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Supporting Information

## Hierarchical $\text{TiO}_{2-x}$ imbedded with graphene quantum dots for high-performance lithium storage

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## Experimental

### Materials preparation

#### Synthesis of ZIF-8 and ZIF-8 derived carbon (ZIF-8C)

ZIF-8 was prepared according to the previously reported works.<sup>S25,S26</sup> In a typical synthesis, 0.395 g of 2-Methylimidazole and 0.387 g of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  were dissolved in 30 mL of methanol to generate two solutions, respectively. Two solutions were mixed and aged for 24 h at room temperature. The as-prepared ZIF-8 were collected by washing with methanol and then dried at 70 °C in air. The white ZIF-8 was heated in a tube furnace at 800 °C and maintained for 4 h in Ar atmosphere, resulting in the formation of ZIF-8C black powder. After washed by 2 M HCl solution and DI water to remove the zinc residue, the product was dried at 60 °C, and then ZIF-8C was retrieved.

#### Preparation of GQDs

0.3 g of ZIF-8C powder was filled in the porous  $\text{SiO}_2$  griddle, the griddle was then transported into a Teflon-lined stainless autoclave with 2 mL of  $\text{HNO}_3$ . After sealling at 160 °C for 5 h, the product was washed with 50 mL of DI water. The yellow filtrate was then transferred into dialysis bag for a week and labelled as GQD solution.

#### Synthesis of $\text{TiO}_{2-x}$ /GQDs hybrid

In a typical synthesis, 5 mL of graphene quantum dots (1 mg/mL) solution was added to 50 mL of 2 M of  $\text{TiCl}_4$  solution in a glass beaker (100 mL). The glass beaker was then sealed and held over an ultrasonic water bath for 20 min, and then the mixture was kept in magnetic stirring at 50 °C for 24 h. After finished reaction, the product was washed with DI water and ethanol for several times, followed by vacuum-drying at 70 °C for 6 h, then calcined in Ar (5%  $\text{H}_2$ ) atmosphere for 2h.

### Characterizations of the samples

The crystalline structures of the as-prepared samples were characterized by X-ray diffraction spectrometry (XRD) on a Rigaku Ultima IV using  $\text{Cu K}\alpha$  radiation (40 kV, 40 mA). Raman spectroscopy (InVia Reflex) was performed with a Renishaw inVia Reflex Raman system using a 532 nm Nd:YAG excitation source. The morphological observation of the as-prepared samples were performed by scanning electron microscopy (SEM, Hitachi S4800 instrument), transmission electron microscopy (TEM, FEI F20 S-TWIN 0 instrument), and selected area electron diffraction (SAED), respectively.  $\text{N}_2$  adsorption-desorption isotherms were carried out on a Micro-meritics ASAP 2020 instrument (Micromeritics, Norcross, GA, USA), pore volumes were determined using the adsorbed volume at a relative pressure of 0.99. The pore size distribution of the as-prepared samples was analyzed using the Barrett-Joyner-Halenda (BJH) method based on the adsorption branch.

### Electrochemical measurements

The lithium storage performances of the as-prepared electrodes were tested using CR2025-type coin cells, in which the 1 M  $\text{LiPF}_6$  solution in the mixture of EC, DEC, and EMC with a mass ration of 1:1:1 were used as the electrolyte solution, the metallic Li was used as a counter electrode, and Celgard 2400 microporous polypropylene membrane was used as a separator, the working electrodes were made of 70%  $\text{TiO}_{2-x}$ /GQDs hybrid, 20% of acetylene black carbon (AC), and 10% of polyvinylidene fluoride (PVDF). The active materials were painted uniformly on the copper foil with 1.2-1.5  $\text{mg cm}^{-2}$  mass loading, and dried at 110 °C under the vacuum for one night. The cells were assembled in a glove box filled with highly pure argon gas ( $\text{O}_2$  and  $\text{H}_2\text{O}$  levels < 0.1 ppm). The electrochemical properties of  $\text{TiO}_{2-x}$ /GQDs anode were evaluated by Cyclic voltammetry (CV) with a scan rate of 0.5  $\text{mV s}^{-1}$  in the potential range from 3.0 to 1.0 V (vs.  $\text{Li/Li}^+$ ). Galvanostatic charge-discharge measurements were performed on an electrochemical workstation (Land CT 2001A, Wuhan, China). Electrochemical impedance spectroscopy (EIS) measurements were carried out on an electrochemical workstation (Chenhua CHI660c, Shanghai, China), and excitation voltage applied to the cells was 5 mV.

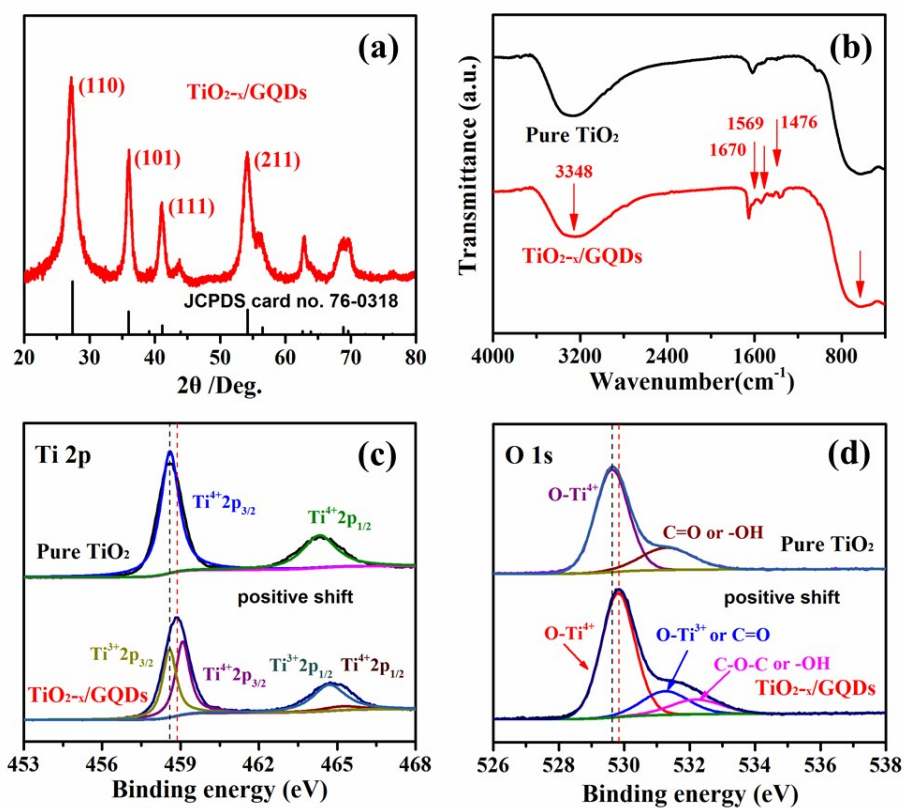


Figure S1 (a) XRD pattern, (b) FT-IR spectra, (c) Ti 2p XPS spectra and (d) O 1s XPS spectra of  $\text{TiO}_2\text{-x/GQDs}$  and pure  $\text{TiO}_2$ , respectively.

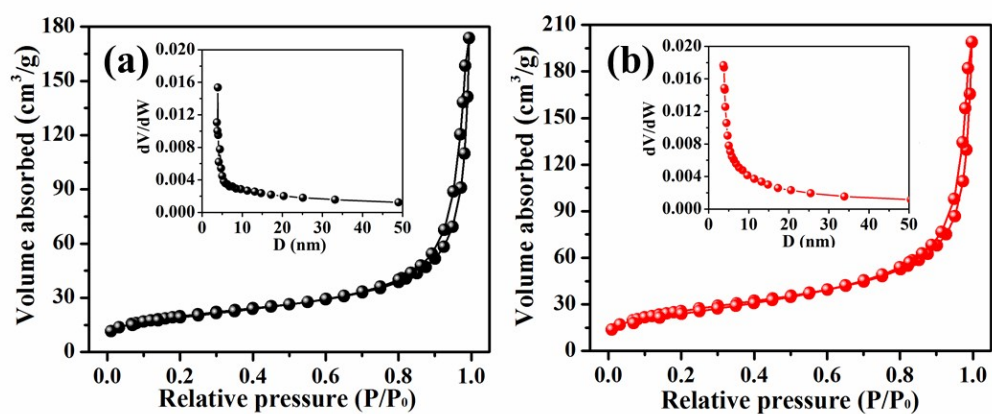
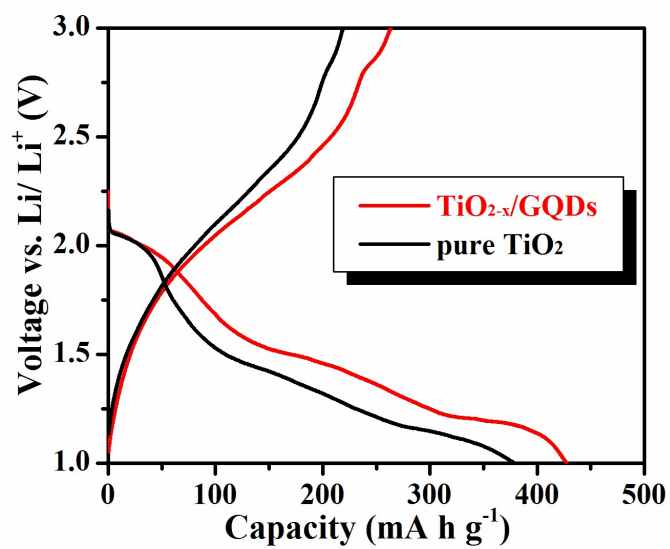
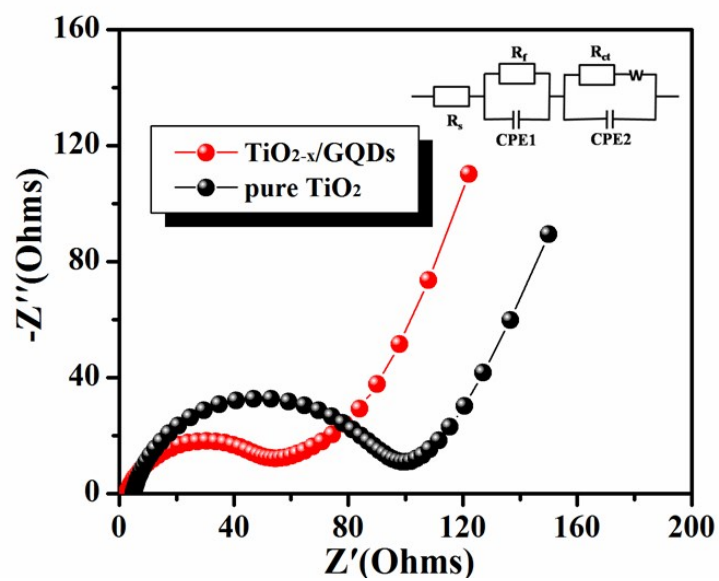


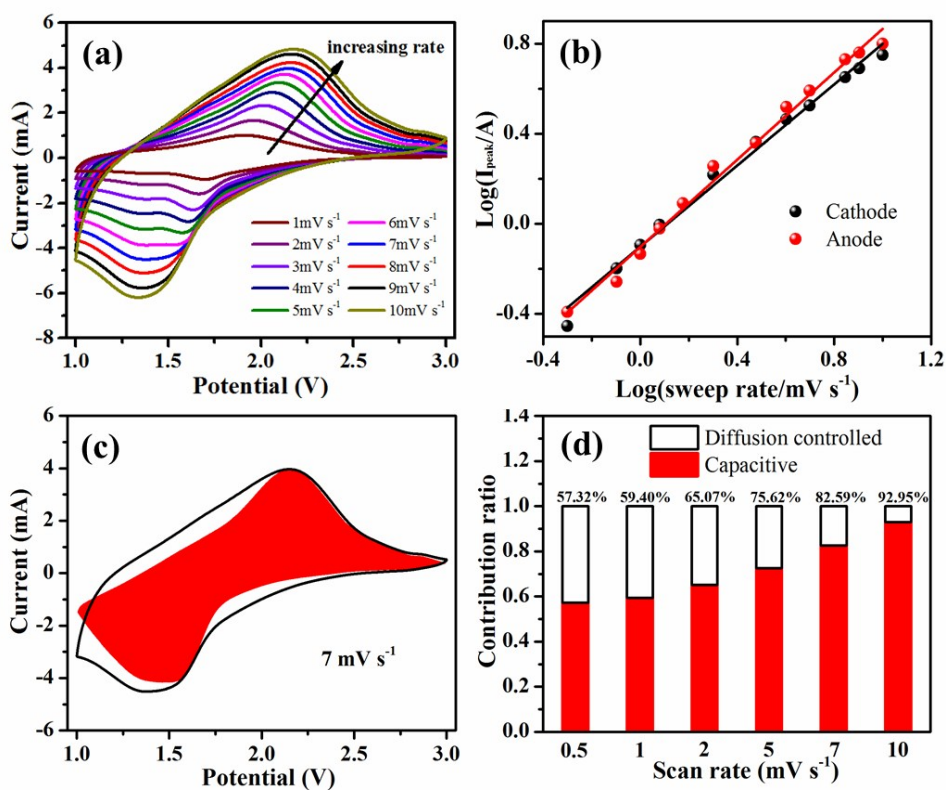
Figure S2 N<sub>2</sub> adsorption-desorption isotherms of (a) pure TiO<sub>2</sub> and (b) TiO<sub>2-x</sub>/GQDs, respectively.



**Figure S3** Initial charge-discharge profiles of pure TiO<sub>2</sub> and TiO<sub>2-x</sub>/GQDs at current rate of 1C.



**Figure S4** Impedance plots of pure  $\text{TiO}_2$  and  $\text{TiO}_{2-x}/\text{GQDs}$  anodes after 20 cycles at 2 C (Inset: the equivalent circuit used to fit the experimental data).



**Figure S5** Kinetics analysis of the electrochemical behavior toward  $\text{Li}^+$  for the  $\text{TiO}_{2-x}/\text{GQDs}$  anode. (a) CV curves at various scan rates from 0.5 to  $10 \text{ mV s}^{-1}$ , (b) determination of the b-value based on the relationship between peak current and scan rate, (c) separation of the capacitive and diffusion currents at a scan rate of  $7 \text{ mV s}^{-1}$ , and (d) contribution ratio of the capacitive and diffusion-controlled charge at various scan rates, respectively.

## References

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S26 N. L. Torad, M. Hu, Y. Kamachi, K. Takai, M. Imura, M. Naito and Y. Yamauchi, *Chem. Commun.*, 2013, **49**, 2521-2523.