Electronic Supplementary Material (ESI) for Nanoscale.

## ***Supporting Information for***

# Tuning and Understanding the Phase Interface of $TiO_2$ Nanoparticles for More Efficient Lithium Ion Storage

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## Material Characterizations

The morphology of samples were characterized using transmission electron microscopy (TEM, JEM-1200EX), selected area electron diffraction (SAED) and HRTEM (JEOL JEM 2010F, 200 kV). The Brunauer-Emmett-Teller (BET) specific surface area and the pore volume were measured using a Micromeritics TriStar Surface Area and Porosity Analyzer by nitrogen absorption/desorption. The phase structure of the samples was characterized by an X-ray Diffractometer (DX-2700, Haoyuan Corporation, China) equipped with Cu Kα radiation between 10 and 80°. Raman spectra were recorded using a Renishaw 2000 system with an Ar-ion laser (514.5 nm) at room temperature. Fourier transforms infrared (FT-IR) spectroscopy measurement was carried out with a Nicolet Nexus 5700 (Thermo Electron Corporation, USA) using KBr pellets. Electrochemical impedance spectroscopy (EIS) was carried out using a CHI750E electrochemical workstation (Chenhua, Shanghai).

**Lithium Ion Battery Performance.** The working electrodes were prepared by compressing a mixture of the active materials, acetylene black, and binder (polytetrafluoroethylene, PTFE) in a weight ratio of 75:15:10 onto pure Cu foil. Celgard 2400 was used as a separator, whereas the lithium foil as the counter electrode. Standard 1 M $LiPF_6$ in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 wt%, DAN VEC) mixture was used as the electrolyte solution. Pouch type half-cells were used to test the electrochemical properties of the active materials. A LAND-CT2001A galvanostatic test equipment was employed to measure electrochemical capacity and cycle life at room temperature of the working electrodes at various rates of 1 C, 2 C, 4 C, 6 C, and 8 C (1 C = 335 mA $g^{-1}$), respectively. The cut-off potentials for charge and discharge were set at 3.0 to 1.0 V (vs. $Li^+/Li$), respectively.

## Experimental Section

**Synthesis of $H_2Ti_3O_7$ nanosheets and their modification.** $H_2Ti_3O_7$ nanosheets were synthesized according to the established method.[1-3] First, titanate precipitate was prepared *via* a hydrothermal reaction between a 15 M NaOH solution and $TiOSO_4•xH_2O$ at 150 °C for 48 h. The precipitate was washed with deionized water and a 0.1 M HCl solution, respectively, followed by being washed with distilled water until pH reaches 7 and further being dried at 80 °C for 12 h. Then, $H_2Ti_3O_7$ nanosheets and triethoxysilane (APTES) were added into 100 mL of toluene and refluxed at 100 °C for 6 h. The resulting product was carefully washed using toluene and then dried at 80 °C for 12 h. Afterwards, the above-obtained product reacted with 1-pyrenebutyric acid for 12 h using 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC•HCl, 98.5%) as coupling agent. Finally, the pyrene surface modified $H_2Ti_3O_7$ nanosheets were centrifuged and dried at 40 °C for 12 h.

**Preparation of G.** The chemically converted G was obtained by the reduction of GO at 95 °C in a hydrazine solution at pH 10.[4-6]

**Preparation of $TiO_2$/G**. 144 mg of G was first dispersed in 1000 mL of water and sonicated at 40 KHz for 4 h to form a homogeneous suspension, followed by the addition of 336 mg of pyrene-modified $H_2Ti_3O_7$. The as-prepared mixture was sonicated for 12 h and filtered to obtain the $H_2Ti_3O_7$/G composite. The as-prepared composite was then calcined at 300, 600, and 700 °C, respectively, for 1 h in a nitrogen atmosphere, to afford the $TiO_2$/G hybrids with different $TiO_2$ phase.

**Table S1** Structural properties of the T(B)/G, T(A)/G and T(AB)/G obtained from $N_2$ sorption curves.

| Samples | Surface area ($m^2$ $g^{-1}$) | Pore Size (nm) | Pore volume ($cm^3$ $g^{-1}$) |
|---|---|---|---|
| T(B)/G | 144 | 4, 10 | 0.51 |
| T(AB)/G | 171 | 4, 10 | 0.55 |
| T(A)/G | 163 | 4, 14 | 0.48 |

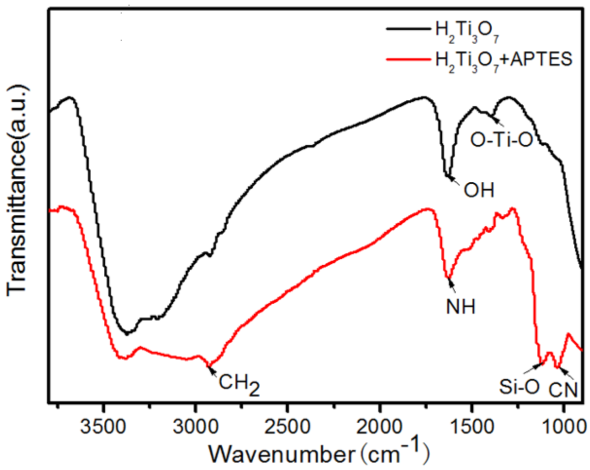

**Fig. S1** FTIR spectra of $H_2Ti_3O_7$ nanosheets before and after their modification with APTES.

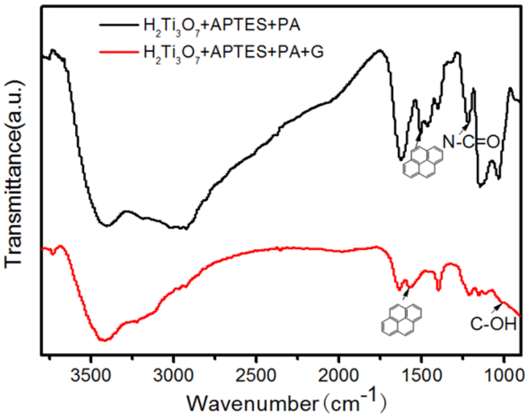

**Fig. S2** FTIR spectra of $H_2Ti_3O_7$ nanosheets grafted with PA and $H_2Ti_3O_7$/G nanosheets.

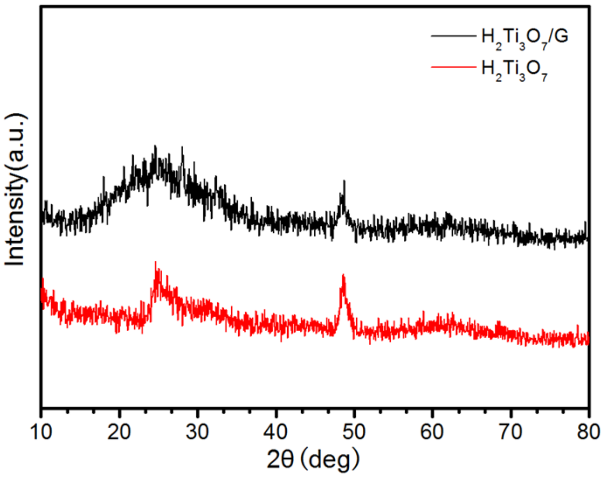

**Fig. S3** XRD patterns of $H_2Ti_3O_7$/G and $H_2Ti_3O_7$ nanosheets.

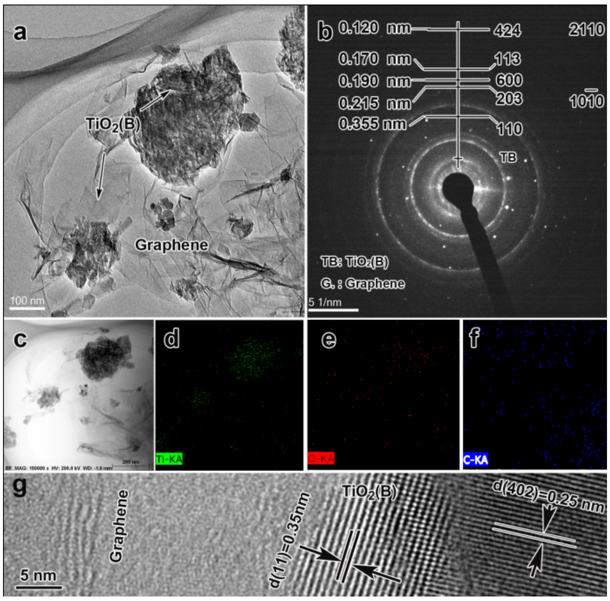

**Fig. S4** (a) TEM image, (b) SAED pattern, (c) STEM DF image, (d-f) elemental mapping and (g) HRTEM image of T(B)/G nanohybrids.

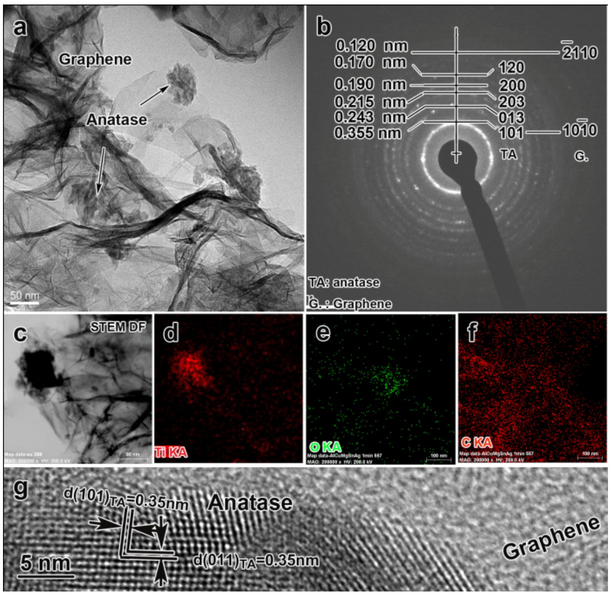

**Fig. S5** (a) TEM image, (b) SAED pattern, (c) STEM DF image, (d-f) elemental mapping and (g) HRTEM image of T(A)/G nanohybrids.

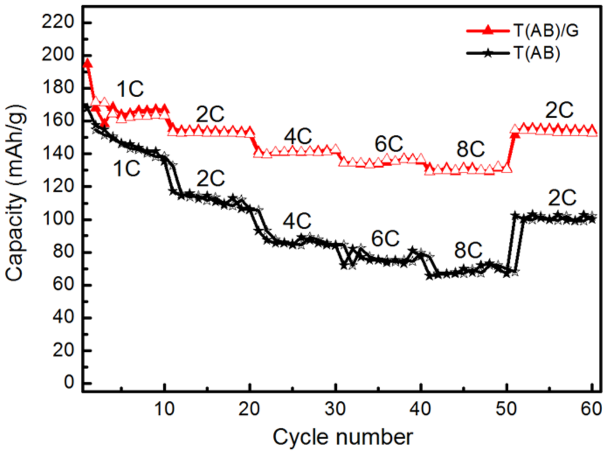

**Fig. S6** Specific capacity of T(AB)/G and T(AB) nanosheets at different C rates: 1 C, 2 C, 4 C, 6 C, and 8 C (1C = 335 mA g−1, open: charge, solid: discharge).

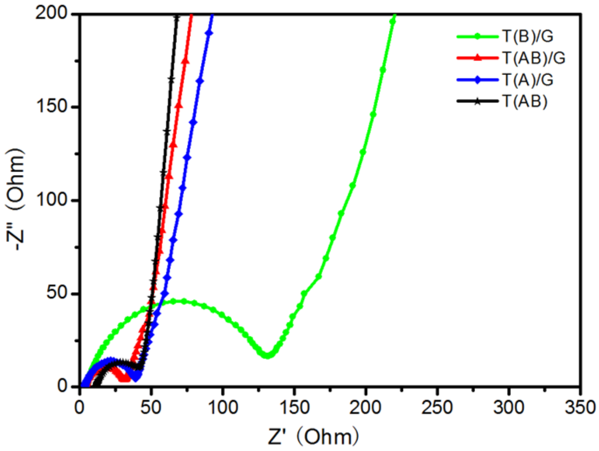

**Fig. S7** Nyquist plots of the electrodes based on T(AB)/G, T(A)/G, T(B)/G and T(AB) .

## References

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