

Supporting Information

Highly Ordered Mesoporous WS₂ Anode Material with Superior Electrochemical Performance for Lithium Ion Battery

Hao Liu,^{a,b} Dawei Su,^b Guoxiu Wang^{*b} and Shi-Zhang Qiao^{* a,c}

^a Australian Institute for Bioengineering and Nanotechnology, The University of Queensland, QLD 4072, Australia

^b Centre for Clean Energy Technology, School of Chemistry and Forensic Science, University of Technology Sydney, Broadway Sydney, NSW 2007, Australia. E-mail:
Guoxiu.Wang@uts.edu.au

^c School of Chemical Engineering, The University of Adelaide, SA 5005, Australia. E-mail:
s.qiao@adelaide.edu.au

Experimental Section

Synthesis of materials

The 2-dimensional (2D) hexagonal mesoporous silica template (SAB-15) was synthesized by following the previously reported method.^[1] The WS₂ replica from the 2D hexagonal SBA-15 was synthesized by a vacuum assisted impregnation route.^[2] Typically, 2.88g phosphotungstic acid (Aldrich, denoted as PTA, H₃O₄₀PW₁₂·xH₂O, FW=2880.05 g mol⁻¹) was dissolved in 15 ml of ethanol to form a transparent solution. Then, 0.5 g of dried SBA-15 was added to the solution. After stirring for 5-10 h, the solvent was removed by evaporation at room temperature in a vacuum oven (<10⁻³ bar). The PTA/SBA15 composite was ground and transferred to a three-zone furnace. A crucible of sulphur was placed at the first heating zone, maintained at 350 °C to produce sulphur vapour. H₂/N₂ (5% H₂) reductive mixture gas carried the sulphur vapour to the PTA/SBA15 composite for sulphuration. After the sulphuration at 600 °C for 5 h with a slow ramping rate (2 °C/min), the WS₂/SBA15 composite was collected and the silica template was removed by 10 wt% HF. The

mesoporous WS₂ product was obtained after filtering and washing by deionised water and ethanol several times, and then dried at 50 °C.

For comparison, the bulk WS₂ was synthesized by the sulphuration of commercial PTA at 600°C in H₂/N₂ atmosphere for 5 h.

Characterisations

The small angle X-ray diffraction (SAXRD) pattern of mesoporous WS₂ was collected by a Bruker D8 Advacned X-ray diffractometer within the scanning range from 0.5° to 5° using a Cu K α radiation ($\lambda=0.15406$ nm). Wide angle X-ray diffraction patterns of bulk and mesoporous WS₂ were obtained from a Rigaku Miniflex XRD device between 10° to 80° (2 θ), by using a Co K α source ($\lambda=0.17902$ nm). N₂ adsorption–desorption isotherms of mesoporous WS₂ was measured by using a Quadrasorb SI analyzer at the testing temperature of 77 K. Brunauer-Emmett-Teller (BET) and Barret-Joyner-Halenda (BJH) analyses were used to determine the surface area, pore volume, and pore size distribution. The BET surface area was calculated using experimental points at a relative pressure of $P/P^0=0.05-0.27$. The pore size distribution was derived from the adsorption branch of isotherm using the BJH method. The total pore volume was determined by the nitrogen amount adsorbed at a relative pressure (P/P^0) of 0.99. The morphologies of bulk and mesoporous WS₂ were obtained from a field emission scanning electron microscope (FESEM, Zeiss Supra 55VP). The crystalline microstructures of bulk and mesoporous WS₂ were observed by transmission electron microscopy (TEM) and high resolution TEM analysis (JEOL 2100, accelerating voltage 200kV).

Cell assembly and electrochemical testing

The bulk and mesoporous WS₂ electrodes were fabricated by mixing the active materials with acetylene black (AB) and a binder, poly(vinylidene fluoride) (PVDF), at weight ratio of

70:20:10. The mixture was dispersed in *n*-methyl pyrrolidone (NMP) solvent to form a slurry. The slurry was uniformly pasted on Cu foil with a blade. The electrodes were dried at 120 °C in a vacuum oven for 12 hours and subsequently pressed under a pressure of 200 kg cm⁻². CR2032-type coin cells were assembled in a glove box for electrochemical characterization. A non-aqueous solution of 1 M LiPF₆ in a 1:1:1 of ethylene carbonate (EC), diethyl carbonate (DEC), and dimethyl carbonate (DMC) was used as the electrolyte. Li metal disks were used as the counter electrodes for electrochemical testing. Cyclic voltammetry (CV) curves were collected by an electrochemistry workstation (CHI660C) at 0.5 mV s⁻¹ within a range of 0.01–3.0 V. The conductivities of bulk and mesoporous WS₂ were measured by a.c. impedance method with an applied frequency from 1 to 100k Hz, using a CHI electrochemical station. The cells were galvanostatically charged and discharged at a current density of 0.1 A g⁻¹ within the voltage range of 0.01–3 V. For the high rate testing, the charge/discharge current gradually increased from 0.1 A g⁻¹ to 0.2, 0.5, 1, 2, 5 and 10 A g⁻¹, then decreased to 1 and 0.1 A g⁻¹, step by step.

Reference

- [1] C. Z. Yu, J. Fan, B. Z. Tian, D. Y. Zhao, G. D. Stucky, *Adv. Mater.*, **2003**, 15, 1742.
- [2] H. Liu, X. W. Du, X. R. Xing, G. X. Wang, S. Z. Qiao, *Chem. Commun.*, **2012**, 48, 865.

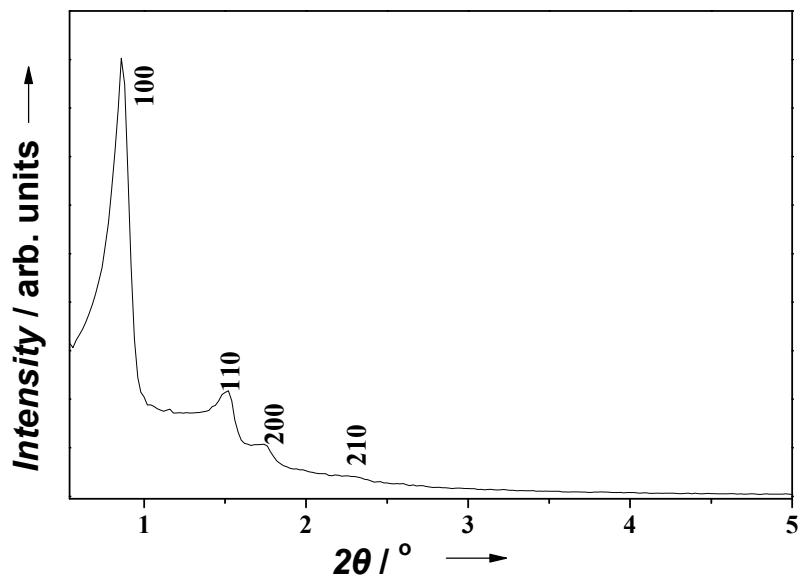


Figure S1. The SAXRD pattern of SBA-15 silica template.

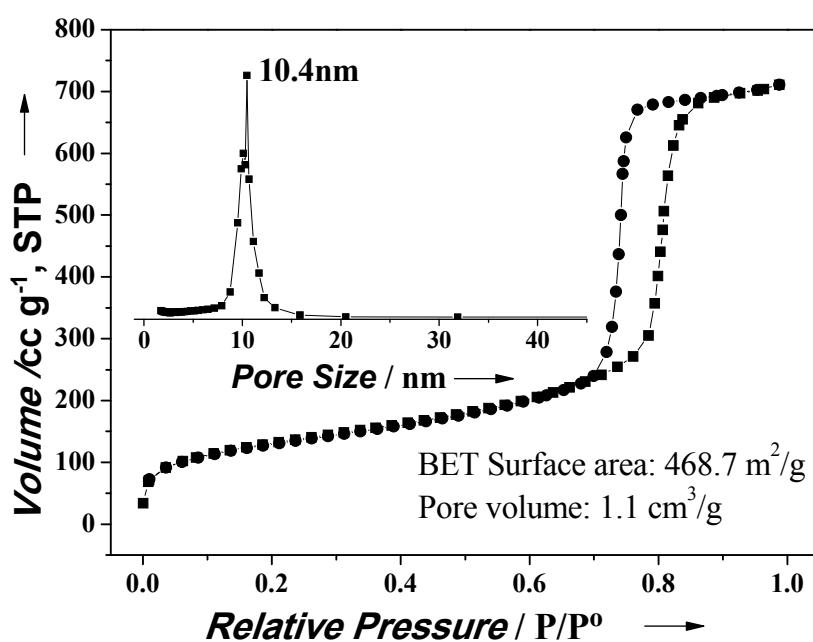


Figure S2. Nitrogen sorption isotherm and corresponding pore size distribution (inset) of SBA-15 silica template .

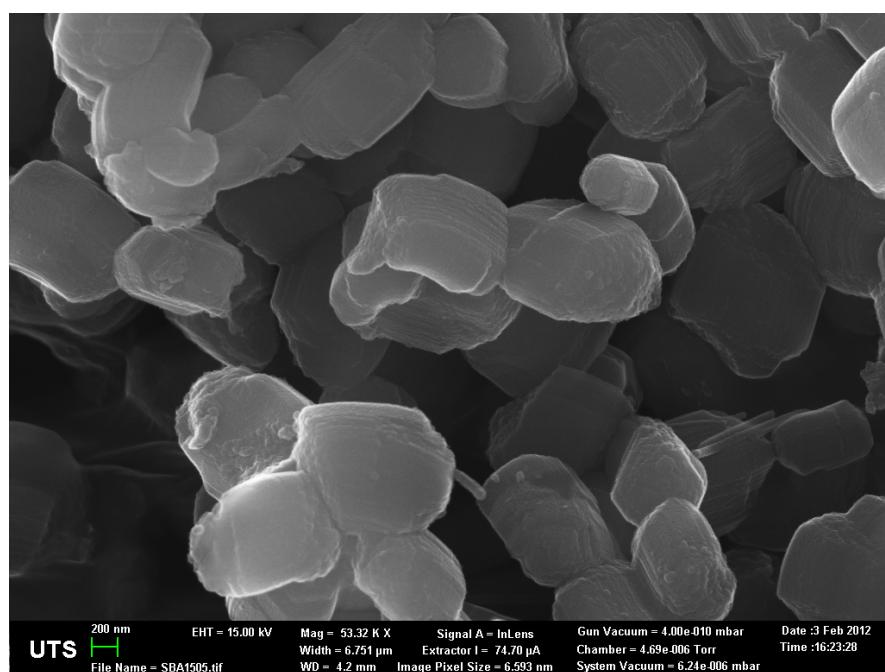


Figure S3. SEM image of SBA-15 template

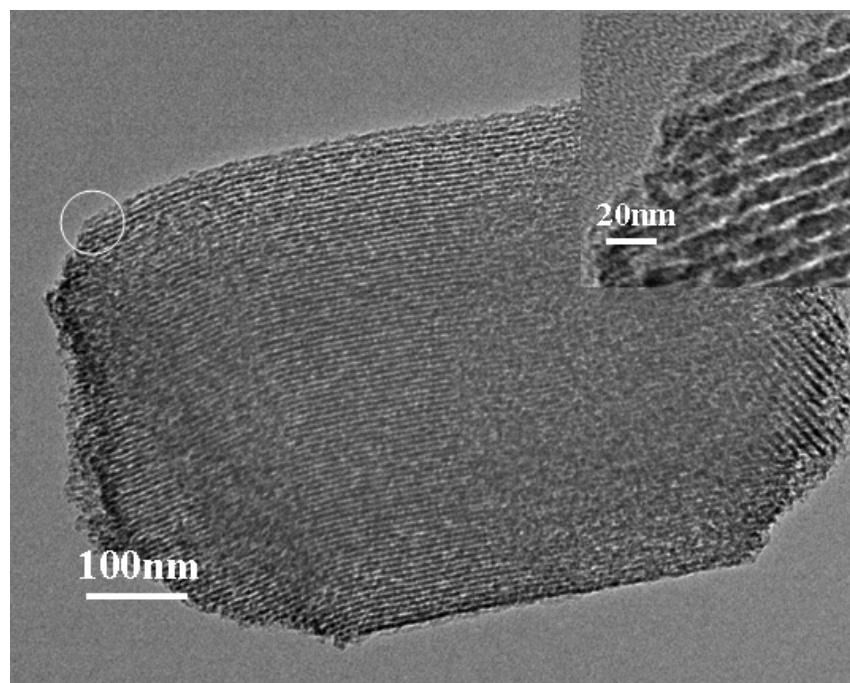


Figure S4. TEM images of SBA-15 template. Inset image is the high magnification image of selected area denoted by the white circle, which demonstrates the mesoporous structure along the [001] direction.

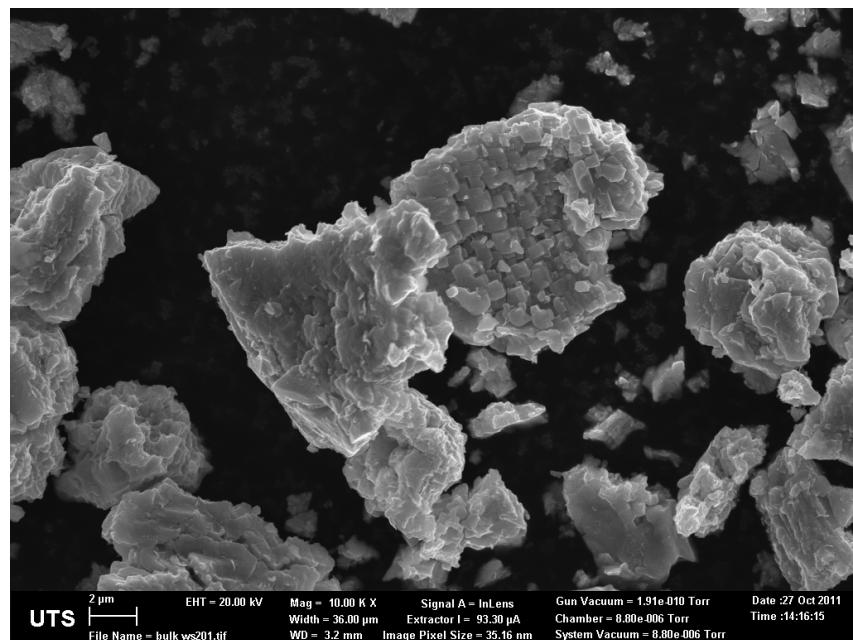


Figure S5. SEM image of bulk WS₂.

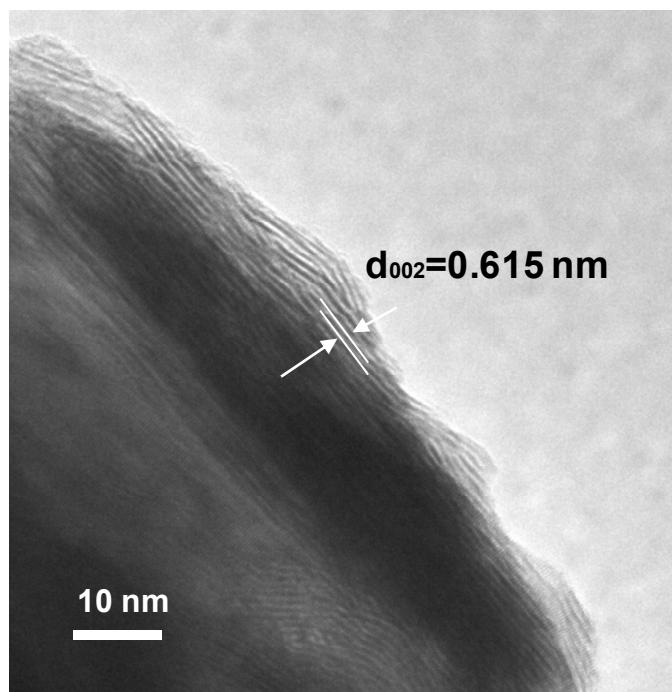


Figure S6. TEM image of bulk WS₂, revealing the (002) d-spacing of 0.615 nm.

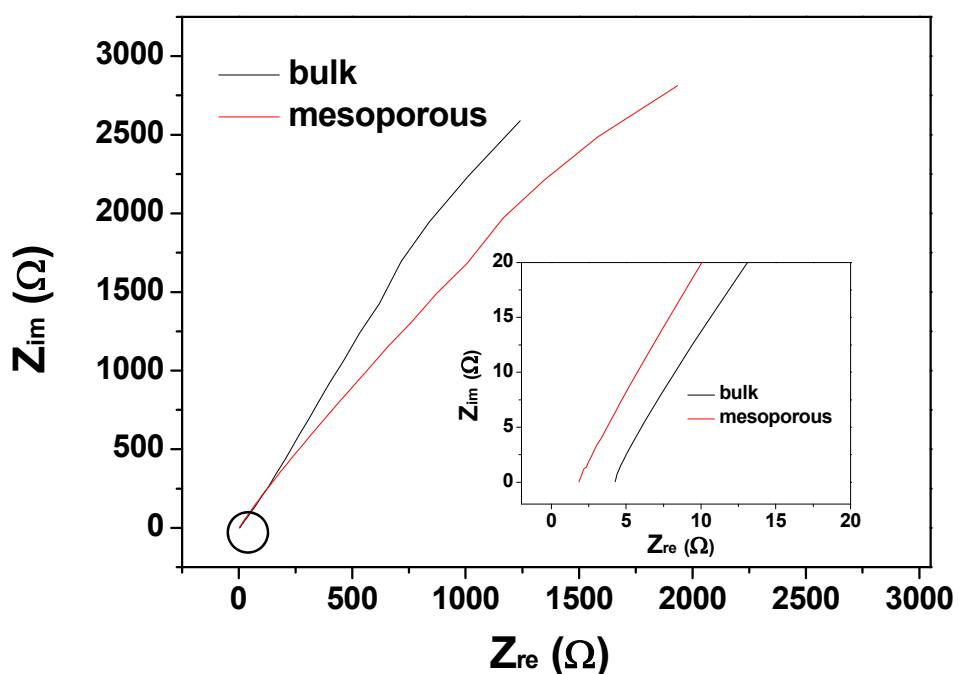


Figure S7. The a.c impedance curves of bulk and mesoporous WS_2 . The inset plot is the impedances in high frequency region as circled, indicating a lower resistance of mesoporous WS_2 .