

Electronic Supplementary Information

Interweaving of multilevel carbon networks with mesoporous TiO₂ for lithium-ion battery anodes

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Experimental

Synthesis of thermally-exfoliated graphene (TEG): Graphite oxide (GO) was prepared from natural graphite powders (universal grade, 99.985%) according to a modified Hummers method. Dried GO was thermally exfoliated at 300 °C for 3 min in air, and subsequently treated at 900 °C for 3 h in Ar atmosphere. The obtained sample was denoted as TEG.

Synthesis of nanocomposite: 0.47 g of Pluronic P123 (EO₂₀PO₇₀EO₂₀) was first dissolved in 10 mL of ethanol. Then, 0.28 g of TiCl₄ and 1.18 g of titanium isopropoxide (TPT) were added in the solution. On the other hand, 0.05 g of TEG was added into 10 mL of ethanol. After ultrasonic for 30min, the TEG suspension was added into the above P123/TiCl₄/TPT ethanol solution. The mixture solution was magnetically stirred for 2 h. The final solution was poured into a petri dish and evaporated in air overnight. The obtained TiO₂/P123/TEG composite material was subsequently treated in Ar at 500 °C for 5 hours.

Synthesis of mesoporous TiO₂: 0.47 g of Pluronic P123 (EO₂₀PO₇₀EO₂₀) was first dissolved in 10 mL of ethanol. Then 0.28 g of TiCl₄ and 1.18 g of TPT were

added in the solution. The solution was magnetically stirred for 2 h. The final solution was poured into a petri dish and evaporated in air overnight. The obtained TiO₂/P123 composite material was subsequently treated in Ar at 500 °C for 5 hours.

Synthesis of simplex TiO₂: 0.28 g of TiCl₄ and 1.18 g of TPT were added in 10 mL of ethanol. The solution was magnetically stirred for 2 h. The final solution was poured into a petri dish and evaporated in air overnight. The obtained material was subsequently treated in air at 500 °C for 5 hours.

Characterization: X-ray powder diffraction (XRD) patterns were recorded on a Bruker D8 powder X-ray diffractometer (Germany). The morphologies of the samples were observed by a scanning electron microscopy (SEM) system (Hitachi S-4800) and a transmission electron microscopy (TEM) system (JEOL, JEM-2100). N₂ adsorption-desorption analysis was performed using a Micromeritics ASAP 2010 instrument. Thermal analysis was performed on NETZSCH STA 409C thermal analyzer (Germany), in which the sample was heated in alumina crucible in air to 800 °C at a heating rate of 10 °C min⁻¹.

Lithium-ion battery performance measurement: Electrochemical measurements were performed using 2032-type coin cells. For the nanocomposite, 80 wt% active material, 10 wt% carbon black, and 10 wt% polyvinylidene fluoride binder were mixed with N-methylpyrrolidone. The obtained slurry was coated onto a copper foil current collector and dried in vacuum at 80 °C for 12 h. Then the electrode was cut into disks (12 mm in diameter) and further dried in vacuum at 80 °C for 12 h. The loading of the tested electrodes in our experiments is around 1.5 mg cm⁻². The coin cells were assembled in an Ar-filled glove-box using an active material as the working electrode, a Li foil as the reference and counter electrode, 1 M LiPF₆ in ethylene carbonate and diethyl carbonate (1:1 vol) as the electrolyte, and Celgard 2250 film as the separator. Charge-discharge measurements were carried out galvanostatically using a battery testing system (LAND, Wuhan Jinnuo Electronics. Ltd.) and the potential window was controlled between 1.0 and 3.0 V at room temperature. 80% of the weight of loading film in the electrode was used to estimate the specific capacity of the batteries. Full cell with LiFePO₄ as the cathode and the nanocomposite as the anode was also

assembled in the same argon-filled glove-box. The LiFePO_4 sample was prepared via Wang's method.¹ The tested cathode was prepared using similar methods as that of the anode slurry. The resultant LiFePO_4 slurry was uniformly pasted onto alumina foil and dried in vacuum. The loading of the LiFePO_4 electrode in our experiments is around 2.5 mg cm^{-2} . In the full cell, LiFePO_4 is slightly excesses over nanocomposite. The full cell was tested between 0.1 and 3 V and the specific capacity is calculated based on the mass of the nanocomposite.

Figures:

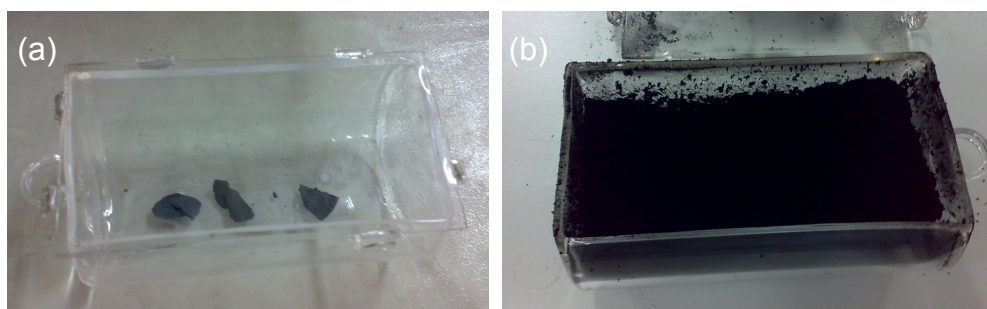


Fig. S1. The photos of (a) GO and (b) TEG. After the thermal exfoliation, the sample has a huge variation in volume.

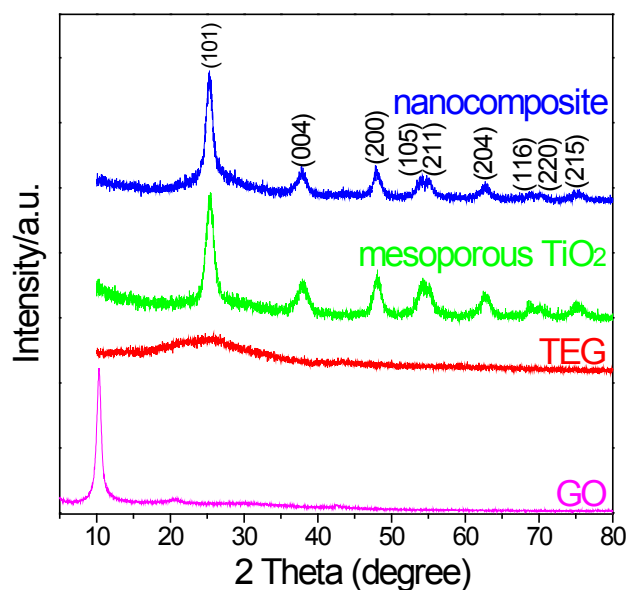


Fig. S2. XRD patterns of GO, TEG, mesoporous TiO_2 , and nanocomposite (anatase TiO_2 , JCPDS File Card No. 21-1272)

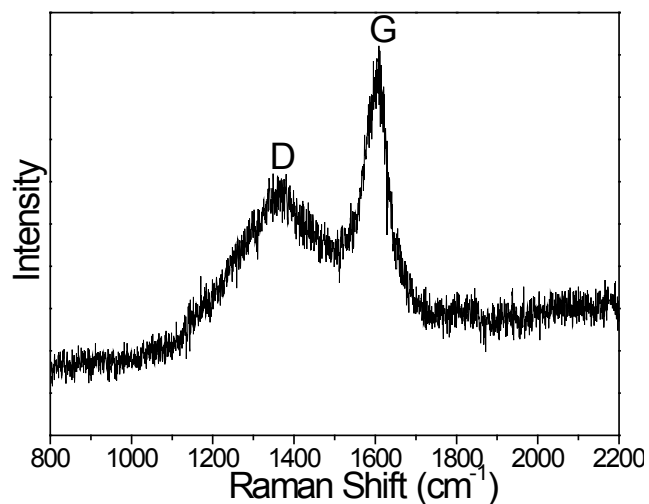


Fig. S3. Raman spectrum of mesoporous TiO₂. Mesoporous TiO₂ is obtained by heating the TiO₂/P123 composite material in Ar at 500 °C for 5 h. Two prominent peaks are obtained at 1365 and 1600 cm⁻¹ for mesoporous TiO₂, and these peaks correspond to the D and G bands of amorphous carbon. Amorphous carbon is formed by the carbonization of P123 micelles during heat treatment.

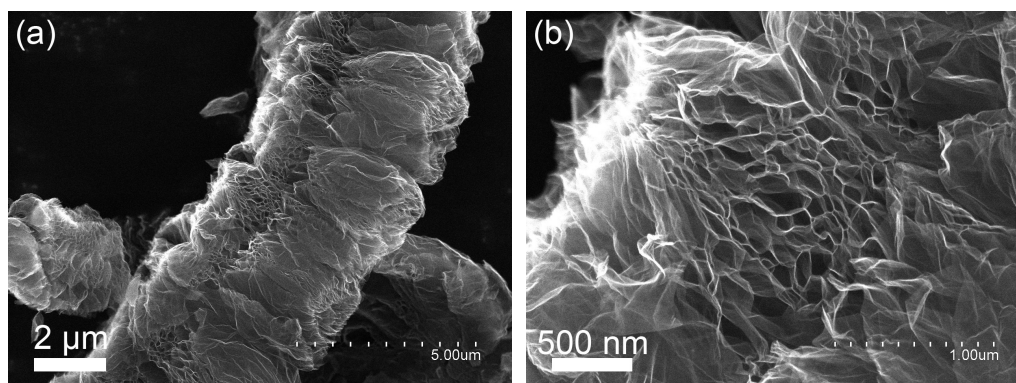


Fig. S4. SEM images of TEG. The TEG sample is composed of micron-sized particles and has a nanosheet structure resulting from the decomposition of the oxygen-containing groups of GO during the thermal exfoliation process.

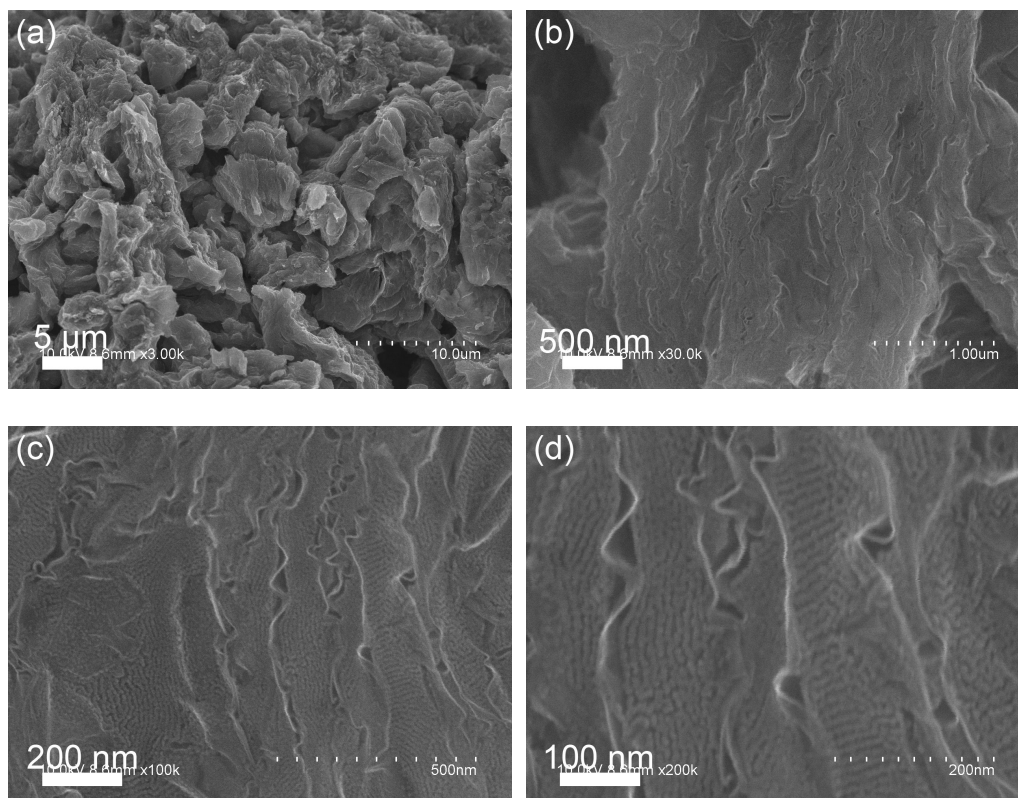


Fig. S5. SEM images of the nanocomposite at different magnifications. Figure a shows that the nanocomposite is composed of micron-sized particles. Figure b-d show that the mesoporous TiO₂ and graphene nanosheets form the three-dimensional continuous complex structure.

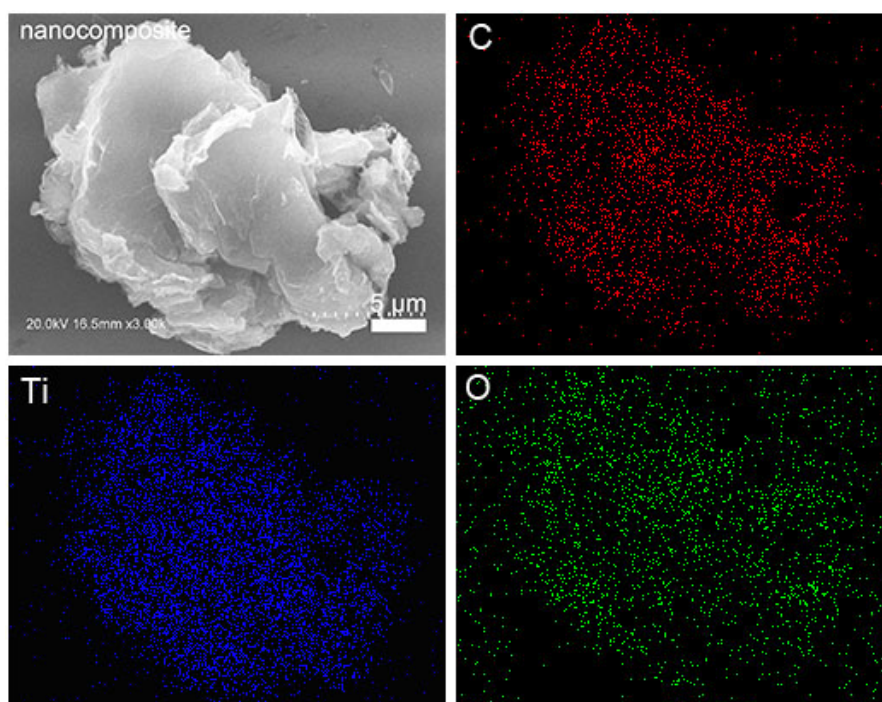


Fig. S6. SEM image and corresponding carbon, titanium, and oxygen elemental mapping of the nanocomposite

Reference:

- [1] Y. Wang, Y. Wang, E. Hosono, K. Wang, H. Zhou. *Angewandte Chemie International Edition* 2008, **47**, 7461.