

Graphene-supported Anatase TiO₂ Nanosheets for Fast Lithium Storage

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Experimental section

The graphene oxide (GO) sheets were first synthesized by a modified Hummers' method.¹⁻² Anatase TiO₂ NSs were then grown onto the GO support following our previous method.³ In a typical synthesis of G-TiO₂ NSs, 40 mg of GO sheets was dispersed into 40 mL of isopropyl alcohol (IPA) by sonication for 20 minutes, followed by the addition of 0.03 mL of diethylenetriamine (DETA; 99 %, Sigma-Aldrich). After the solution was gently stirring for 2 minutes, 0.6 mL of titanium (IV) isopropoxide (TIP; 97 %, Sigma-Aldrich) was added. The reaction solution was then transferred into a 60 mL Teflon-lined stainless steel autoclave and kept in an electric oven at 200 °C for 24 h. The autoclave was then taken out of the oven and left to cool down to room temperature. The black precipitate was collected by centrifugation, washed thoroughly with ethanol, and dried at 60 °C overnight. The as-prepared GO-TiO₂ NSs were treated at 400 °C in H₂/Ar for 2 h with a heating rate of 1 °C min⁻¹ to obtain G-TiO₂ NSs. In the absence of GO, TiO₂ NS spheres were obtained, and also treated at 400 °C in N₂ for 4 h as a comparison.

The product morphology and structure of samples were investigated using field-emission scanning electron microscopy (FESEM; JEOL, JSM-6700F, 5 kV) and transmission electron microscopy (TEM; JEOL, JEM-2100F, 200 kV). Crystallographic information of the samples was collected using powder X-ray diffraction (XRD; Bruker, D8 Advance X-ray diffractometer, Cu K α radiation, $\lambda = 1.5406 \text{ \AA}$). The surface area and pore size distribution of the sample were measured using a Quantachrome Instrument (Autosorb AS-6B). Thermogravimetric analysis (TGA) was carried out under a flow of air with a temperature ramp of 10 °C min⁻¹ from room temperature to 800 °C.

The electrochemical measurements were carried out using two-electrode Swagelok cells (X2 Labwares, Singapore) with pure lithium foil as both the counter and the

reference electrodes at room temperature. The working electrode consists of active material, conductive agent (carbon black, Super-P-Li), and polymer binder poly(vinylidene difluoride) (PVDF; Aldrich) in a 70:20:10 weight ratio. The electrolyte used was 1.0 M LiPF₆ in a 50:50 (w/w) mixture of ethylene carbonate and diethyl carbonate. Cell assembly was carried out in an Ar-filled glovebox with concentrations of moisture and oxygen below 1.0 ppm. Cyclic voltammetry (1–3 V, 0.5 mV s⁻¹) was performed using an electrochemical workstation (CHI 660C). The charge/discharge tests were performed using a NEWARE battery tester at different current rates (1C = 170 mA g⁻¹) with a voltage window of 1–3 V.

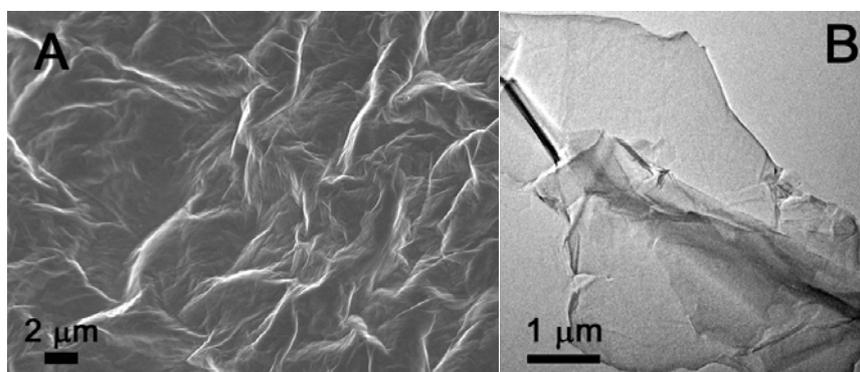


Fig. S1 Electron microscopy images of as-prepared graphene oxide sheets.

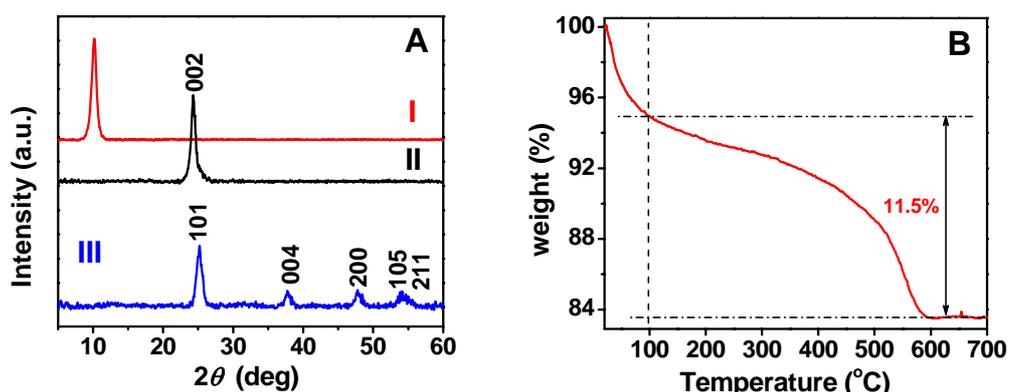


Fig. S2 (A) X-ray diffraction (XRD) patterns of the samples: graphene oxide (I), graphene (II) and G-TiO₂ NSs (III). (B) Thermogravimetric analysis (TGA) of the G-TiO₂ NSs. The weight loss of ~5% below 100 °C is probably due to the evaporation of the absorbed moisture contents, which is common for materials with large surface area.

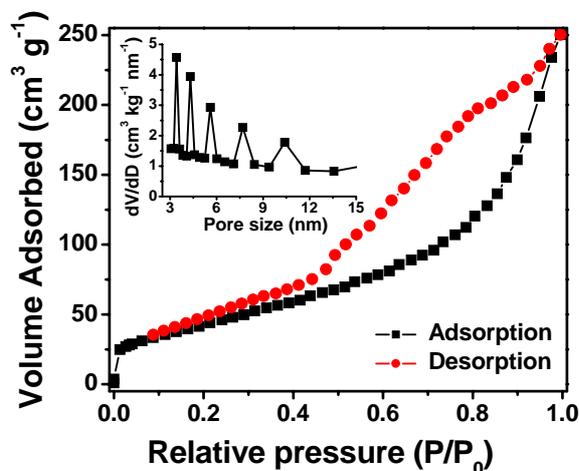


Fig. S3 N₂ adsorption-desorption isotherm of the G-TiO₂ NSs. The inset shows the pore size distribution calculated from the adsorption branch of the isotherm.

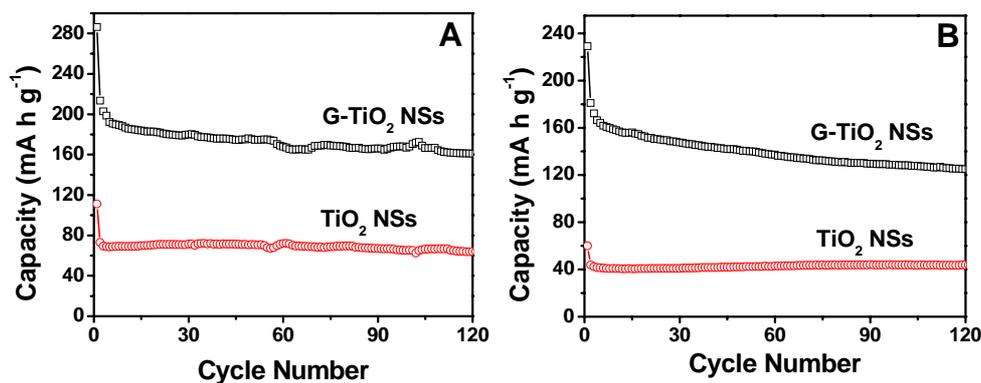


Fig. S4 Comparative cycling performance between G-TiO₂ NSs and pure TiO₂ NSs prepared using similar method without graphene support at the current rate of 1 C (A) and 5 C (B). All measurements were conducted between 1 V and 3 V.

References

1. W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339.
2. Y. Y. Liang, H. L. Wang, H. S. Casalongue, Z. Chen and H. J. Dai, *Nano Res.*, 2010, **3**, 701.
3. J. S. Chen, Y. L. Tan, C. M. Li, Y. L. Cheah, D. Y. Luan, S. Madhavi, F. Y. C. Boey, L. A. Archer and X. W. Lou, *J. Am. Chem. Soc.*, 2010, **132**, 6124.