Supporting Information

A Sol-Gel Design Strategy Towards Ultra-dispersed TiO_2 Nanoparticles on Graphene for High-Performance Lithium Ion Batteries

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Experimental Section

Chemicals. Concentrated H_2SO_4, KNO_3, $KMnO_4$, tetrabutyl titanate (TBOT) and ethanol were of analytical grade and purchased from Shanghai Chemical Corp. Concentrated ammonia solution (28 - 30 wt%) and graphite were purchased from Sigma–Aldrich. All chemicals were used as received without further purification. Deionized water was used for all experiments.

Synthesis of Graphene Oxide (GO). GO was synthesized from graphite *via* a modified Hummers method. Briefly, the commercial graphite (5.0 g) was added into a solution of concentrated H_2SO_4 (115 mL) cooled in an ice-water bath. KNO_3 (2.5 g) and $KMnO_4$ (15 g) were added very slowly (with a period more than 15 min) into the mixture. All the operations were carried out very slowly in a fume hood. The solution was allowed to stir in an ice-water bath for 2 h, then at 35 °C for 1 h. Afterwards, 115 mL of water was added to the flask. After 1 h, 700 mL of water was added. After 15 min, the solution was removed from the oil bath and 50 mL of 30% H_2O_2 were added to end the reaction. This suspension was stirred at room temperature for 5 min. The suspension was then repeatedly centrifuged and washed twice with 5% HCl solution and then dialyzed for a week.

Synthesis of the TiO_2 nanocrystals/RGO sheets. The TiO_2 nanocrystals/RGO sheets were prepared *via* a simple sol-gel design approach. In detail, GO was transferred from the as-made suspension to ethanol and sonicated in an ultrasound bath cleaner for 6 h, then centrifuged and re-dispersed in pure ethanol with a concentration of ~ 0.05 mg/mL. In the first sol-gel process, a low content of concentrated ammonia solution (0.10 mL, ~ 28 wt%) was added into 100 mL of the GO sheets ethanol suspension. After stirring for 30 min at 25 °C, 0.75 mL of TBOT was added dropwise to the above solution. The mixture was then kept at 25 °C with stirring for 24 h to uniformly create the amorphous TiO_2 nanoparticles on the GO sheets. The as-made composites were collected by centrifugation and washing with water, then dried at 60 °C overnight. In the second thermal treatment process, the as-made TiO_2/GO composites were calcined at 500 °C in Ar for 2 h to give rise to the grain growth of TiO_2 nanoparticles and the reduction of graphene oxide.

Electrochemical Tests: The working electrodes were prepared by mixing the TiO_2 nanocrystals/RGO sheets, Super P, and polyvinylidene difluoride (PVDF) at a weight ratio of 85:10:5, and dissolved in N-methyl-2-pyrrolidinone (NMP). Then, the slurries of the mixture were cast onto a copper foil current collector. After coating, the

electrodes were dried at 80 °C for 1 h to remove the solvent before pressing. The electrodes were punched in the form of disks typically with a diameter of ~ 12 mm, then vacuum-dried at 80 °C for 24 h. The mass loading of the working electrode materials was ~ 5 mg. The weight ratio of the active material TiO_2 was ~ 52 wt%. The cell assembly was operated in a glove box (model 100G, MBraun, Germany) filled with a high purity argon. The electrolyte solution was 1.0 M $LiPF_6$/ethylene carbonate (EC)/diethyl carbonate (DMC)/ethyl methyl carbonate (EMC) (1: 1: 1 by volume). The cells were assembled with the as-prepared positive electrode, lithium metal, and separators made of a Celgard 2300 film. The electrochemical tests of the samples were evaluated using an automatic battery testing system (LAND CT2001A model). The specific capacity of the electrode material was calculated from the weight of the TiO_2 nanocrystals/RGO sheets.

Characterization. Wide-angle XRD patterns were recorded on a Bruker D8 diffractometer (Germany) with Ni-filtered Cu Kα radiation (40 kV, 40 mA). Nitrogen sorption isotherms were measured at 77 K with a Micromeritcs Tristar 3020 analyzer. All of the samples were degassed under vacuum at 180 °C for at least 8 h prior to measurement. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas using adsorption data in a relative pressure range from 0.05 to 0.25. The pore size distributions (PSD) were derived from the adsorption branch of the isotherms using the Barrett-Joyner-Halenda (BJH) model. Thermogravimetric analysis was conducted on a Mettler Toledo TGA-SDTA851 analyzer (Switzerland) from 40 to 800 °C under O_2 with a heating rate of 10 °C/min. Transmission electron microscopy (TEM) experiments were conducted on a JEOL JEM-2100 F microscope (Japan) operated at 200 kV. The samples for the TEM measurements were suspended in ethanol and supported onto a holey carbon film on a Cu grid. The particle size distribution curve was derived from 200 TiO_2 nanoparticles. Field-emission scanning electron microscopy (FESEM) images were taken on a Hitachi S-4800 microscope. Raman spectra were collected by using Raman microscopes (Renishaw, UK) under a 632.8 nm excitation

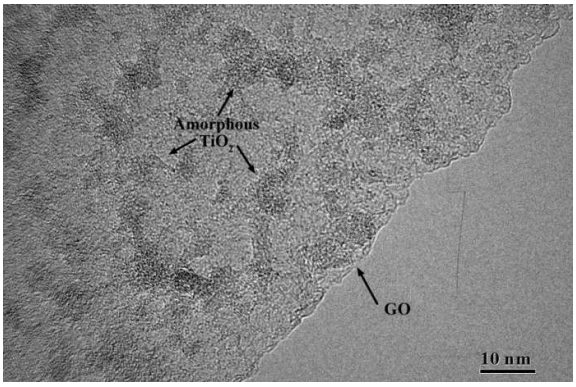

Figure S1. HRTEM image of the amorphous TiO_2/GO nanosheets. The amorphous TiO_2 nanoparticles and the edge of GO (≤ 3 layers) can be clearly observed as indicated by the arrows.

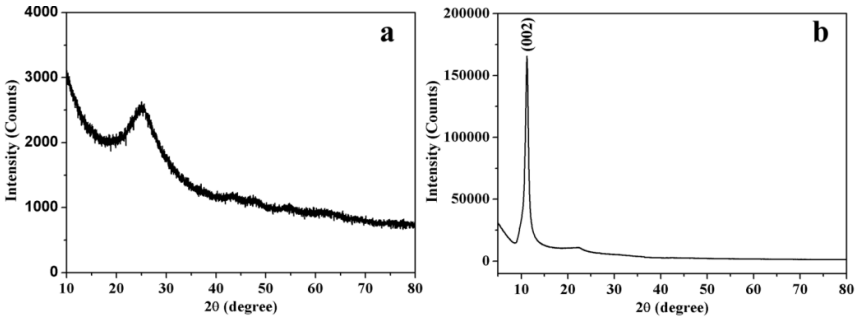

Figure S2. XRD patterns of (a) the amorphous TiO_2/GO sheets prepared *via* the sol-gel design strategy with 0.1 mL ammonia and (b) the initial GO sheets obtained by directly drying the GO suspension at 60 °C.

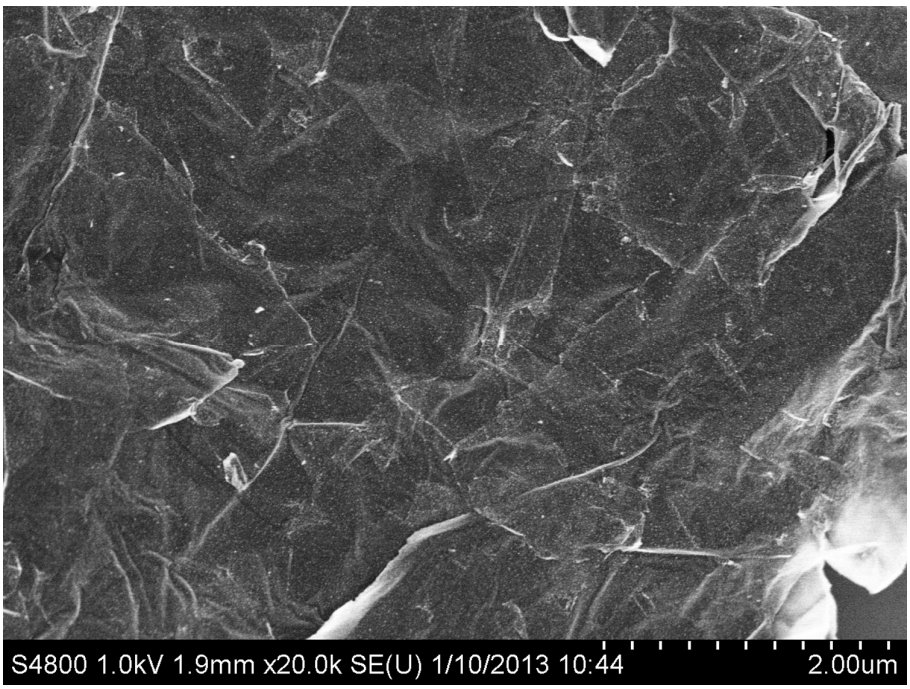

Figure S3. The FESEM image of the TiO_2 nanocrystals/RGO sheets prepared *via* the sol-gel design strategy with 0.1 mL ammonia and a calcination at 500 °C in Ar.

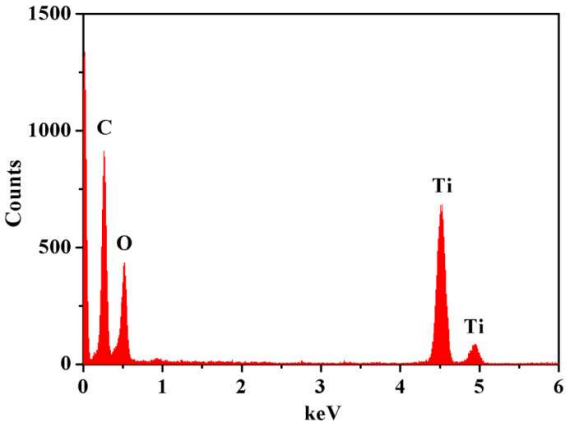

Figure S4. The energy dispersive X-ray (EDX) spectrum of the TiO_2 nanocrystals/RGO sheets prepared *via* the sol-gel design strategy with 0.1 mL ammonia and a calcination at 500 °C in Ar.

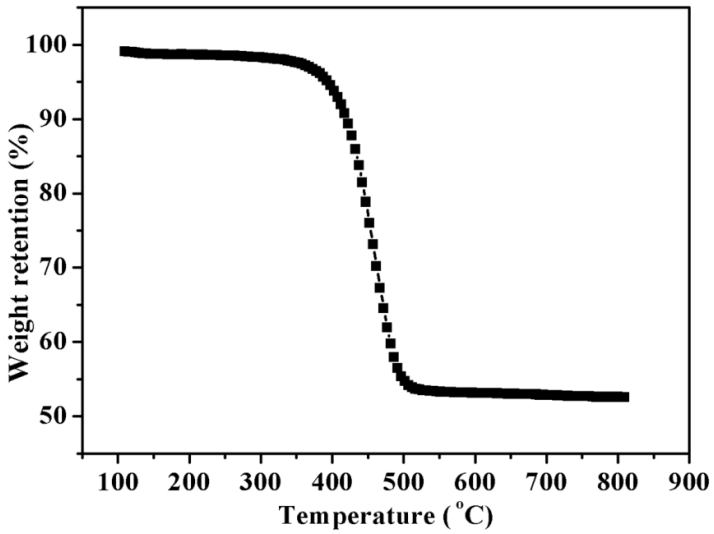

Figure S5. A typical TGA curve obtained for the TiO_2 nanocrystals/RGO sheets under O_2. Approximately 48% weight loss was observed at a temperature around 450 °C.

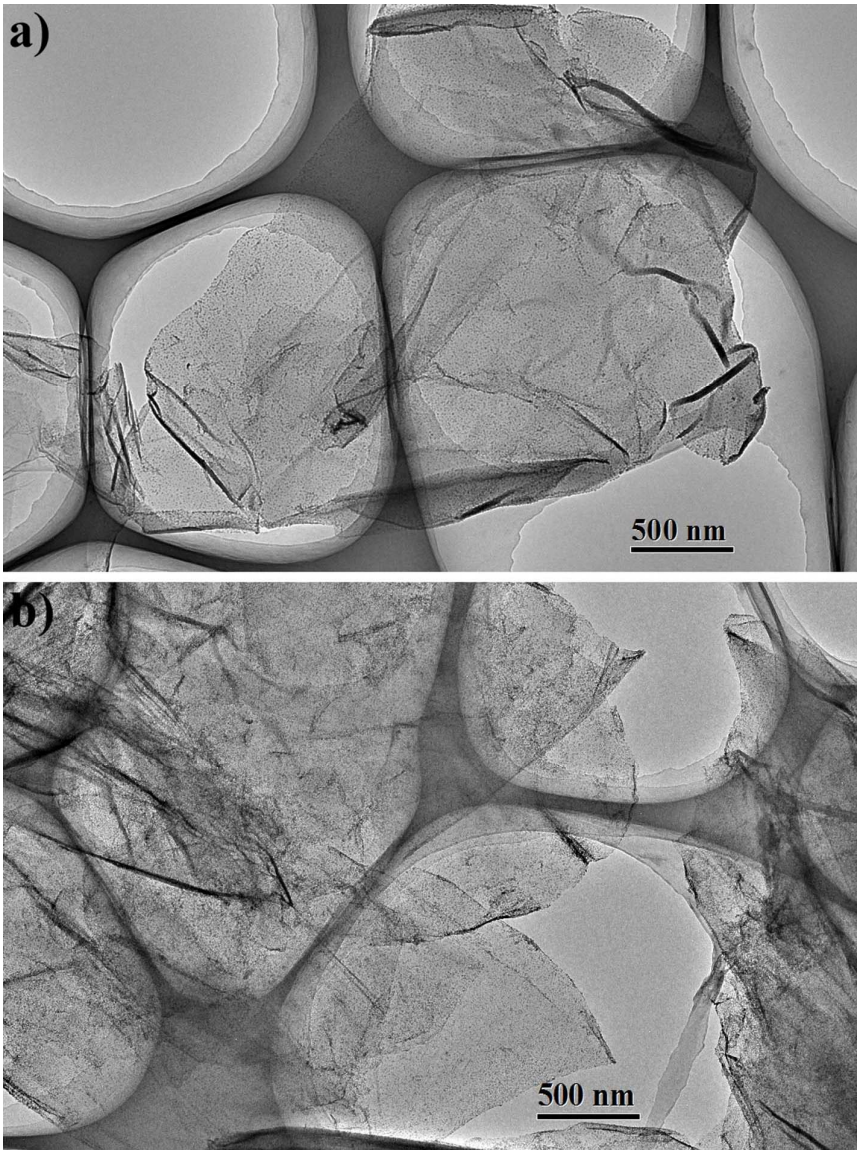

Figure S6. TEM images of the TiO_2 nanocrystals/RGO sheets prepared *via* the sol-gel design strategy with 0.1 mL ammonia and a calcination at 500 °C in Ar.

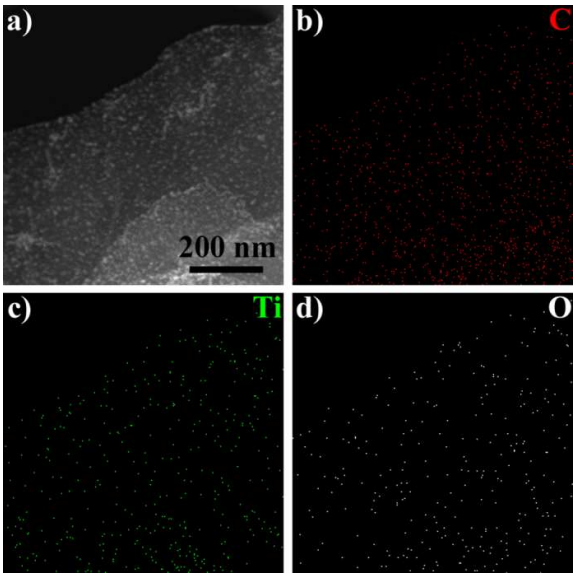

Figure S7. (a) The STEM image of the TiO_2 nanocrystals/RGO sheets prepared *via* the sol-gel design strategy with 0.1 mL ammonia and a calcination at 500 °C in Ar. (b-d) The corresponding EDX elemental maps of C, Ti and O, respectively. It clearly shows that the TiO_2 nanoparticles are uniformly dispersed on graphene sheets.

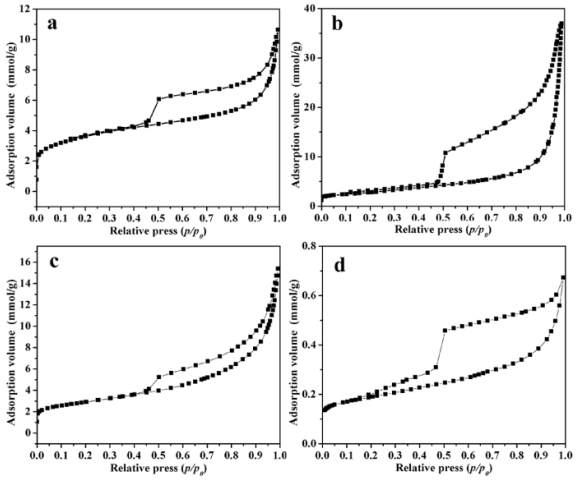

Figure S8. N_2 sorption isotherms of (a) the amorphous TiO_2/GO sheets prepared *via* the sol-gel design strategy with 0.1 mL ammonia, (b) the freeze-dried GO sheets obtained by freeze-drying the initial GO suspension, (c) the TiO_2 nanocrystals/RGO sheets *via* the sol-gel design strategy with 0.1 mL ammonia and a calcination at 500 °C in Ar and (d) the RGO sheets obtained by directly reducing the initial GO sheets.

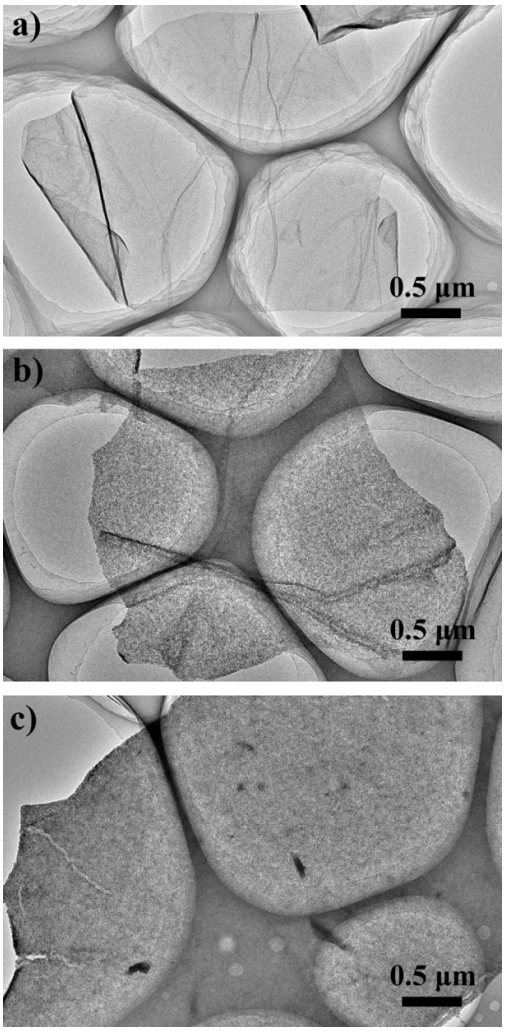

Figure S9. TEM images of the amorphous TiO_2/GO sheets prepared *via* the sol-gel design strategy with different content of ammonia: (a) 0.1 mL, (b) 0.2 mL and (c) 0.3 mL. It can be clearly observed that the density and thickness of the amorphous TiO_2 layer is well controlled by varying the content of ammonia in the system.

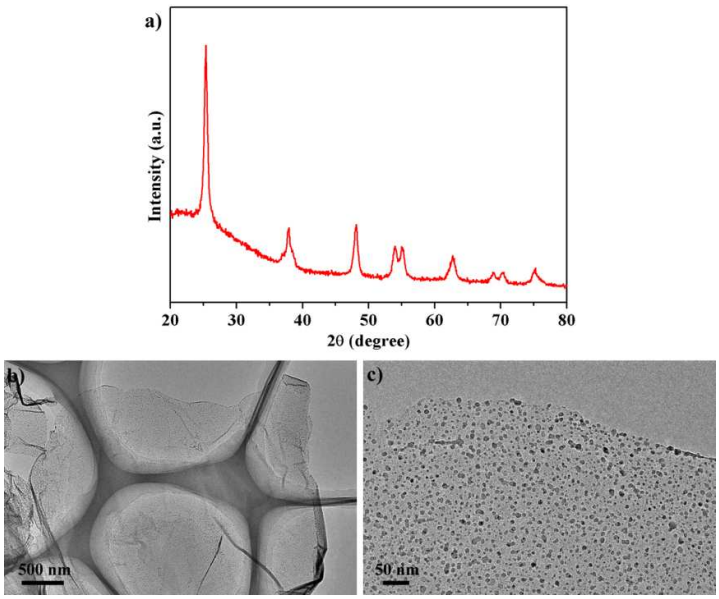

Figure S10. (a) The XRD pattern and (b, c) TEM images of the TiO_2 nanocrystals/RGO sheets prepared *via* the sol-gel design strategy with 0.1 mL ammonia and a calcination at 700 °C in Ar. Compared with the samples calcinated at 500 °C, the crystallinity of the TiO_2 nanoparticles can be effectively improved; and simultaneously, the fascinating nanostructures of the hybrid materials can be well retained.

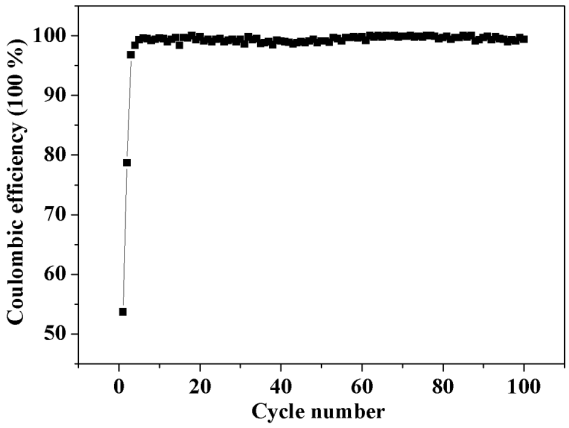

Figure S11. The Coulombic efficiency of the TiO_2 nanocrystals/RGO sheets electrode at a current density of 0.1 A g^{-1} (~ 0.59 C).

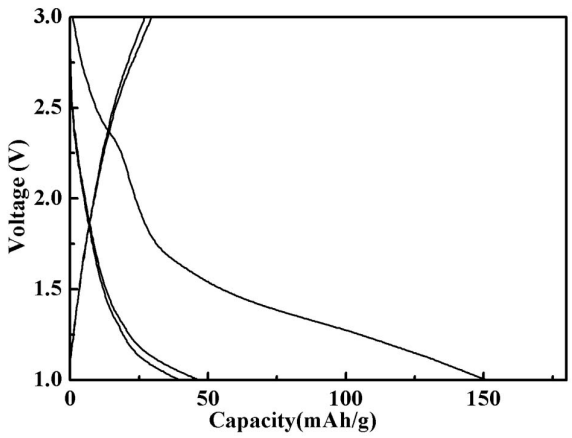

Figure S12. Charge–discharge curves of the RGO sheets from the pure GO ones at a current density of 0.1 A g^{-1} (~ 0.59 C).

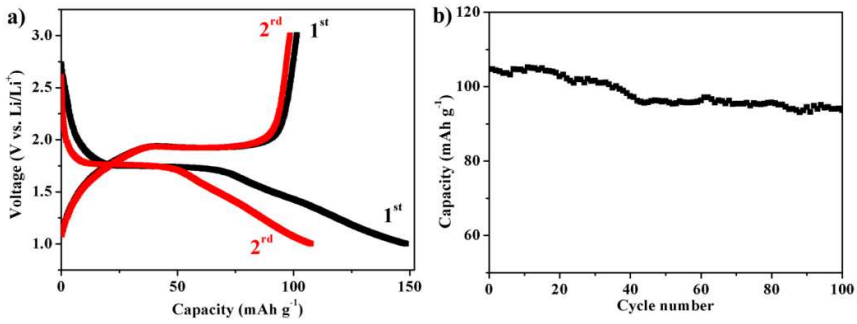

Figure S13. (a) Charge–discharge curves and (b) cycling performance of the mechanically mixed TiO_2-RGO composites electrode at a current density of 0.1 A g^{-1} (~ 0.59 C).

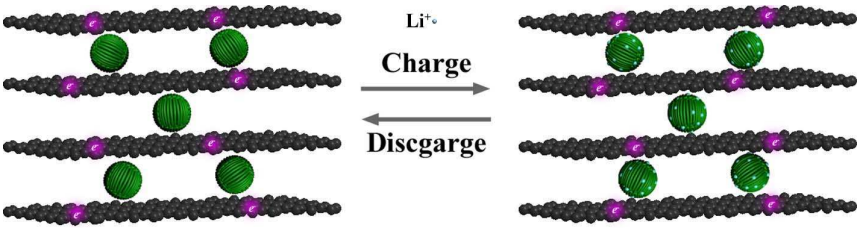

Figure S14. Schematic drawing of the charge/discharge processes of the TiO_2 nanocrystals/RGO sheets anode.