Electronic Supplementary Information for

SnO₂@graphene Nanocomposites as Anode Materials for Na-ion Battery with Superior Electrochemical Performance

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Experiment details

Synthesis. Graphene oxide nanosheets were synthesised from natural graphite powders by a modified Hummer's method.¹ To synthesize bare graphene, the obtained graphene oxide was dispersed in distilled water and then exfoliated to generate graphene oxide nanosheets by ultrasonication using a Brandson Digital Sonifer (S450D, 40% amplitude). The brown graphene oxide nanosheet dispersion was poured into a round-bottomed flask, to which hydrazine monohydrate (as reducing agent) was added. The mixed solution was then refluxed at 130 °C for 3 h, during which the colour of the solution gradually changed to dark black as the graphene nanosheet dispersion was formed. The bare SnO2 and SnO2@graphene nanocomposites were produced via hydrothermal method. In a typical process, 2 mmol $SnCl_2 \cdot 5H_2O$ (Sigma-Aldrich, $\geq 98\%$) were dissolved in 20 mL distilled water. Then 0.315 g poly vinyl pyrrolidone (PVP) as surfactant was added. After stirring for at least 20 mins, 0.4 ml 37.5% H₂SO₄ was added. After stirring for another several minutes, the precursor solution was separated by two parts (10 ml each). One part was added with 10ml GO ethylene glycol solution (20g L⁻¹) and was treated by ultrasonic for 30 mins. Then both two mixtures were heated up to 200 °C in the Teflon-lined autoclave (25 mL in capacity) and maintained at that temperature for 12 h. The precipitates were cooled down to room temperature naturally, collected and washed with distilled water and ethanol several times. After drying at 60 °C in vacuum oven overnight, the final products were obtained.

Structural and physical characterization. The crystal structure and phases of as-prepared materials were characterized by X-ray diffraction (XRD, Siemens D5000) using a Cu K α radiation at a scanning step of 0.02° min⁻¹. The morphology was analysed by field emission scanning electron microscope (FESEM, Zeiss Supra 55VP). The crystal structure details were further characterized by transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2011). Selected area electron

diffraction (SAED) patterns were recorded by a Gatan CCD camera in a digital format. TGA/DTA was performed to analyse the weight ratio of nanocomposite at a heating rate of $5 \,^{\circ}$ C min⁻¹ in air from room temperature to 900 °C with a 2960 SDT system.

Electrochemical testing. The electrodes were prepared by dispersing the as-prepared material (80 wt %), acetylene carbon black (10 wt %), and poly (Vinylidene fluoride) binder (PVDF, 10 wt %) in N-methyl-2-pyrrolidone (NMP) to form a slurry. The resultant slurry was pasted onto copper foil using a doctor blade and dried in vacuum oven for 12 h, followed by pressing at 200 kg cm⁻². Electrochemical measurements were carried out using two-electrode coin cells with Na metal as counter and reference electrodes and the glass microfibre (Whatman) as the separator. The CR2032-type coin cells were assembled in an argon-filled glove box (UniLab, Mbraun, Germany). The electrolyte solution was 1 M NaClO₄ dissolved in a mixture of ethylene carbonate (EC) and propylene carbonate (PC) with a volume ratio of 1:1. Cyclic voltammetry (CV) was conducted on a CHI 660C instrument between 0.01 and 3 V *vs.* Na/Na⁺ at room temperature. The charge-discharge measurements were performed at ambient temperature at different current densities in the voltage range from 0.01 to 3 V *vs.* Na/Na⁺.



Figure S1. a and b are low magnification FESEM images of $SnO_2@graphene$ nanocomposites. c and d are high magnification FESEM images of $SnO_2@graphene$ nanocomposites.



Figure S2. TG/DTA curves of SnO₂@graphene nanocomposites.



Figure S3. The 1st, 2nd 5th, 20th, 50th, and 100th cycles discharge and charge profiles of $SnO_2@$ graphene nanocomposites at <u>40</u> mA g⁻¹.



Figure S4. Cycling performance of bare SnO_2 (a) and graphene (b) at current densities of 40, 80, 160, 320, and 640 mA g⁻¹, which are recorded from the 2^{nd} cycle.



Figure S5. (a) Low magnification, (b) medium magnification, and (c) high magnification SEM images of SnO₂@graphene nanocomposite electrodes taken from fully charged state at 20 mA g⁻¹ current rate after 100 cycles.



Figure S6. (a) Low magnification, (b) medium magnification, and (c) high magnification <u>SEM images of bare SnO_2 nanoparticle electrodes taken from fully charged state at 20 mA g⁻¹</u> <u>current rate after 100 cycles.</u> Electronic Supplementary Material (ESI) for Chemical Communications This journal is C The Royal Society of Chemistry 2013

Reference:

1. W. S. Hummers and R. E. Offeman, J. Am. Chem. Soc. 1958, 80, 1339.