Electronic Supplementary Information for

Wet milled synthesis of Sb /MWCNT nanocomposite for improved sodium storage

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Experimental Section

Synthesis of Sb nanoparticle/multiwalled carbon nanotube nanocomposite (SbNP/MWCNT): 700 mg of Sb powders (200 mesh, Alfa Aesar) and 200 mg of MWCNTs (40-60 nm in diameter and 5-15 μm in length, Shenzhen Nanotech Port Co., Ltd.) were wet milled in acetone at 1200 rpm for 12 h using a WL-IA planetary mill. After centrifugating and subsequently drying the resulting mixture at 60 ^{o}C under vacuum, the final product SbNP/MWCNT was obtained. In addition, Sb powders were wet milled through the same procedures as synthesizing SbNP/MWCNT without adding any MWCNTs. MWCNTs were wet milled through the same procedures as synthesizing SbNP/MWCNT without adding any Sb powders.

Structural and electrochemical characterization: SEM measurements were carried out on a Hitachi S-4800 field emission scanning electron microscope operated at 15 kV. TEM and HRTEM characterizations were performed on a Tecnai G2 F20 U-TWIN field emission transmission electron microscope operated at 200 kV. EDX

analysis was conducted on an EDAX system. XRD pattern was conducted on a Rigaku D/max2500 diffractometer using Cu Kα radiation. Thermogravimetric (TG) analysis was investigated with a NETZSCH STA 409 PC/PG instrument. Nitrogen adsorption and desorption isotherms at 77.3 K were determined by a Nova 2000e surface area-pore size analyzer. Electrochemical experiments were performed using CR2032 coin cells. To make working electrodes, Sb/MWCNTs, Super-P carbon black, and carboxymethyl cellulose sodium with mass ratio of 80:10:10 were added to water, and mixed into homogeneous slurry with mortar and pestle. The resulting slurry was pasted onto pure Cu foil (99.9 %, Goodfellow). The electrolyte was 1 M $NaClO_4$ in ethylene carbonate (EC)/propylene carbonate (PC) (1:1 v/v) with addition of 5% or 10% fluoroethylene carbonate (FEC). Glass fibers (GF/D) from Whatman were used as separators and sodium metal was utilized as the counter electrode. The coin cells were assembled in an argon-filled glove box (H_2O, O_2 < 0.1 ppm, Mbraun, Germany). Cyclic voltammetry was conducted on a CHI 733D electrochemical workstation at a scan rate of 0.1 mV s^{-1}. The charge and discharge measurements of the batteries were performed on a Land CT2001A multi-channel battery testing system in the fixed voltage window between 0 and 2 V *vs.* Na^+/Na at room temperature. Electrochemical impedance spectral measurements were carried out on a PARSTAT 2273 advanced electrochemical system in the frequency range from 100 kHz to 100 mHz.

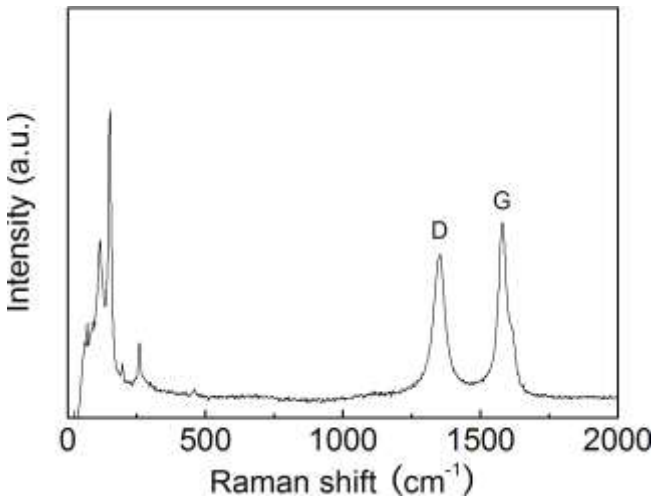

Figure S1. Raman spectrum of SbNP/MWCNT.

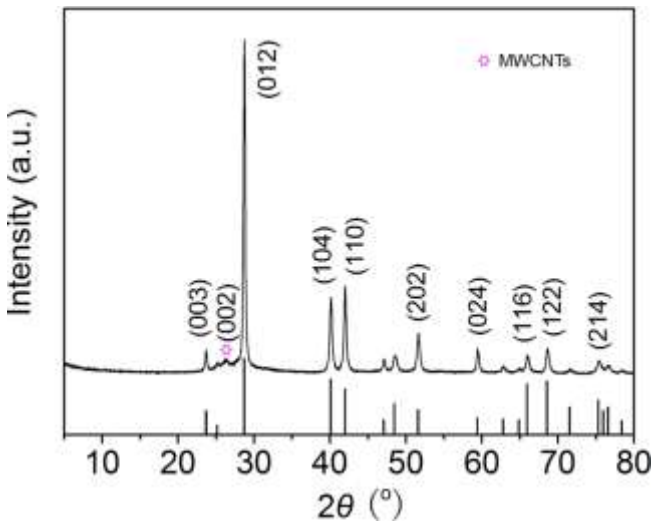

Figure S2. XRD pattern of SbNP/MWCNT. The peak marked with a red asterisk corresponds to the (002) plane of MWCNTs.

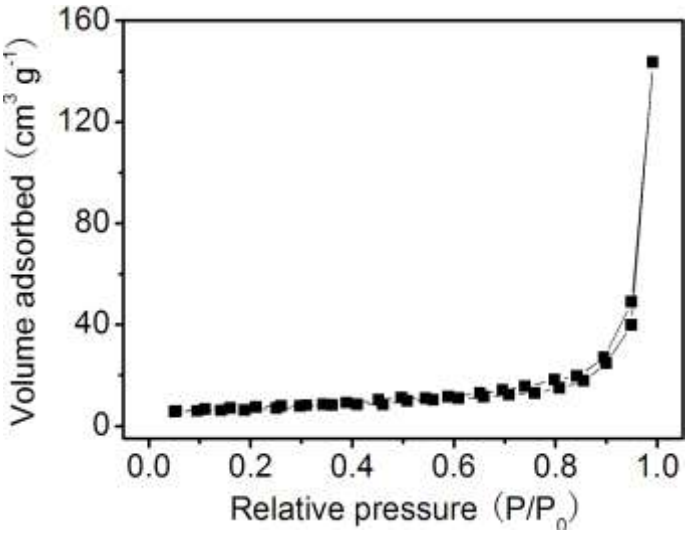

Figure S3. Nitrogen adsorption/desorption isotherms of SbNP/MWCNT.

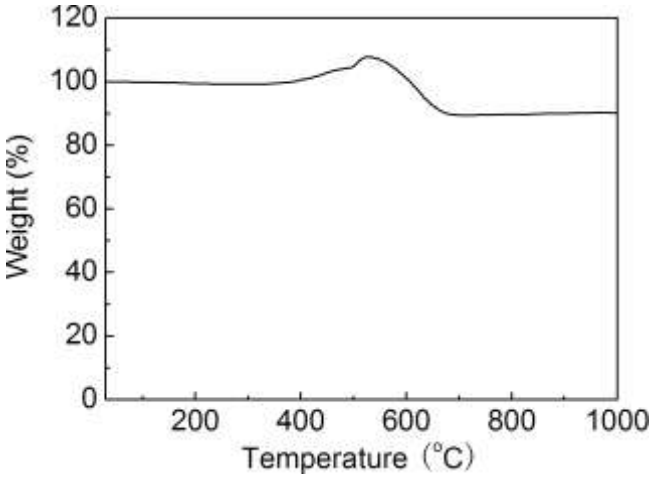

Figure S4. TG analysis curves of SbNP/MWCNT under air atmosphere at a heating rate of 10 ^{o}C min^{-1}.

Table S1. Summary of specific capacities of the Sb electrodes reported previously and in this work.

Current density (mA g^{-1})	Voltage range (V) *vs.* Na^+/Na	Initial capacity (mA h g^{-1})	Cycle number (n)	Residual capacity (mA h g^{-1})	Ref.
100	0−2	610	100	~580	36
330	0.02−1.5	537	80	576	37
100	0−2	422	300	350	38
100	0−1.2	544	50	453	39
200	0−2	502	120	382	This work

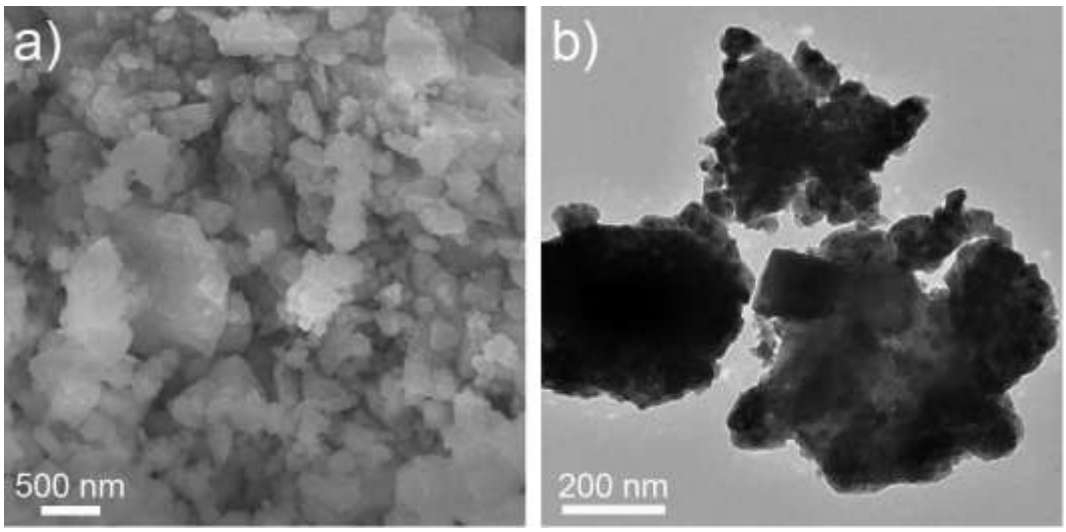

Figure S5. (a) SEM and (b) TEM images of wet milled Sb powder.

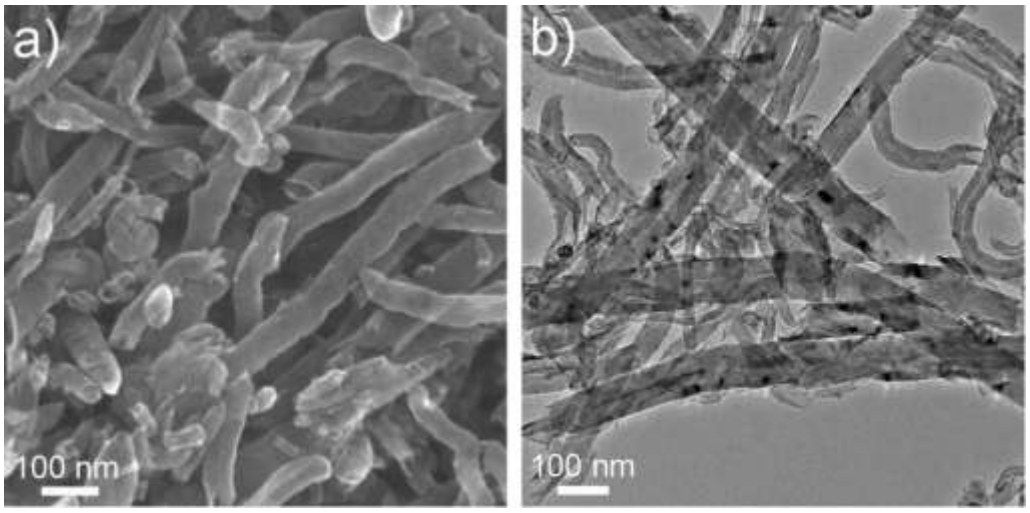

Figure S6. (a) SEM and (b) TEM images of wet milled MWCNTs.

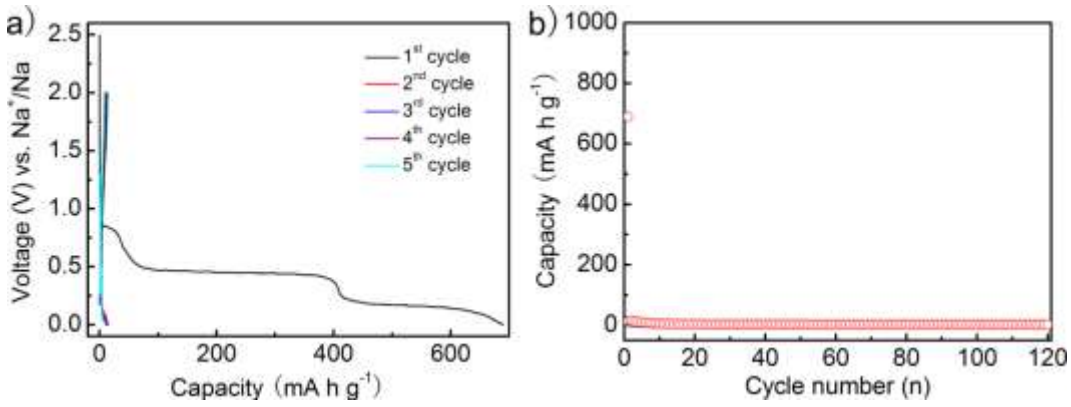

Figure S7. a) Galvanostatic charge/discharge profiles and b) cycling performance of the Sb electrode in the voltage range of 0 to 2 V *vs.* Na^+/Na. The first ten cycles are under 0.1 A g^{-1} and the remaining cycles are under 0.2 A g^{-1}.

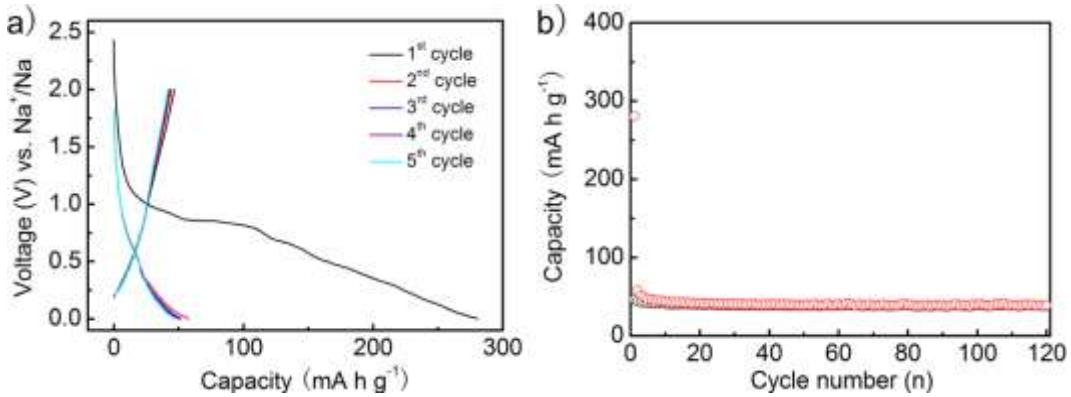

Figure S8. a) Galvanostatic charge/discharge profiles and b) cycling performance of the MWCNT electrode in the voltage range of 0 to 2 V *vs.* Na^+/Na. The first ten cycles are under 0.1 A g^{-1} and the remaining cycles are under 0.2 A g^{-1}.

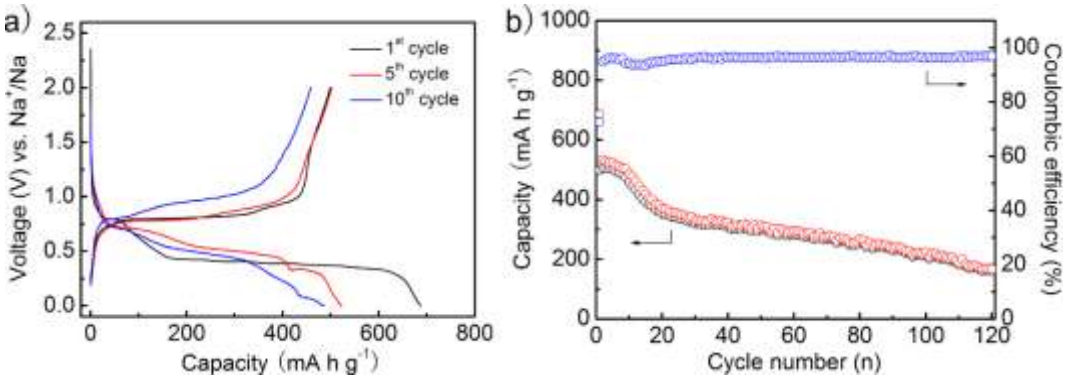

Figure S9. a) Galvanostatic charge/discharge profiles and b) cycling performance and Coulombic efficiency of the SbNP/MWCNT electrode in the voltage range of 0 to 2 V *vs.* Na^+/Na using 1 M $NaClO_4$ in EC/PC with addition of 10% FEC as the electrolyte. The first ten cycles are under 0.1 A g^{-1} and the remaining cycles are under 0.2 A g^{-1}.

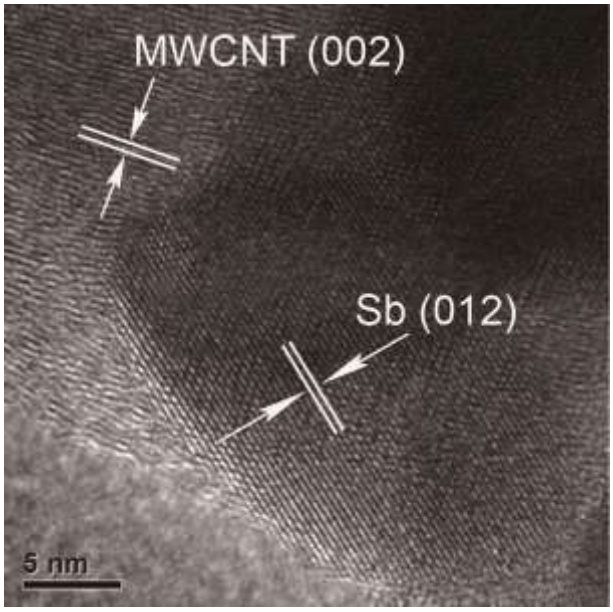

Figure S10. HRTEM of the SbNP/MWCNT electrode after 120 cycles.

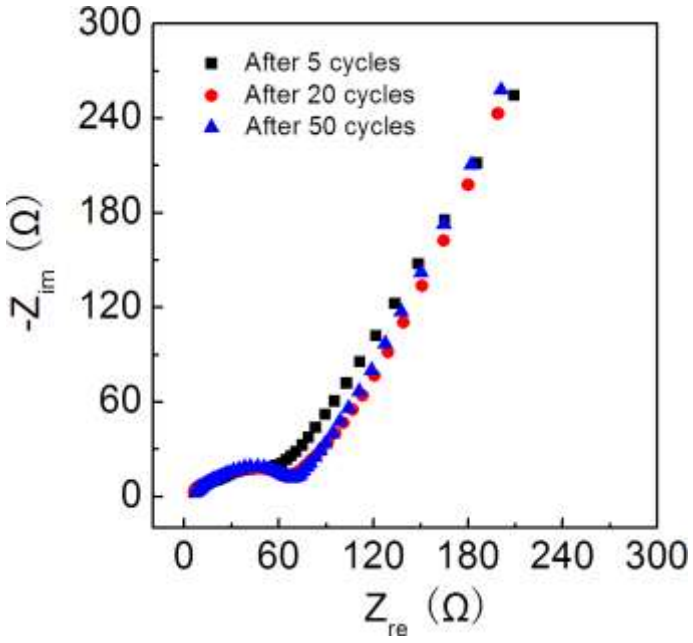

Figure S11. Nyquist plots of the SbNP/MWCNT electrode for different cycles.