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## **Electronic Supplementary Information**

## Sandwich-like porous TiO<sub>2</sub>/reduced graphene oxide (rGO) for highperformance lithium-ion batteries

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*Materials*: TiCl<sub>4</sub> and ethanol were provided by Beijing Chemical Reagent Company. Graphenen 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.

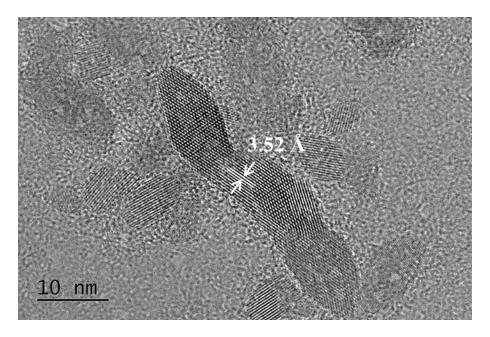
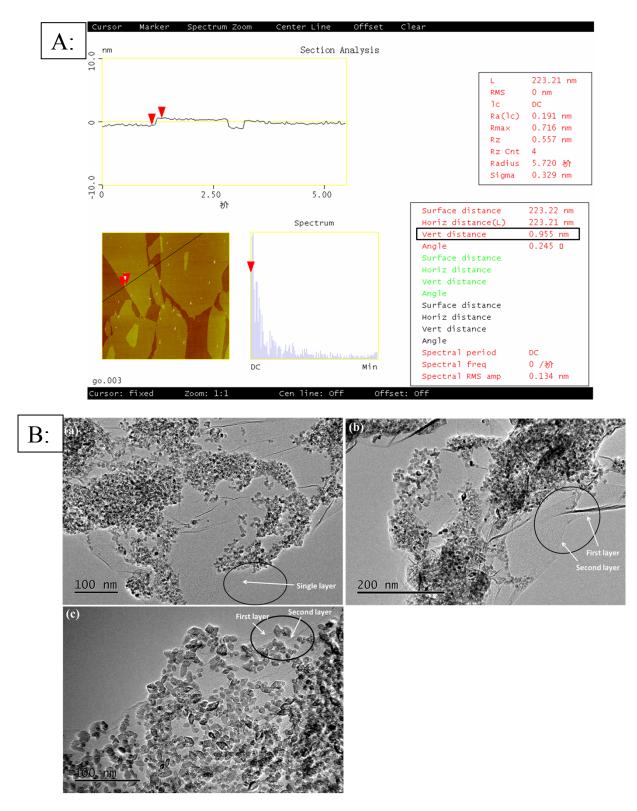


Fig. S1 HRTEM image of T-200. The (101) crystal face (3.52 Å) of anatase could be seen.



**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).

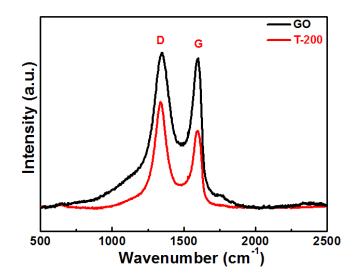
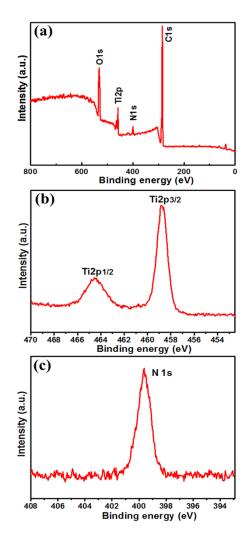


Fig. S3 Raman spectra ( $\lambda = 532 \text{ nm}$ ) of GO (black) and T-200 (red).



**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).

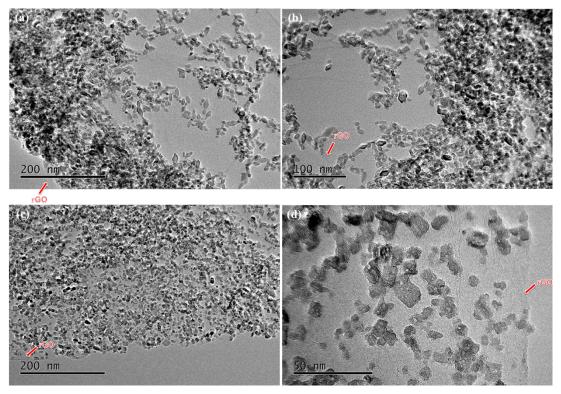


Fig. S5 TEM images of  $TiO_2$ -graphene with  $H_2O$  (a-b) and triethylene glycol (c-d) as the solvent respectively.

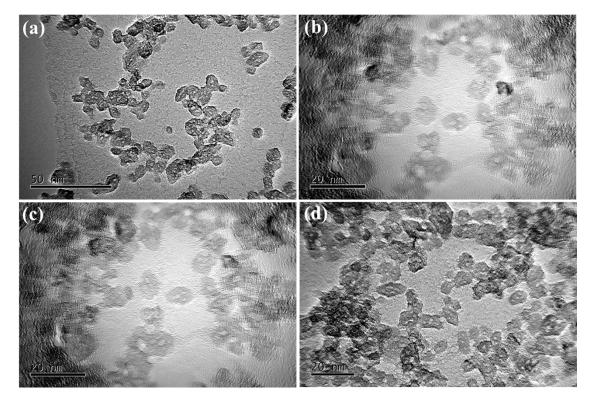


Fig. S6 TEM images (a-d) of  $TiO_2$ -graphene composites where the amount of PVP was quartered. When the amount of PVP was decreased, the  $TiO_2$  nanocrystals was not loaded so uniformly when comparing with **T-200**. However, the pores could still be seen clearly.

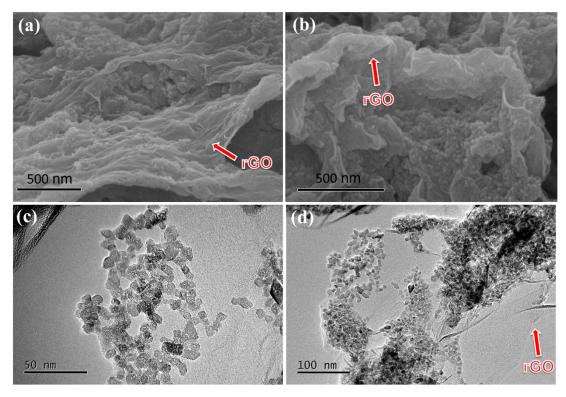


Fig. S7 SEM images (a-b) and TEM images (c-d) of  $TiO_2$ -graphene composites. It was found that when the PVP molecules were absent, the pores were still present. However, the  $TiO_2$  nanocrystals aggregated on the graphene surface.

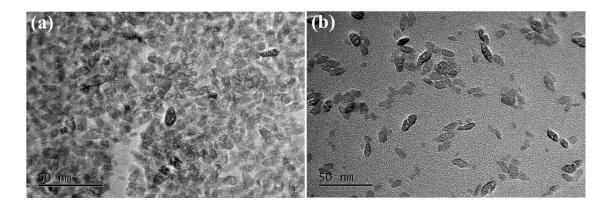
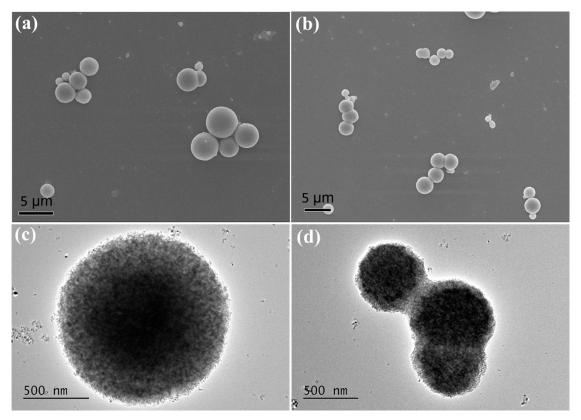
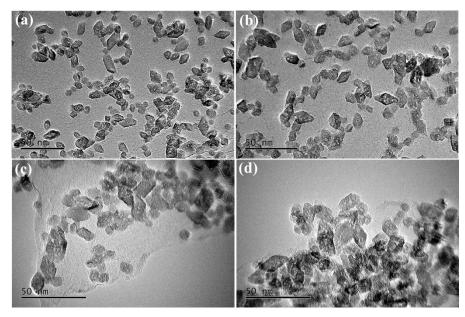


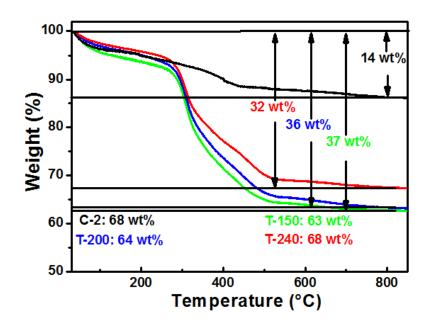
Fig. S8 TEM images (a, b) of  $TiO_2$  nanocrystals. The  $TiO_2$  nanocrystals were prepared using PVP as the stablizer.



**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 temprature 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.

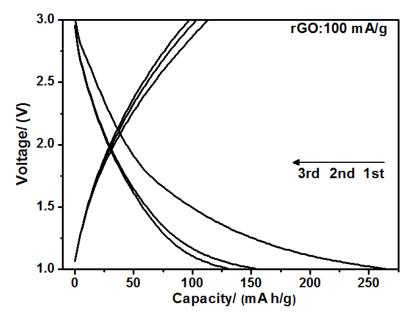


Fig. S12 Charge–discharge curves of rGO cycled at 1.0-3.0 V under a current density of 100 mA g<sup>-1</sup>.