Well-Distributed TiO$_2$ 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) H$_2$SO$_4$ (98%), followed by slow addition of KMnO$_4$ (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 H$_2$O$_2$ (30%) was injected into the suspension to completely react with the excess KMnO$_4$, 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 TiO$_2$/RGO Nanocomposites

The TiO$_2$/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 Li$_2$SO$_4$·H$_2$O and 2 ml TiCl$_3$ (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 TiO$_2$ were prepared under similar conditions but without Li$_2$SO$_4$·H$_2$O and TiCl$_3$ or GO, respectively.

Materials Characterization

The obtained samples were characterized by X-ray diffraction (XRD, Rigaku D/Max III diffractometer with Cu Kα radiation, λ = 1.5418 Å), 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 LiPF$_6$ 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.

![AFM images of GO nanosheets prepared through a modified Hummers method.](image)

*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 Li$_2$SiO$_4$·H$_2$O) and TiO$_2$-2 (synthesized without Li$_2$SiO$_4$·H$_2$O). SEM images of TiO$_2$/RGO nanocomposites (B), TiO$_2$-1 (C) and TiO$_2$-2 (D).
Fig. S3. TG-DTA curves of TiO$_2$/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.