

## Electronic Supplementary Material for

### Spontaneous Redox-Reaction-Mediated Interface Charge Transfer in Titanium Dioxide/Graphene Oxide Nanoanodes toward the Rapid and Durable Lithium Storage

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## 1. Experimental section

### 1.1. Materials synthesis and characterization

P25 powders were purchased from Degussa Co., Ltd. Other analytical grade chemicals were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. All reagents were used directly without any further purification. GO material with a concentration of  $1 \text{ mg mL}^{-1}$  was obtained by a modified Hummers method.<sup>25</sup> P25 powders were reduced by  $\text{NaBH}_4$  solution to generate oxygen vacancies. Typically, P25 powders (0.5 g) were transferred to a freshly synthesized  $\text{NaBH}_4$  solution (100 mL) with various concentrations (50 mM, 1 M, and 2 M). The mixture was gently agitated for 1 h at ambient temperature. The sample was collected via centrifugation, followed by three washes with deionized water and a final drying at  $60 \text{ }^\circ\text{C}$  for 12 h. The modified sample was named as  $\text{TiO}_2\text{-}x$  ( $x = 50 \text{ mM}$ , 1 M, and 2 M) and redispersed in DI water with a sample concentration of  $5 \text{ mg mL}^{-1}$ . The solution-phase reduced P25 sample was then mixed with the as prepared GO solution with a proportion of 100:3. The mixed solution was stirred for 2 h and then freeze-dried. The composites were named as  $\text{GTiO}_2\text{-}x$  ( $x = 50 \text{ mM}$ , 1 M, and 2 M). As a control, the as received P25 powders were also mixed with GO and named as  $\text{GTiO}_2\text{-AR}$ .

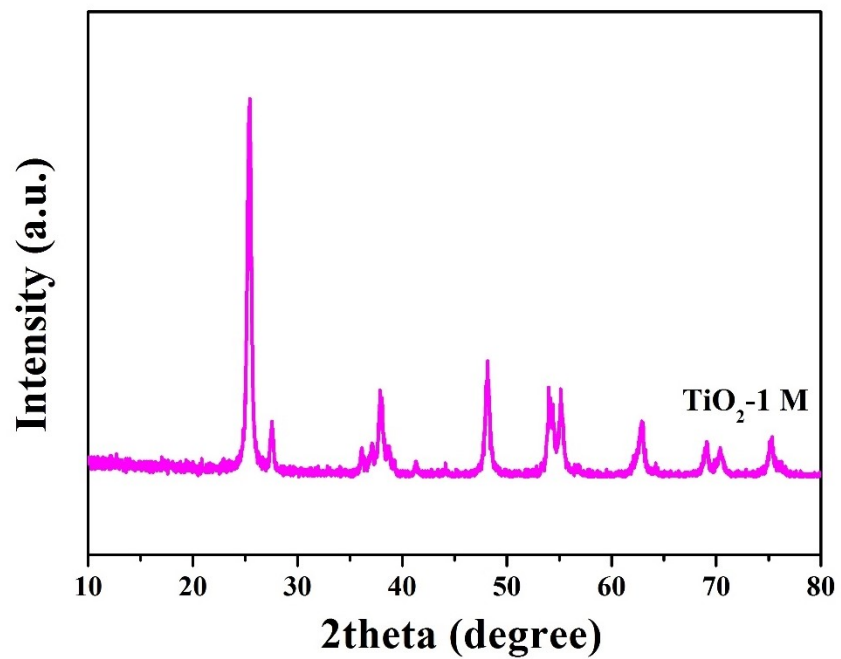
X-ray diffraction (XRD) characterization was carried out on a DX-2500 X-ray diffractometer with  $\text{Cu-K}\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). scanning electron microscopy (SEM) and transmission electron microscopy were obtained with a Hitachi S-4800 (15 kV) and a JEM 2100F (200 kV). The X-ray photoelectron spectroscopy (XPS) was executed using a Thermo Scientific  $\text{K}\alpha$  XPS spectrometer. Fourier transform infrared spectrometry (FTIR) and Raman were performed using Nicolet IS 10 and LabRam HR Evolution. The Brunauer-Emmett-Teller (BET) specific surface area and Barret-Joyner-Halenda (BJH) pore structure of the samples were measured and analyzed by a surface area-pore size analyzer (SSA-4300).

### 1.2. Electrochemical measurements

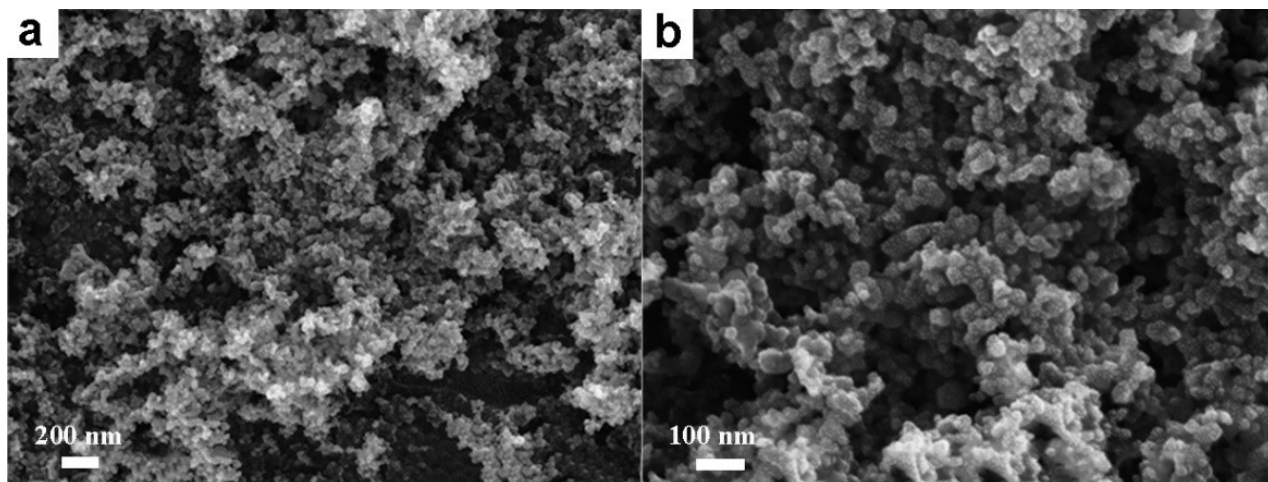
To measure the electrochemical performance, the CR2032 coin cells were mounted in an glovebox filled with argon. The working electrodes were prepared as follows. Active materials (80 wt%), acetylene back (10 wt%), and poly(vinylidene fluoride) binder (10 wt%) were mixed in N-methyl-2-pyrrolidinone solvent. The

mixture was stirred for 3 h to obtain a homogeneous slurry, which was then coated on a Cu foil that used as current collector, and heated in a vacuum oven at 60 °C for 8 h. The disks ( $\Phi$  12 mm) were cut from the electrode and subjected to vacuum oven drying for 8 h at 120 °C. As for the counter/reference electrode and separator, the common lithium foil and Celgard 2400 were employed, respectively. The electrolyte was  $\text{LiPF}_6$  (1 M) dissolved in a mixture of ethylene carbonate (EC) and dimethylcarbonate (DMC) (weight ratio 1:1). All cells were standing for 24 h before tests. The electrochemical performance was measured by using LAND CT2001A apparatus. The charge-discharge curves and cyclic performance were tested at 1 C between the potential range from 0.01 to 3.0 V. The rate capability was collected at various current densities ranging from 1 C to 50 C. The CV curves were measured at a scan rate of 0.2  $\text{mV s}^{-1}$  between 0.01 V and 3.0 V on an electrochemical workstation (CHI1000C, Chenhua Instrument, Shanghai).

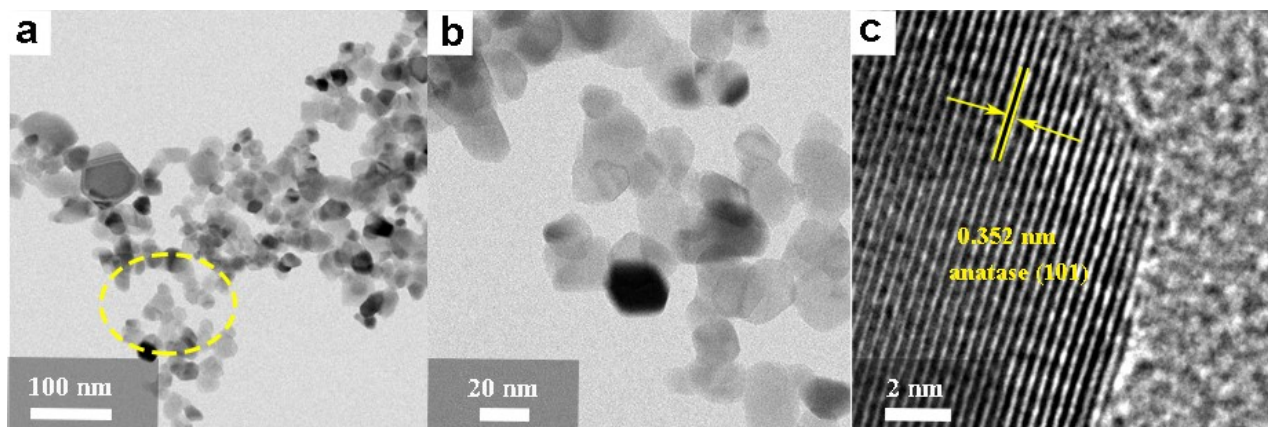
## 2. Supplementary figures



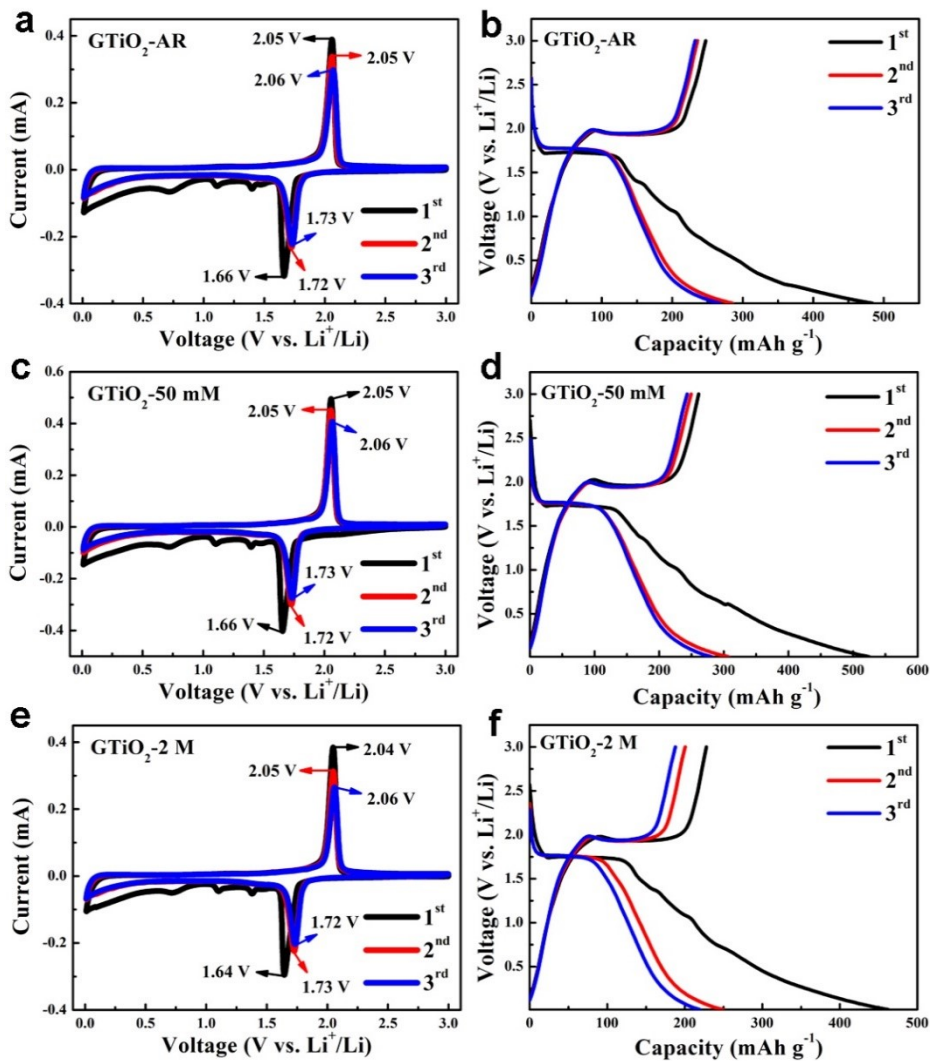
**Figure S1.** XRD pattern of TiO<sub>2</sub>-1 M sample.



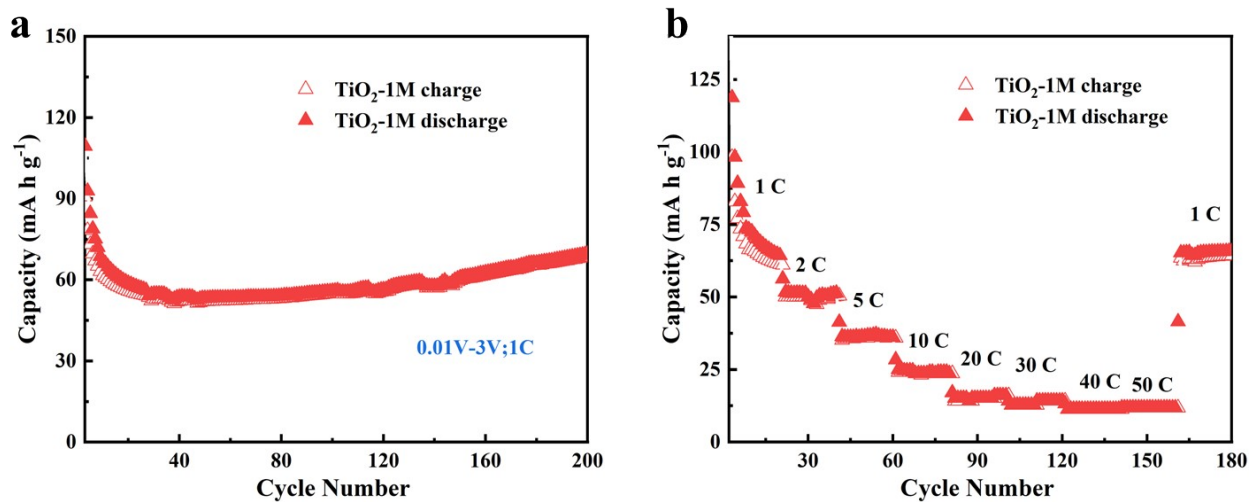
**Figure S2.** (a) Low- and (b) high-magnification SEM images of TiO<sub>2</sub>-1 M sample.



**Figure S3.** (a, b) TEM and (c) HRTEM images of  $\text{TiO}_2$ -1 M sample.



**Figure S4.** (a, c, e) CV curves of the electrodes for the first three cycles between potential window of 0.01 - 3.0 V (vs. Li<sup>+</sup>/Li) at a scan rate of 0.2 mVs<sup>-1</sup>, and (b, d, f) galvanostatic charge-discharge voltage profiles of the samples for the first three cycles between 0.01 and 3.0 V (vs. Li<sup>+</sup>/Li) at a current density of 1 C. (a, b) GTiO<sub>2</sub>-AR, (c, d) GTiO<sub>2</sub>-50 mM, and (e, f) GTiO<sub>2</sub>-2 M.



**Figure S5.** Cycling stability and rate capability of the TiO<sub>2</sub>-1 M sample.