

Supporting Information

Effective Wrapping of Graphene on Individual $\text{Li}_4\text{Ti}_5\text{O}_{12}$ Grains for High-Rate Li-Ion Batteries

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Experimental Methods

Preparation of Graphene Oxide: Graphene oxide was synthesized from natural graphite flakes (325 mesh, Sigma-Aldrich) by modified Hummers' method.¹ In an ice bath, 1 g of graphite, 1 g of NaNO_3 , and 46 ml of concentrated H_2SO_4 were stirred for 30 min. Then, 5 g of KMnO_4 was slowly added into the mixture and stirred at 35°C. After 2 h, 100 ml of deionized (DI) water was slowly added to the mixture and stirred for 30 min at 98°C. In order to reduce the residual permanganate (MnO_4^-) and MnO_2 to soluble MnSO_4 , 8 ml of H_2O_2 (30%) was slowly added to the solution. The solution was centrifuged and washed with HCl (10%) and DI water, and the final product was dried in vacuum overnight. The dried graphite oxide was added to DI water, and the mixture was sonicated for 2 h to exfoliate the graphite

oxide to graphene oxide. In order to confirm the formation of graphite oxide, x-ray diffraction (XRD) was measured. The peak shift of the (002) plane from 3.39 Å to 8.16 Å by XRD was observed (Fig. S8), confirming graphite oxide. The atomic force microscopy (AFM) observation of graphene oxides clearly revealed that the synthesized graphene oxides by Hummers' method had a width of $\sim 3 \mu\text{m}$ and a thickness of $\sim 1 \text{ nm}$ (Fig. S9, Supporting Information). Since graphene, by definition, is a one-atom-thick layer of graphite, the graphene used in this study should be referred to as reduced graphene oxide. The terminology "graphene" is used throughout this article for convenience's sake.

Synthesis of Graphene-Wrapped LTO: 0.5 g of P25 (TiO_2 nanoparticles with $\sim 25 \text{ nm}$ in diameter: Degussa) nanoparticles were dispersed in distilled water by ultrasonication for 1 h. Then, the P25 aqueous solution was added into the different amounts of 0.5 mg ml^{-1} graphene-oxide aqueous solution under magnetic stirring at pH 2, and the relative amounts of graphene oxide with respect to P25 corresponded to 5, 10, or 15 wt. %. After 4 h, the product was collected by centrifugation, and was dried at room temperature in vacuum overnight. Then, the resultant graphene-oxide-wrapped P25 nanoparticles were mixed mechanically with Li_2CO_3 (as a lithium precursor) at a Li:Ti molar ratio of 4.1:5 using acetone to form a slurry. Finally, the resulting products were annealed at 850°C for 10 h under H_2/Ar (4 vol. % H_2 in argon) atmosphere. After the pyrolysis, the graphene oxide turned into graphene (reduced graphene oxide), and the resultant graphene contents were found to be 1.0, 2.1, or 4.5 wt. % in graphene-wrapped LTO. For comparison, bare $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was also prepared in a similar manner without the use of graphene oxide. The XRD peaks (Fig. S10) of the bare and graphene-wrapped LTO particles with various amounts of the graphene (1.0, 2.1, or 4.5 wt. % of graphene) were ascribed to the pure phase of well-crystallized LTO^2 with negligible impurity phases such as Li_2TiO_3 , TiO_2 , and so on.

Materials Characterization: The crystal structure of the prepared samples was characterized by XRD (New D8 Advance: Bruker). The morphology of synthesized materials was analyzed using field-emission scanning electron microscopy (FE-SEM, SU70: Hitachi), and transmission electron microscopy (TEM) was carried out on a JEOL 2100 microscope operated at 200 kV. The relative compositions of graphene were measured using CHNS

analyzer (Flash EA 1112: Thermo Electron Corp.), and the results are listed in Table S1 (Supporting Information). Raman spectra were collected with a “Labram” Raman microscope system from ISA Group Horiba. The samples were excited with a 488 nm Ar⁺ laser with the power adjusted to ≤ 2 mW. The system was setup in the backscattering configuration with an 80 \times objective, providing a beam diameter of ~ 2 μ m. As shown in Fig. S11, broad peaks at ~ 1360 and ~ 1600 cm^{-1} are assigned to the *D* and *G* bands of graphene, respectively, which indicate the reduction of graphene oxide to graphene. The nitrogen adsorption/desorption isotherms were obtained at 77 K using a Micromeritics ASAP 2010 instrument. The specific surface areas of the graphene (incorporated in the composite) and 2.1 wt.%-graphene-wrapped LTO were obtained by the Brunauer-Emmet-Teller (BET) methods (Fig. S12, Supporting Information). The obtained specific surface areas of graphene and the 2.1 wt. %-graphene-wrapped LTO are ~ 49 m^2 g^{-1} and ~ 31 m^2 g^{-1} , respectively.

Electrochemical Measurement: Electrochemical performance of graphene-wrapped LTO was measured using coin-type half cells (2016 type) with a Li counter electrode. The working electrodes were prepared with active materials, carbon black, and PVDF binder at a weight ratio of 8:1:1. In the case of the working electrode without carbon black, the electrode consisted of a mixture of 90 wt. % of active materials and 10 wt. % of PVDF binder. The slurry was cast on Cu foil and dried at 110 $^{\circ}$ C in vacuum for 10 h. The electrolyte contained 1 M LiPF₆ in ethylene carbonate and diethylene carbonate (1/1 vol. %) (Cheil Industries Inc.). The loading density of the electrodes was 1.40 – 1.65 mg cm^{-2} . The cells were charged and discharged between 2.5 and 0.9 V by applying various current densities. Electrochemical impedance spectra were measured using a potentiostat (CHI 608C: CH Instrumental Inc.) at 1.5 V after 100 cycles with AC amplitude of 5 mV in the frequency range from 10 mHz to 10⁵ Hz.

References

1. W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.* 1958, **80**, 1339.
2. L. V. Nowack, O. Waser, O. Yarema, and V. Wood, *RSC Advances* 2013, **3**, 15618.

Sample	Li ₄ Ti ₅ O ₁₂ [wt. %]	C [wt. %]
1.0 wt. %-Graphene-Wrapped LTO	98.9	1.04
2.1 wt. %-Graphene-Wrapped LTO	97.8	2.14
4.5 wt. %-Graphene-Wrapped LTO	95.5	4.46

Table S1. The relative graphene compositions of graphene-wrapped LTO samples. The compositions were measured by a CHNS elemental analysis.

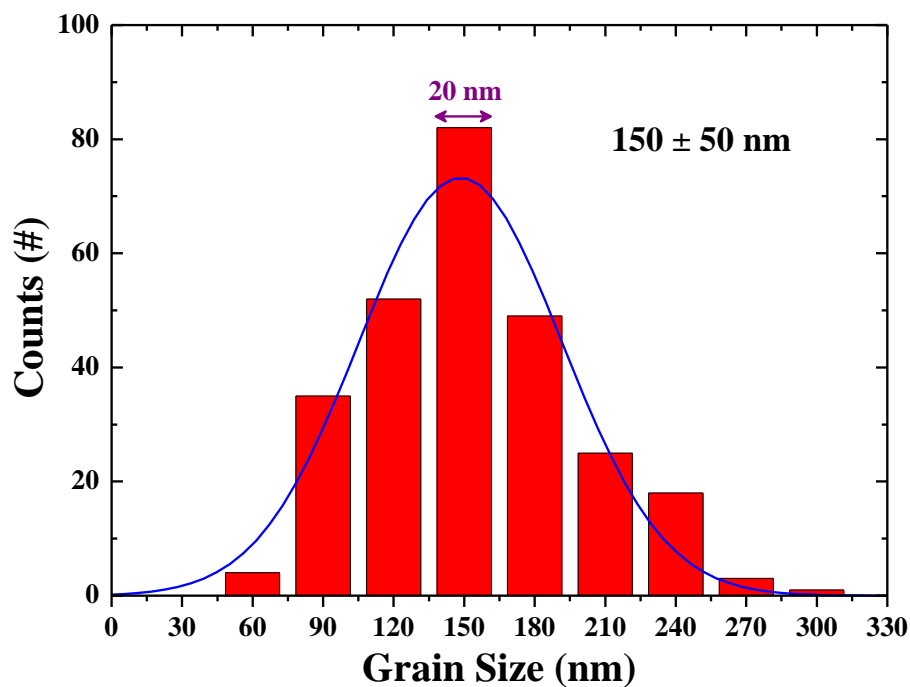


Fig. S1. Grain-size distribution of the 2.1-wt.-% graphene-wrapped LTO.

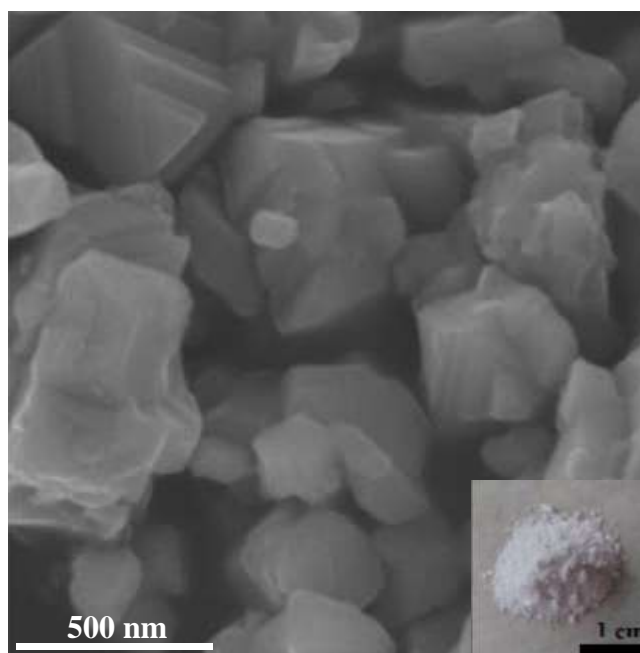


Fig. S2. SEM image of the bare LTO.

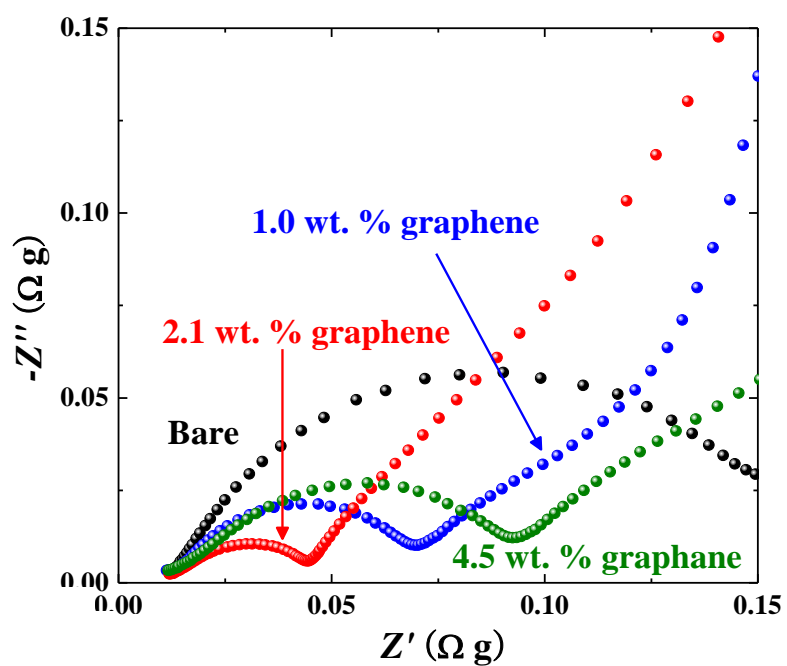


Fig. S3. Electrochemical impedance spectroscopy of the bare and graphene-wrapped LTO with various amounts of graphene measured at 1.5 V after 100 cycles.

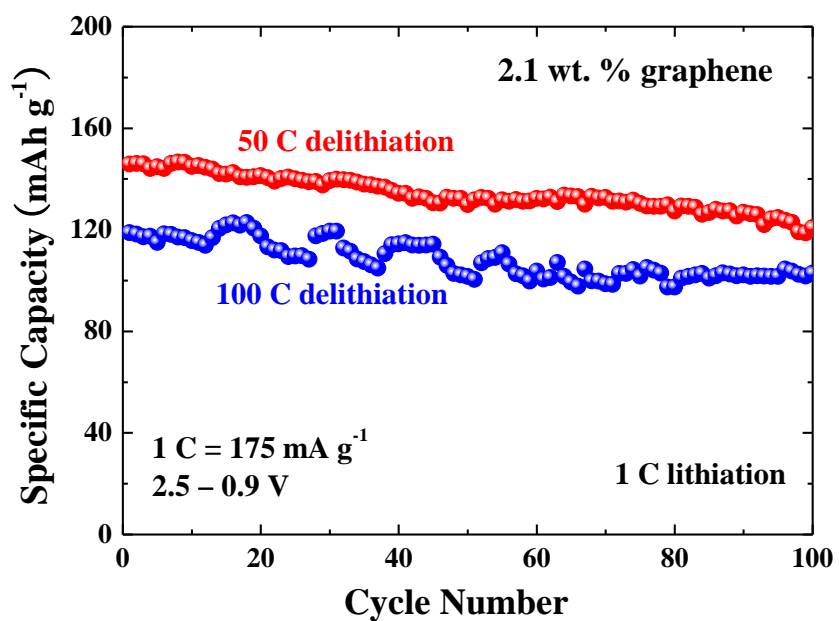


Fig. S4. Capacity retention of the graphene-wrapped LTO with 2.1 wt. % graphene at 50 and 100 C delithiation (lithiation rate = 1 C).

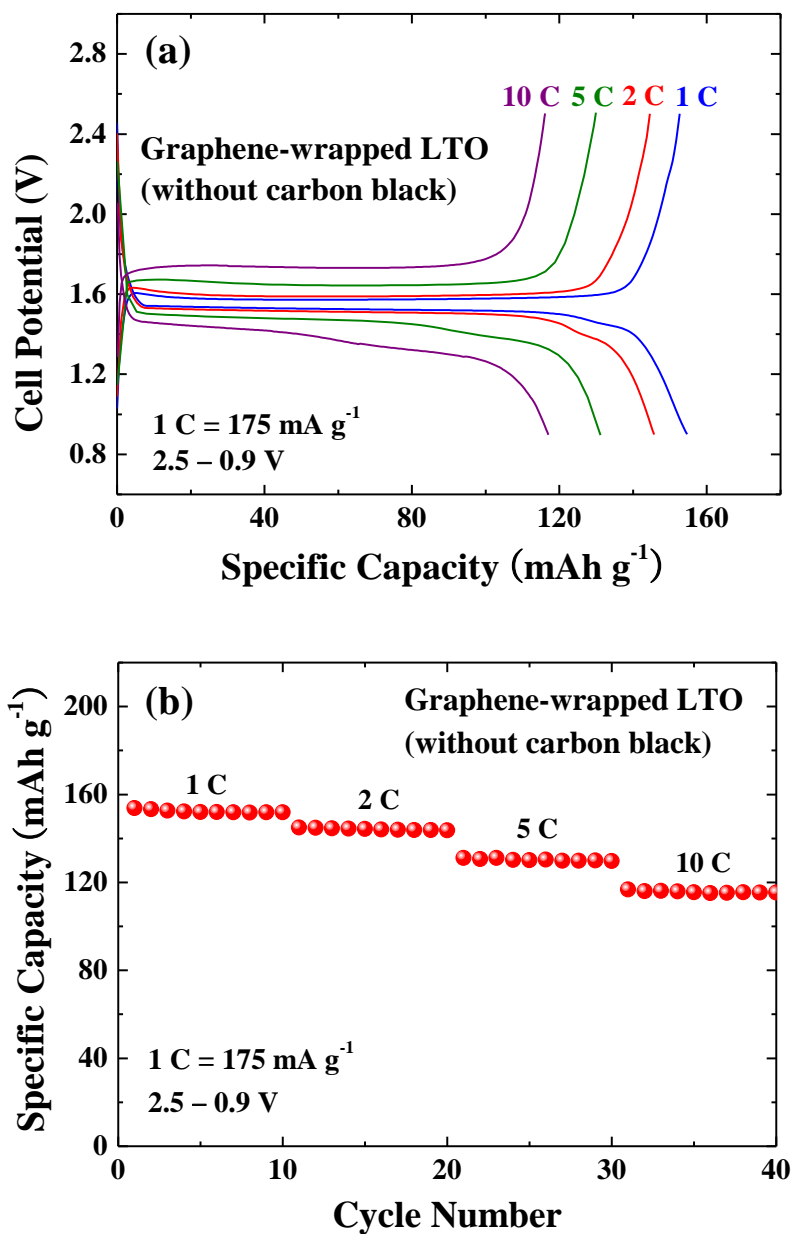


Fig. S5. Coin cells without carbon black: (a) Rate capability (first cycle at the given rate) and (b) rate retention of the graphene-wrapped LTO (3.0 wt. % graphene) at different current rates.

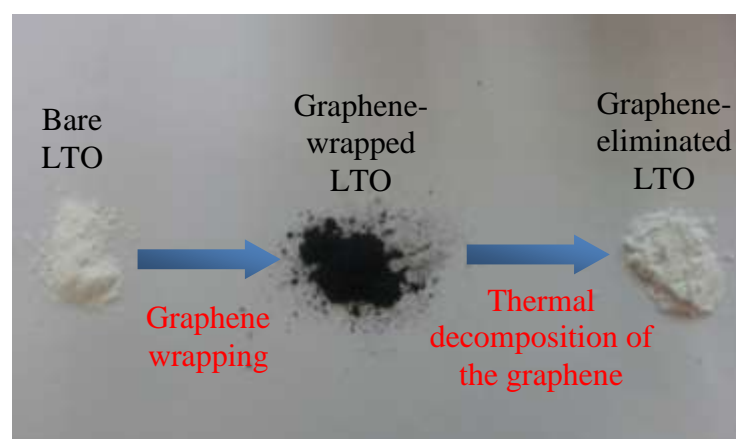


Fig. S6. Comparison of the individual colors of the prepared samples.

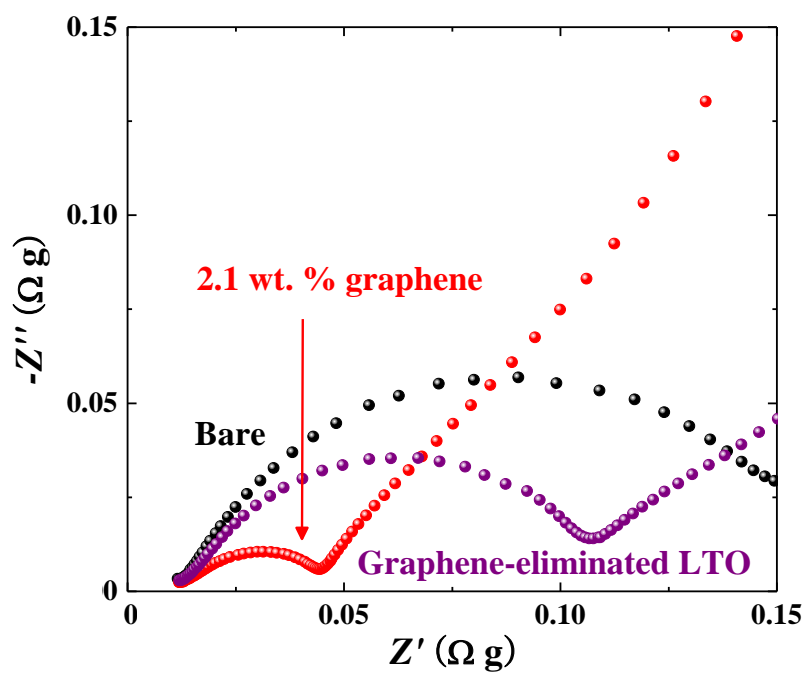


Fig. S7. Electrochemical impedance spectroscopy of the bare, graphene-wrapped LTO, and graphene-eliminated LTO measured at 1.5 V after 100 cycles.

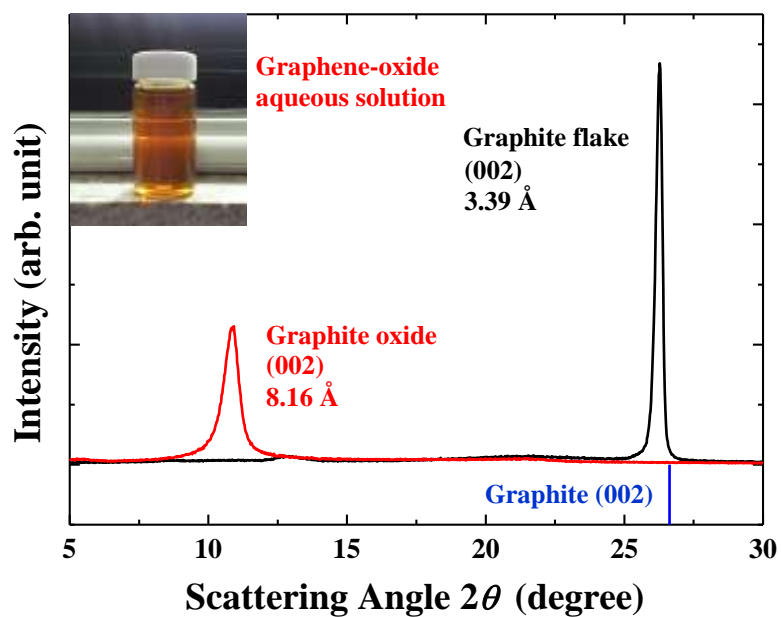


Fig. S8. XRD patterns of the natural graphite and graphite oxide.

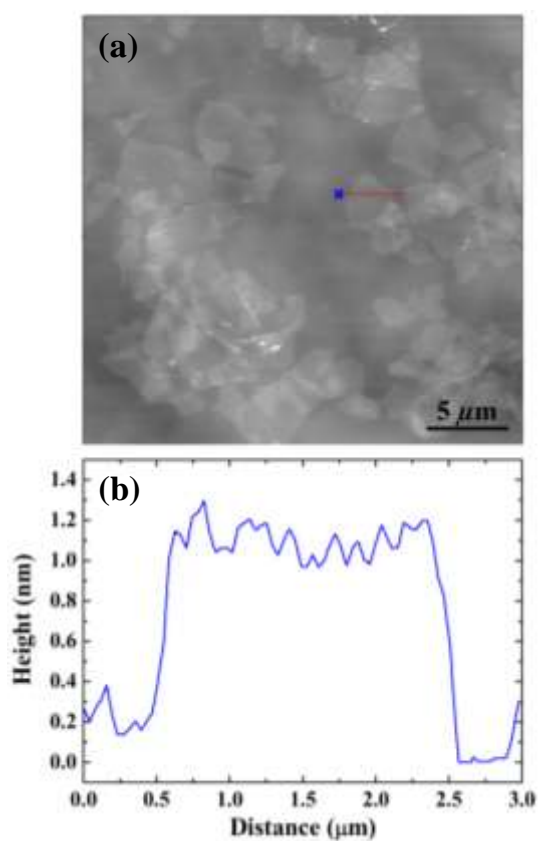


Fig. S9. (a) An AFM image of graphene oxides dispersed in aqueous solution and (b) respective height profile.

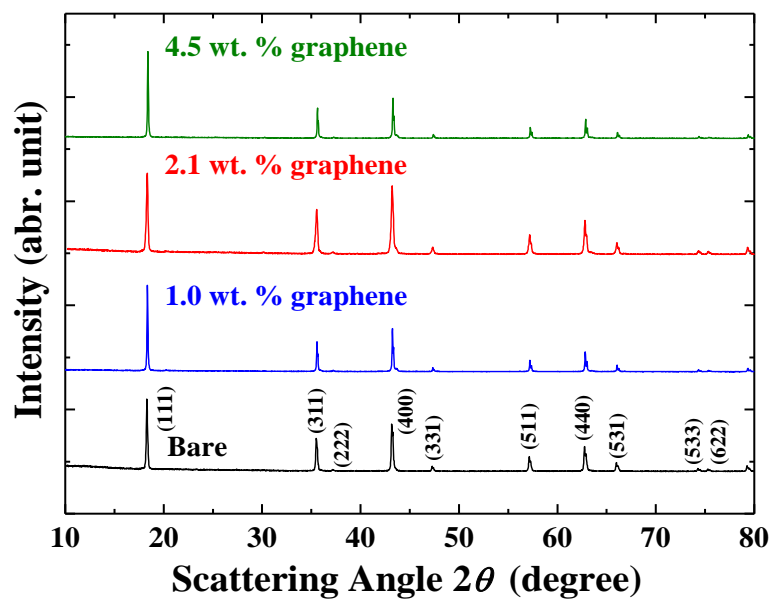


Fig. S10. XRD patterns of the bare and graphene-wrapped LTO with various amounts of graphene.

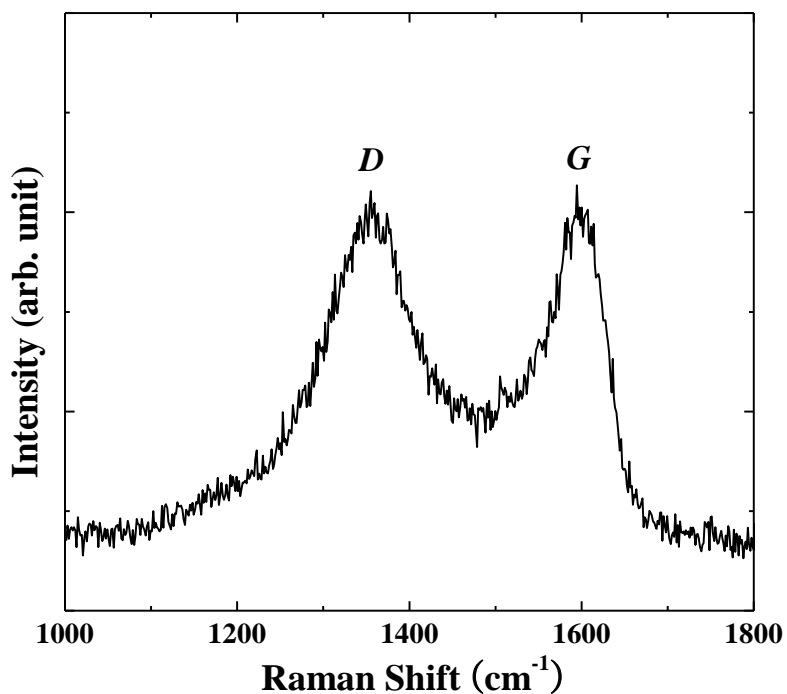


Fig. S11. Raman spectrum of the 2.1-wt.-% graphene-wrapped LTO.

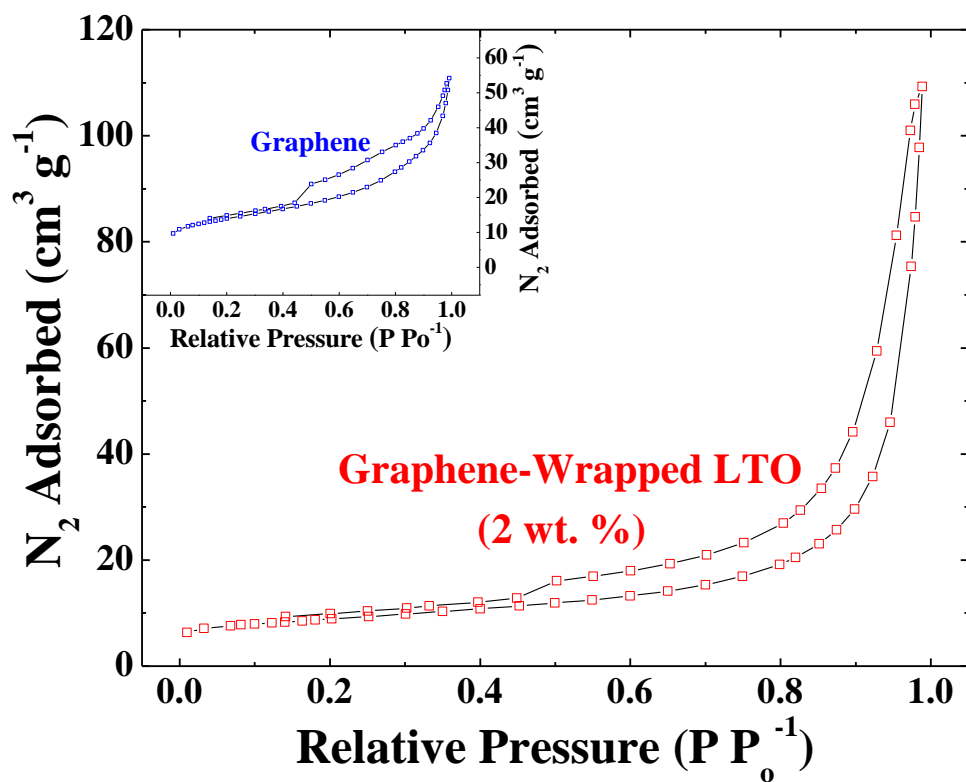


Fig. S12. N₂ adsorption/desorption isotherm of 2.1 wt. %-graphene-wrapped LTO. The inset displays that of graphene only.