Electronic Supplementary Information

WS$_2$@graphene Nanocomposites as Anode Materials for Na-ion Batteries with Enhanced Electrochemical Performances

Dawei Su,$^{a,b}$ Shixue Dou$^*,a$ and Guoxiu Wang$^*,b$

$^a$ Institute for Superconducting and Electronic Materials, University of Wollongong, Wollongong, NSW 2522, Australia. Fax: +61-2-4221-5731; Tel: +61-2-4221-4558; E-mail: shi@uow.edu.au

$^b$ Centre for Clean Energy Technology, School of Chemistry and Forensic Science, Faculty of Science, University of Technology, Sydney, NSW 2007, Australia. Fax: +61-2-9514-1460; Tel: +61-2-9514-1741; E-mail: Guoxiu.Wang@uts.edu.au
Experiment details

Synthesis of WS$_2$@graphene. To synthesize the WS$_2$@graphene nanocomposites, graphite oxide nanosheets were first prepared from natural graphite powders by a modified Hummers’ method.$^1$ Briefly, 1 g graphite powder and 0.5 g sodium nitrate (NaNO$_3$, Sigma-Aldrich, ≥ 99.0%) were poured into 70 ml concentrated sulfuric acid (H$_2$SO$_4$, Sigma-Aldrich, 99.99 %) in an ice bath. Then, 3 g potassium permanganate (KMnO$_4$, Sigma-Aldrich, ≥ 99.0%) was gradually added. The mixture was stirred for 2 h and then diluted with distilled water. After that, 5 % hydrogen peroxide solution (H$_2$O$_2$, Chem-Supply) was added into the solution until the colour of the mixture changed to brilliant yellow. The obtained graphite oxide was dispersed in distilled water and then exfoliated to generate graphite oxide nanosheets by ultrasonication using a Brandson Digital Sonifer (S450D, 40 % amplitude).

The hydrothermal synthesis of the WS$_2$@graphene nanocomposite can be described as follows: 0.125 mmol tungsten chloride (WCl$_6$, Sigma-Aldrich, ≥ 99.9 %) was added into 20 ml graphite oxide aqueous suspension (2 mg ml$^{-1}$), and the mixture was treated ultrasonically for 30 min. Subsequently, 0.3 mmol cysteine (C$_3$H$_7$NO$_2$S, Sigma-Aldrich, ≥ 97 %) was added into the solution and stirred for another few minutes. Then, the mixture was heated to 200 °C in a Teflon-lined autoclave (25 mL in capacity) and maintained at that temperature for 12 h. The precipitates were cooled down to room temperature, collected, and washed with distilled water and ethanol several times. After drying at 60 °C in a vacuum oven overnight, the final products were obtained.

Synthesis of bare graphene and WS$_2$. Bare graphene was synthesized by a chemical reduction approach. In the typical process: the obtained graphite oxide solution 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 black as the graphene nanosheet dispersion was formed.
The bare WS\textsubscript{2} was produced via the hydrothermal method without the addition of graphite oxide solution.

**Structural and physical characterization.** The crystal structure and phase of the as-prepared material were characterized by X-ray diffraction (XRD, Siemens D5000) using Cu K\textalpha\, radiation. The morphology was analysed by field emission scanning electron microscopy (FESEM, Zeiss Supra 55VP). The details of the structure were further characterized by transmission electron microscopy (TEM) and high-resolution TEM (HRTEM, JEOL JEM-2011). Selected area electron diffraction (SAED) patterns were collected by a Gatan charge-coupled device (CCD) camera in a digital format. Thermogravimetric/differential thermal analysis (TG/DTA) was performed at a heating rate of 5 °C min\textsuperscript{-1} under air flow from room temperature to 900 ºC with a 2960 SDT system.

**Electrochemical testing.** The electrodes were prepared by dispersing 70 wt. % as-prepared materials, 20 wt. % acetylene carbon black, and 10 wt. % poly (vinylidene fluoride) binder (PVDF, (CH\textsubscript{2}CF\textsubscript{2})\textsubscript{n}, Sigma-Aldrich) in N-methyl-2-pyrrolidone (NMP, C\textsubscript{5}H\textsubscript{9}NO, Sigma-Aldrich, 99.5 %) to form a slurry. The resultant slurry was pasted onto copper foil using a doctor blade and dried in a vacuum oven for 12 h, which was followed by pressing at 200 kg cm\textsuperscript{-2}. The typical loading of each electrode was approximately 1.2 mg cm\textsuperscript{-2}. Electrochemical measurements were carried out using two-electrode coin cells (CR2032) with Na metal (Sigma-Aldrich, 99.95%) as reference and counter electrode and glass microfiber (Whatman) as the separator. The CR2032 coin cells were assembled in an argon-filled glove box (UniLab, Mbraun, Germany). The electrolyte solution was 1 M sodium perchlorate (NaClO\textsubscript{4}, Sigma-Aldrich, ≥ 99 %) dissolved in a mixture of ethylene carbonate (EC, C\textsubscript{3}H\textsubscript{4}O\textsubscript{3}, Sigma-Aldrich, 99 %) and propylene carbonate (PC, C\textsubscript{4}H\textsubscript{6}O\textsubscript{3}, Sigma-Aldrich, 99.7 %) with a volume ratio of 1:1. Cyclic voltammetry (CV) was carried out on a CHI 660C electrochemistry workstation with a scan rate of 0.04 mV s\textsuperscript{-1} from 0.01 to 3 V. The charge-discharge
measurements were performed at ambient temperature at different current densities in the voltage range from 0.01 to 3 V. A.C. Impedance spectra were collected in the frequency range from 0.01 to 100 kHz on a CHI 660C electrochemistry workstation.
Figure S1. XRD pattern of bare graphene.
Figure S2. Cyclic voltammograms of bare WS$_2$ (a) and WS$_2$@graphene nanocomposites (b), respectively.
Figure S3. Low (a) and high (b) magnification FESEM images of the as-prepared bare WS₂.
Figure S4. 1\textsuperscript{st} and 2\textsuperscript{nd} cycles discharge and charge profiles of MoS\textsubscript{2} at the current density of 20 mA g\textsuperscript{-1}. 
Figure S5. Nyquist plots of WS$_2$ and WS$_2$@graphene nanocomposites. A.c. impedance spectra were collected in the frequency range from 0.01 to 100 kHz. The inset is the magnified plot at low Z'.
Figure S6. Schematic diagram of the $\text{WS}_2@\text{graphene}$ nanocomposites.
Figure S7. (a) 1st, 2nd, and 3rd cycles discharge and charge profiles of the as-prepared bare WS$_2$ at 20 mA g$^{-1}$ current density. (b) Cycling performance of bare WS$_2$ at 20 mA g$^{-1}$ current density.
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