

Electronic Supplementary Information

Well-Distributed TiO₂ Nanocrystals on Reduced Graphene Oxides as High-Performance Anode Materials for Lithium Ion Batteries

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Experimental

Preparation of GO Nanosheets

All the reagents are of analytic grade and were used without any purification. Graphene oxide (GO) nanosheets were prepared by a modified Hummers method. In detail, graphite powder (2.0 g) was dispersed into 100 ml cooled (0 °C) H₂SO₄ (98%), followed by slow addition of KMnO₄ (6.0 g). Then, the suspension was stirred at 35 °C for 3 days. Afterwards, 200 ml distilled water was added and kept at 98 °C for 2 h. When cooled to 60 °C, 10 ml H₂O₂ (30%) was injected into the suspension to completely react with the excess KMnO₄, and a bright yellow mixture was obtained. The suspension was centrifuged and washed with HCl (5%) and distilled water until the pH value was ~6. The precipitate was collected and stored for further use.

Preparation of TiO₂/RGO Nanocomposites

The TiO₂/RGO nanocomposites were synthesized by two steps of hydrothermal treatments. Graphene oxide (GO) nanosheets were prepared by a modified Hummers method first. Then, 7 mg as-prepared GO, 0.2 g NaOH, 2.64 g Li₂SO₄·H₂O and 2 ml TiCl₃ (15-20 wt.%) were dispersed or dissolved in 40 ml deionized water under continuous agitation for 30 min. The mixture was transferred into a 50 ml Teflon-sealed autoclave and maintained at 150 °C for 18 h. After the hydrothermally-treated solution was cooled to room temperature, 0.5 g ascorbic acid (AA) was added under agitation and kept heating at 150 °C for another 6 h. The obtained products were centrifuged and washed with deionized water and ethanol at least 5 times separately, and dried at 80 °C overnight for further characterization. As references, pure RGO and TiO₂ were prepared under similar conditions but without Li₂SO₄·H₂O and TiCl₃ or GO, respectively.

Materials Characterization

The obtained samples were characterized by X-ray diffraction (XRD, Rigaku D/Max III diffractometer with Cu K α radiation, $\lambda = 1.5418 \text{ \AA}$), scanning electron microscope (SEM, FEI Nanosem 430), high-resolution transmission electron microscope (HRTEM, FEI Tecnai G²F-20), thermogravimetry analysis (TGA, Rigaku PTC-10A TG-DTA analyzer), and atomic force microscope (AFM, MMAFM/STM, D3100M, Digital Ltd.).

Electrochemical Measurements

For electrochemical tests, the working electrodes were comprised of active materials, acetylene black (AB), and polytetrafluoroethylene (PTFE) at the weight ratio of 75 : 15 : 10. The average weight of the electrodes was ~2 mg. In the test cells, lithium metal was used as the counter and reference electrode. The electrolyte was 1 M LiPF₆ dissolved in a 1 : 1 : 1 mixture of ethylene

carbonate (EC), ethylene methyl carbonate (EMC) and dimethyl carbonate (DMC). The cells were assembled in a glove box filled with high-purity argon. Discharge/charge tests of the cells were performed between 0.01-3.0 V (vs. Li/Li⁺) under a LAND-CT2001A instrument at room temperature. Cyclic voltammetry (CV) tests were performed at different scanning rates from 0.1 to 5 mV s⁻¹ between 1.0-3.0 V (vs. Li/Li⁺) after the initial 5 charge/discharge cycles. Electrochemical impedance spectroscopy (EIS) was taken by using an IM6e electrochemical workstation at 25 °C with the frequency range from 10 kHz to 100 mHz and an AC signal of 5 mV in amplitude as the perturbation. The specific capacity was calculated according to the corresponding entire weight of active material in each electrode.

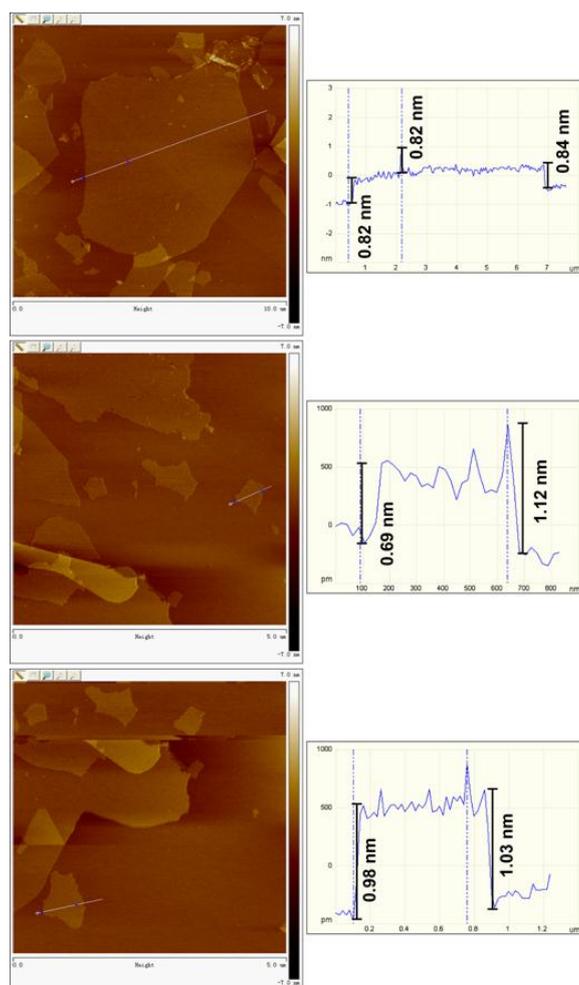


Fig. S1. AFM images of GO nanosheets prepared through a modified Hummers method.

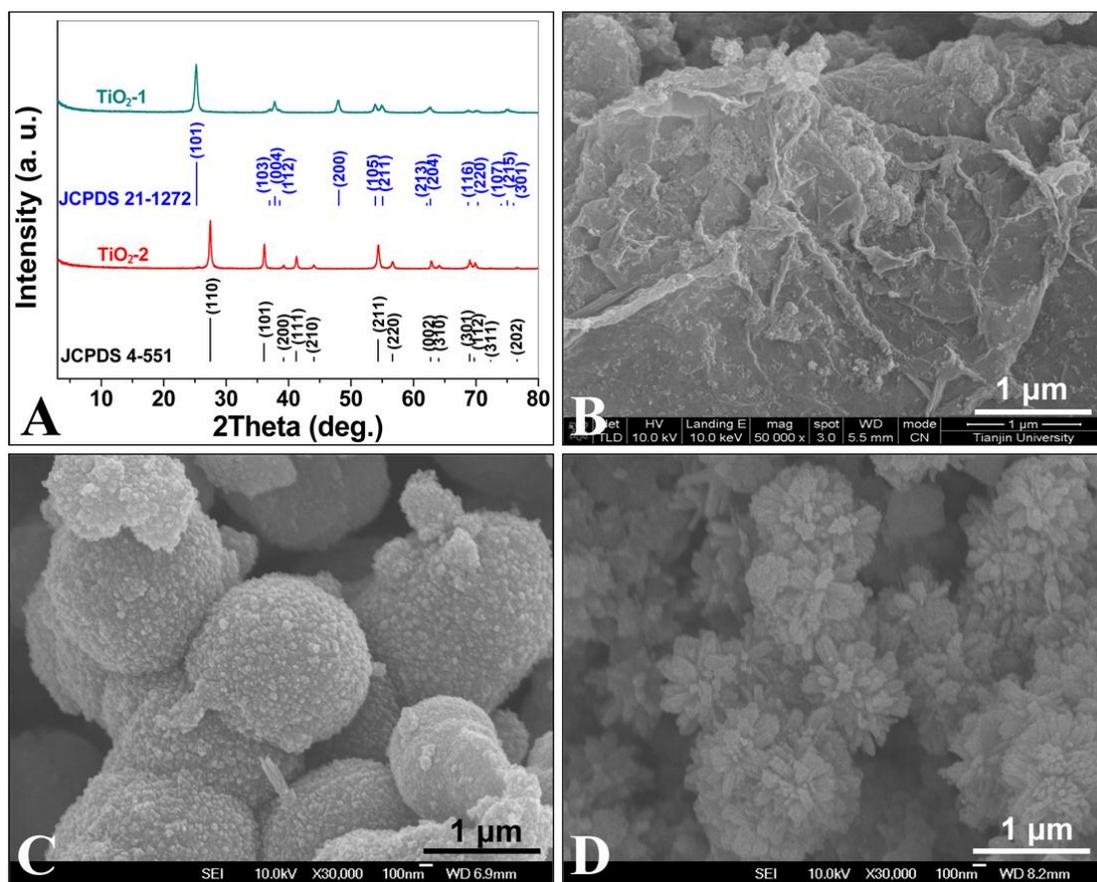


Fig. S2. (A) XRD patterns of pure TiO_2 -1 (synthesized under the existence of $\text{Li}_2\text{SiO}_4 \cdot \text{H}_2\text{O}$) and TiO_2 -2 (synthesized without $\text{Li}_2\text{SiO}_4 \cdot \text{H}_2\text{O}$). SEM images of TiO_2/RGO nanocomposites (B), TiO_2 -1 (C) and TiO_2 -2 (D).

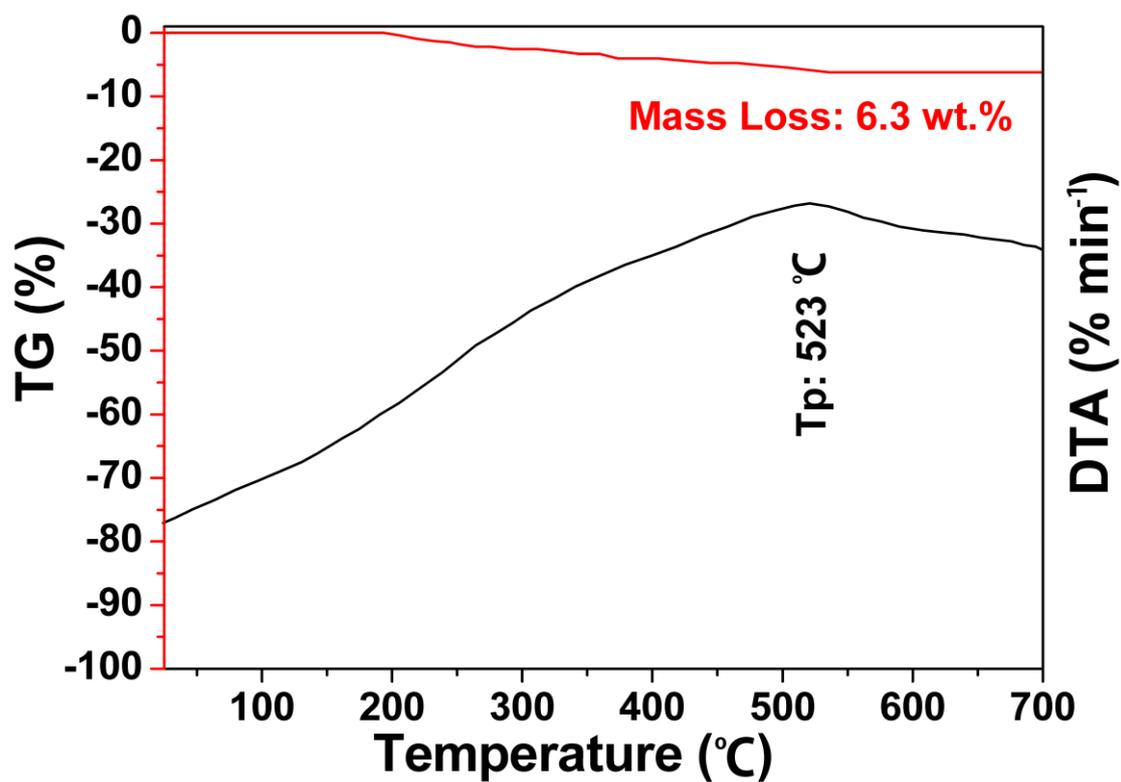


Fig. S3. TG-DTA curves of TiO₂/RGO nanocomposites in air.

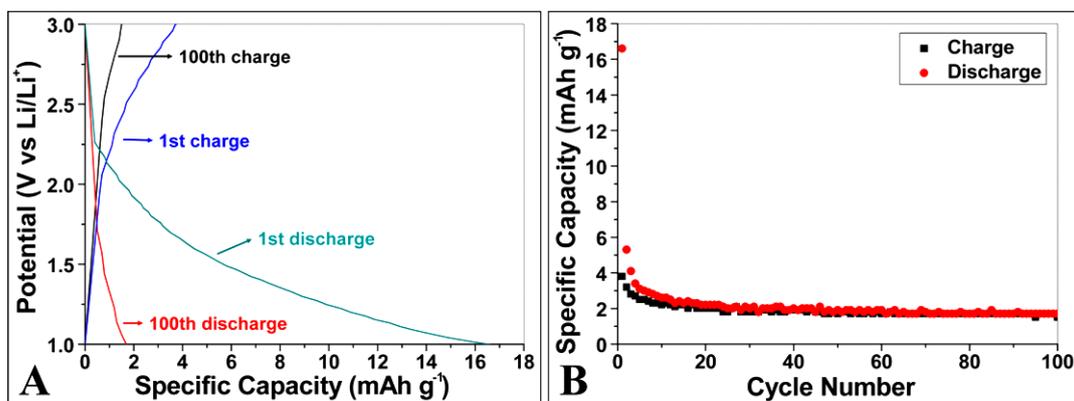


Fig. S4. Discharge/charge curves (A) and cyclic performance (B) of pure RGO electrodes at the potential range of 1.0-3.0 V at 1.2 C.