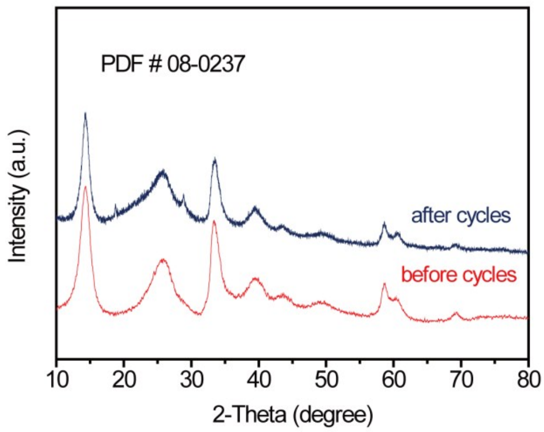

Figure S6. XRD of the A-WS_2 electrode before and after 10000 cycles.

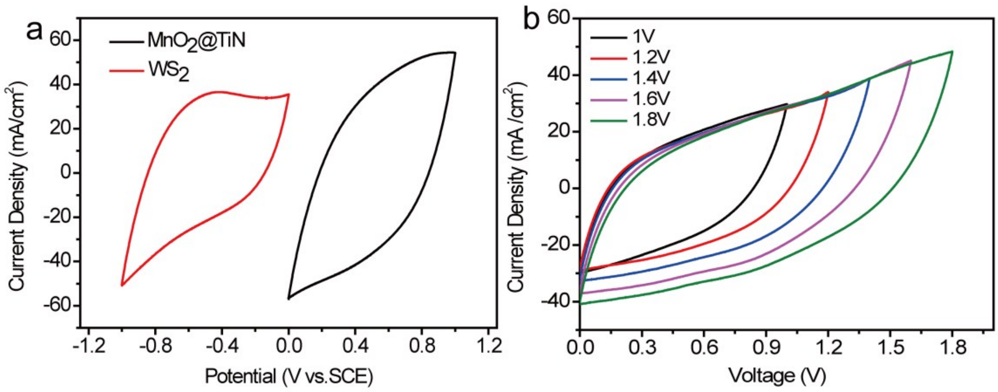

Figure S7. (a) CV curves collected for A-WS_2 and MnO_2@TiN electrodes at a scan rate of 100 mV/s and (b) CV curves in different voltage window at same current density of 100 mV/ s

Balance the charge of electrodes in ASC device:

As for a SC, the charge balance will follow the relationship $q^+ = q^-$. The charge stored by each electrode depends on the capacitance (C_s), the potential range for the charge/discharge process (ΔE) and the volume of the electrode (V) follows the Equation (9):

$$q = C_s \times \Delta E \times m \qquad (9)$$

In order to get $q^+ = q^-$ at 100 mV/ s, the volume balancing between MnO_2 and WON electrode will be calculated as follow:

$$\frac{V_{MnO_2@TiN}}{V_{A-WS_2}} = \frac{C_{V(A-WS_2)} \times \Delta E_{(A-WS_2)}}{C_{V(MnO_2@TiN)} \times \Delta E_{(MnO_2@TiN)}} \approx \frac{1.38}{1}$$

Therefore, the calculated volumetric ration betweenMnO_2@TiN electrode and A-WS_2 electrode is about 1.38 : 1, meanwhile, the mass ratio of MnO_2@TiN toA-WS_2 is 1:1.42.

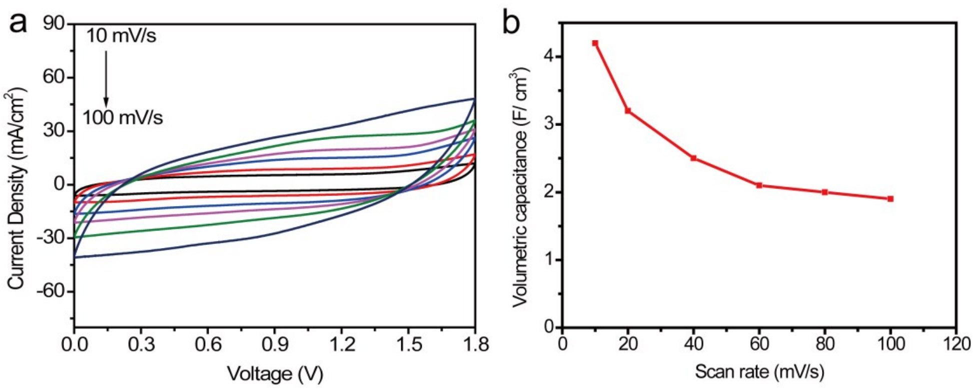

Figure S8. (a) CV curves of the MnO_2@TiN//A-WS_2-ACS device and (b) Capacitance as a function of various scan rates of the MnO_2@TiN//A-WS_2-ACS device.