Electronic Supplementary Information

Sandwich-like porous TiO$_2$/reduced graphene oxide (rGO) for high-performance lithium-ion batteries

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Materials: TiCl$_4$ and ethanol were provided by Beijing Chemical Reagent Company. Graphene oxide (GO) was synthesized from natural graphite powder by a modified Hummers method, as reported elsewhere. Titanium(III) chloride, 20% in 3% hydrochloric acid) was produced by Alfa Aesar.

![Fig. S1 HRTEM image of T-200. The (101) crystal face (3.52 Å) of anatase could be seen.](image)
Fig. S2 AFM image and height profiles of the GO (Fig. S2A). TEM images of TiO$_2$-graphene composites. (a): without PVP, 150 °C/5 h; (b): without PVP, 200 °C/5 h; (c): with PVP, 240 °C/5 h (T-240). According to the TEM images, we think less than three layers of rGO were inserted in the TiO$_2$/rGO composites (Fig. S2B).
Fig. S3 Raman spectra ($\lambda = 532$ nm) of GO (black) and T-200 (red).

Fig. S4 XPS spectrum of T-200 (a), high resolution XPS Ti 2p spectrum (b), high resolution XPS N 1s spectrum (c). The sample T-200 was composed of C, O, N and Ti. It can be found Ti was Ti(+4) and the nitrogen was as pyrrolic nitrogen atoms (399.6 eV).
Fig. S5 TEM images of TiO$_2$-graphene with H$_2$O (a-b) and triethylene glycol (c-d) as the solvent respectively.

Fig. S6 TEM images (a-d) of TiO$_2$-graphene composites where the amount of PVP was quartered. When the amount of PVP was decreased, the TiO$_2$ nanocrystals was not loaded so uniformly when comparing with T-200. However, the pores could still be seen clearly.
Fig. S7 SEM images (a-b) and TEM images (c-d) of TiO$_2$-graphene composites. It was found that when the PVP molecules were absent, the pores were still present. However, the TiO$_2$ nanocrystals aggregated on the graphene surface.

Fig. S8 TEM images (a, b) of TiO$_2$ nanocrystals. The TiO$_2$ nanocrystals were prepared using PVP as the stabilizer.
**Fig. S9** SEM (a,b) and TEM (c,d) images of TiO$_2$. The TiO$_2$ was prepared through adding the TiCl$_3$ solution into the ethanol directly and no PVP and GO was used. It can be seen that the TiO$_2$ nanocrystals aggregated seriously and the TiO$_2$ microspheres with different diameters were observed.

**Fig. S10** TEM images of TiO$_2$-graphene with solvothermal temperature at 200 °C. The solvothermal time was 24 h (a,b) and 72 h (c,d) respectively.
Fig. S11 TGA analysis of T-150, T-200, T-240 under a flow of air with a temperature ramp of 5 °C/min from room temperature to 850 °C.

Fig. S12 Charge–discharge curves of rGO cycled at 1.0-3.0 V under a current density of 100 mA g⁻¹.