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Electronic Supplementary Information (ESI)

In situ Fabrication of Lithium Titanium Oxide by Microwave-Assisted Alkalization for High-Rate Lithium-Ion Batteries

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Experimental details

The graphene oxide (GO) used in this study was prepared by the modified Hummers method, starting from purified graphite powder (SP-1, 200 meshes, Bay Carbon).[2] The as-prepared GO was used for the synthesis of Li-Ti-O/RGO precursor. In the typical procedure, GO powder (0.1 g) was sonicated in diethylene glycol (DEG; >99%, Fluka, 80 mL) for 30 min. The pH of the resulting solution was adjusted as 9–10 using NaOH (1 M). Following that, the titanium and lithium precursors, namely titanium ethoxide (Aldrich, 0.025 mL) and aqueous LiOH solution (0.1 M, 20 mL), respectively, were added to the sonicated solution. The solution was then transferred to a 100-mL Teflon vessel (MARS-5, CEM Corporation) and microwaved at 200 ºC for 30 min. Upon completion of the reaction, the resulting powder (Li–Ti–O/RGO nanocomposite) was repeatedly washed with ethanol and distilled water, and freeze-dried for 24 h. Finally, the as-obtained Li–Ti–O/RGO nanocomposite was heat treated at 700 °C for 2 h in a 5 wt% H_2–Ar atmosphere, to obtain phase-pure $Li_4Ti_5O_{12}$/RGO nanocomposite.

The structure and morphology of the resulting samples were characterized by using XRD (Cu K_α, 40 kV, 20 mA, λ=0.15406 nm; Rigaku DMAX 2200), TEM (200 kV; CM200, Philips), SEM (JSM-7001F, JEOL Ltd.), Raman spectroscopy (LabRam, Jobin Yvon-Spex), and AFM (PSIA XE-100, Park Systems). Additionally, elemental analysis of the prepared samples was performed using FT-IR (Vertex 70, Bruker) and XPS (15 kV, 150 W; ESCALAB 250, Thermo Electron Corporation). The thermal data of the samples were collected using a thermogravimetric analyzer (TGA; STA 409 PC, Netzsch) that was operated in air from room temperature to 800 °C, at a heating/cooling rate of 10 °C min^{-1}. The electrical conductivity was measured using the two-point probe method in a poly methyl methacrylate (PMMA) cell.

Furthermore, the electrochemical properties were investigated at room temperature using a CR2032 coin cell, with metallic lithium as the negative electrode. The working electrode consisted of a mixture of $Li_4Ti_5O_{12}$/RGO nanocomposite (90 wt%) prepared in this study and polyvinylidene fluoride (PVDF; 10 wt%) dissolved in binder N-methylpyrrolidone (NMP). The slurry mixture was coated on copper foil (99.7% purity, Aldrich) and then dried at 100 °C for 24 h. Each working electrode had an area of 1 cm2 and contained the dried slurry (3–4 mg). The electrolyte was LiPF6 (1 M) dissolved in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) at a weight ratio of 1:1. The coin cells were assembled in an Ar-filled glove box using a microporous polyethylene film (Celgard 2400) as separator. Charge–discharge tests and cyclic voltammetry were performed using a potentiostat/galvanostat (VMP3, Princeton Applied Research).

Electrochemical impedance spectroscopy (EIS) was carried out using an impedance analyzer at a DC bias voltage of 10 mV at AC frequencies ranging from 200 kHz to 30 mHz.

Supplementary Figures

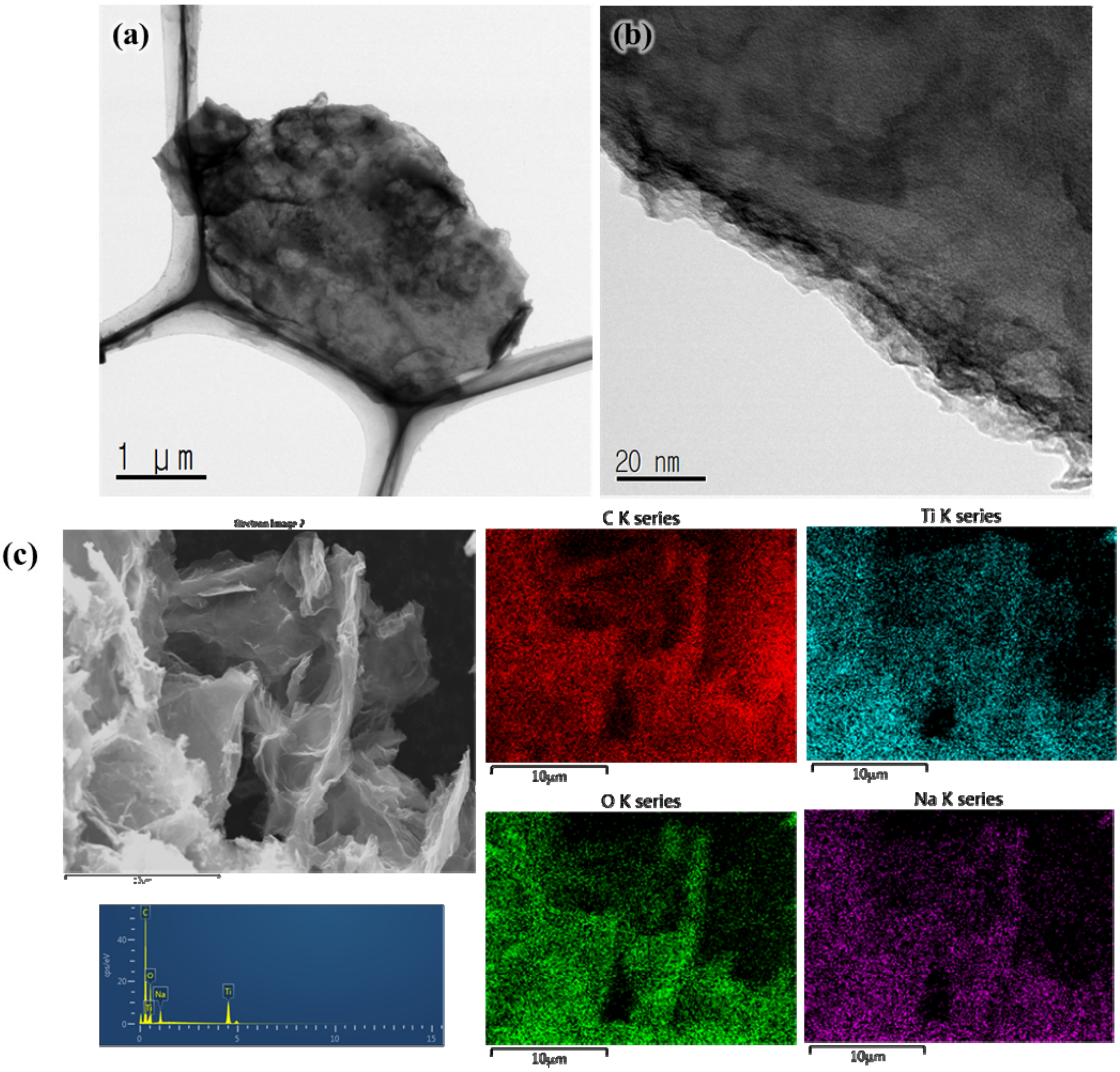

Figure S1. (a–b) TEM images and (c) EDS elemental map of the amorphous alkali titanate/GO composite. During the initial stages of the reaction, titanate is formed on the surface of GO in aqueous solution, with increase in reaction temperature. The as-formed titanate spontaneously transforms to amorphous alkali titanate in the alkali solution.

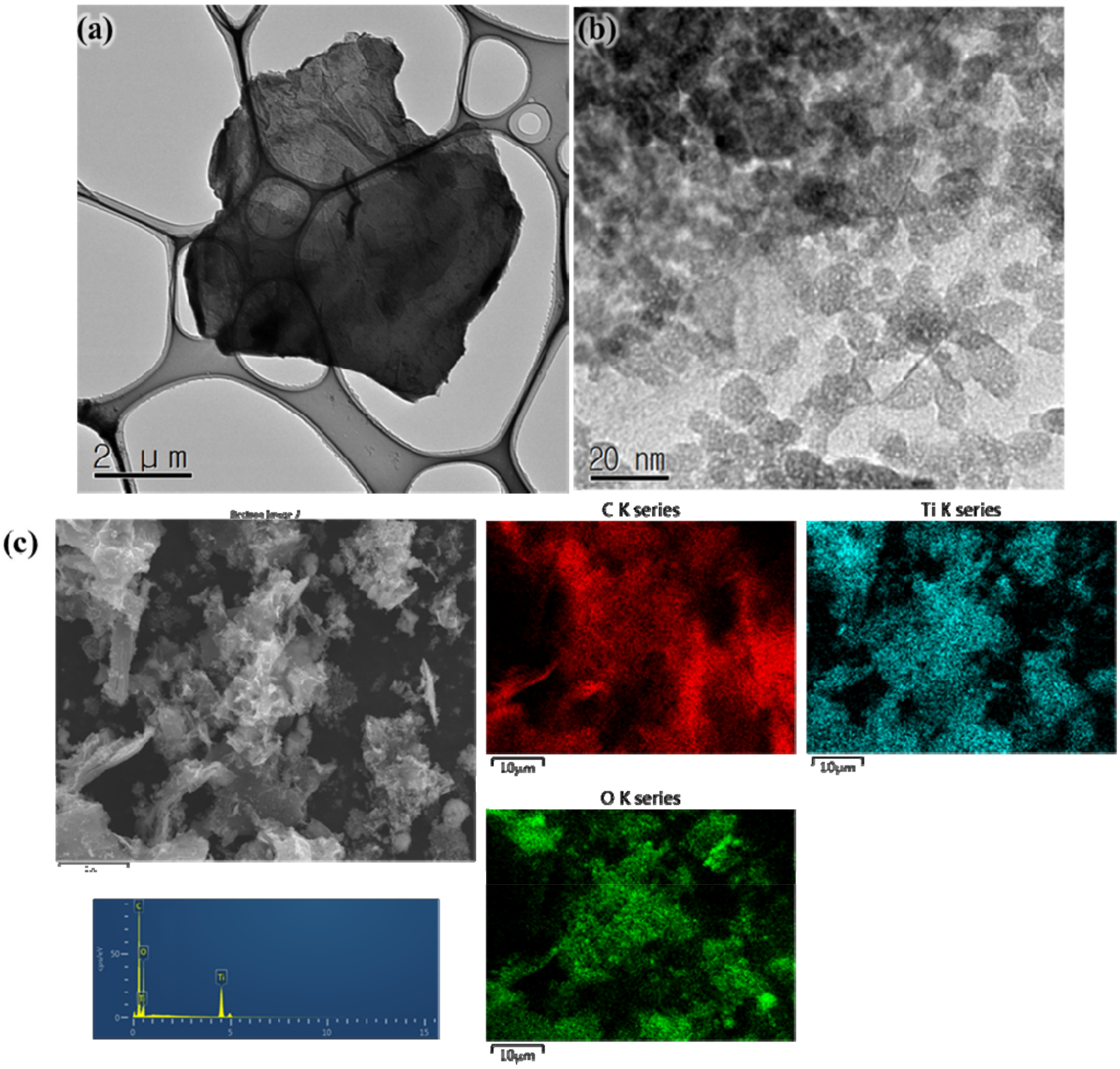

Figure S2. (a–b) TEM images and (c) EDS elemental map of the Li–Ti–O/RGO nanocomposite. The TEM image of the prepared composite shows the formation of Li–Ti–O precursor nanoparticles of size 7–10 nm uniformly supported on RGO.

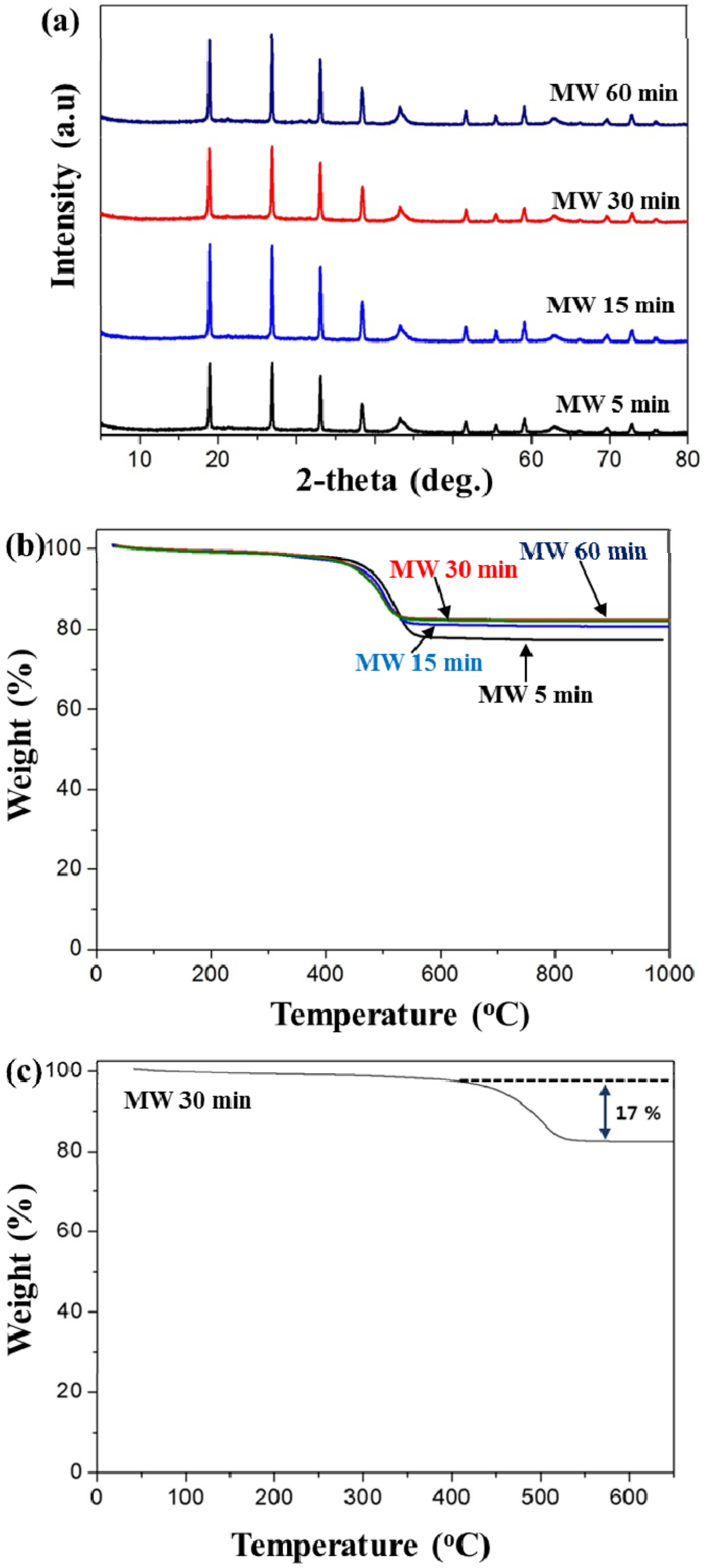

Figure S3. (a) XRD patterns and (b–c) Thermogravimetric analysis (TGA) of the Li–Ti–O/RGO nanocomposite synthesized at different time durations of microwave treatment.

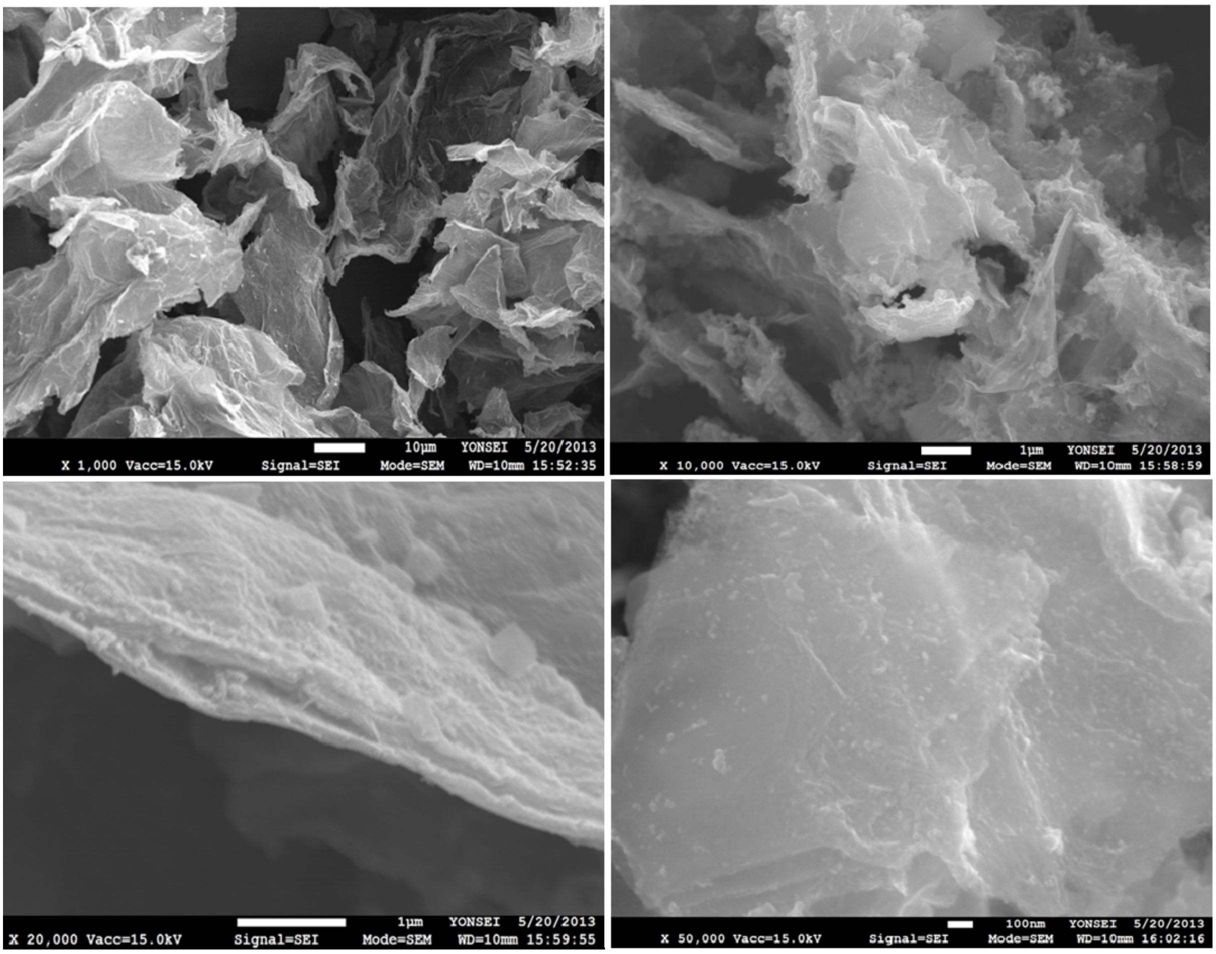

Figure S4. SEM images of the $Li_4Ti_5O_{12}$/RGO nanocomposite confirming the uniform decoration of $Li_4Ti_5O_{12}$ nanoparticles on the RGO surface.

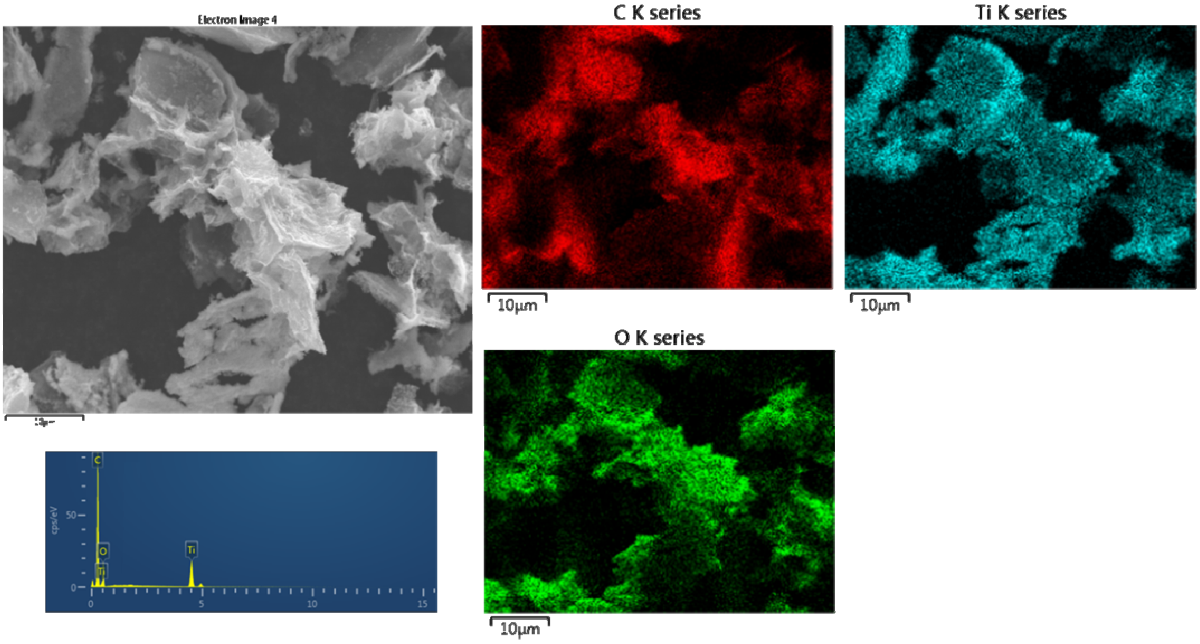

Figure S5. EDS elemental map of the prepared $Li_4Ti_5O_{12}$/RGO nanocomposite.

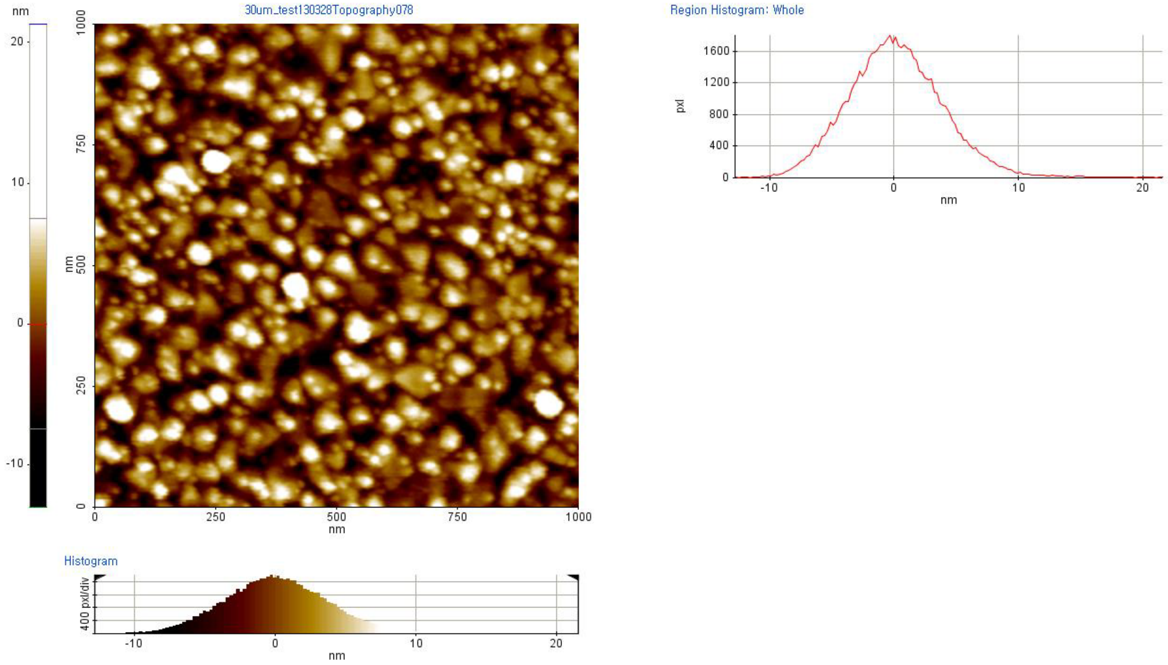

Figure S6. AFM profile indicating the formation of $Li_4Ti_5O_{12}$ nanoparticles on the surface of RGO.

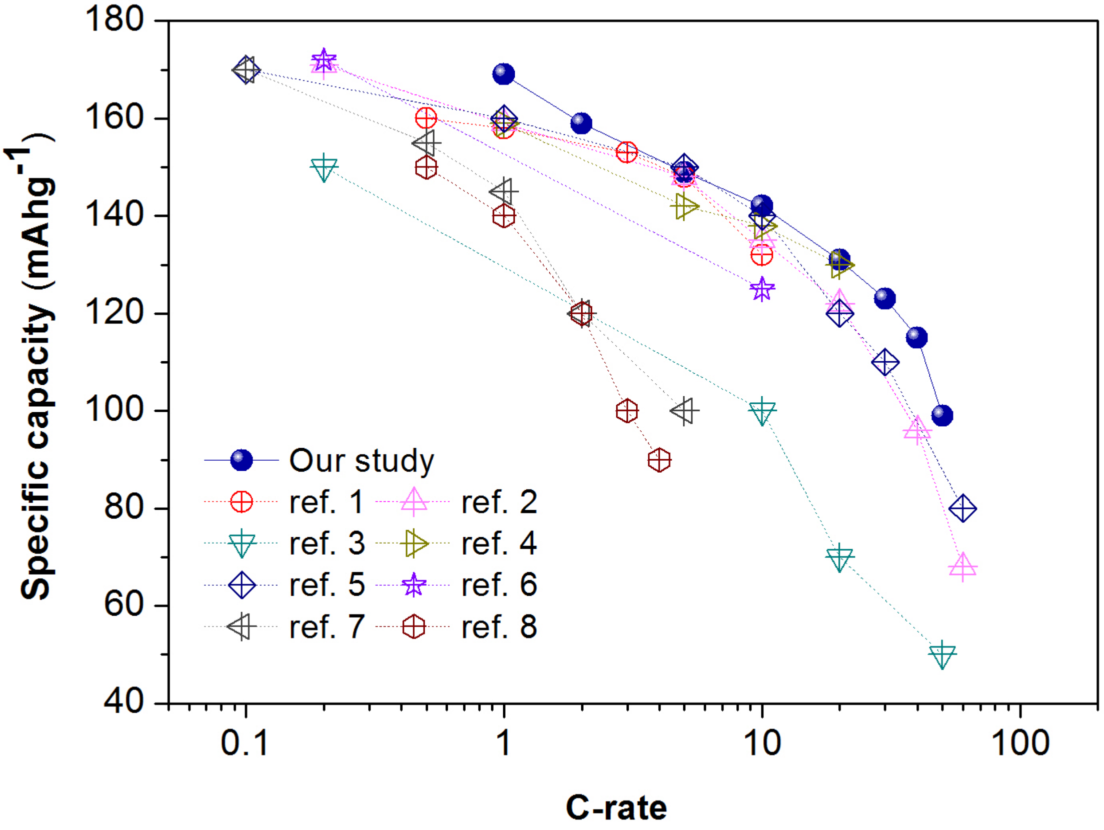

Figure S7. Comparison of rate capabilities (discharge capacity versus discharge rate) of the $Li_4Ti_5O_{12}$/CNT nanocomposite prepared in this study with that of the reported $Li_4Ti_5O_{12}$/CNT composite (refs.1, 2, 3) and $Li_4Ti_5O_{12}$/graphene composite. (refs.4, 5, 6, 7, 8) $Li_4Ti_5O_{12}$/RGO nanocomposite shows a specific discharge capacity of 98 mA h g^{-1} was achieved even at 50 C-rate, a value that is 59% of the 1 C-rate specific capacity, indicating the excellent high-rate capability of the prepared $Li_4Ti_5O_{12}$ / RGO nanocomposite. We compare the electrochemical performance of $Li_4Ti_5O_{12}$ / RGO nanocomposite prepared by the microwave-assisted alkalization method with other $Li_4Ti_5O_{12}$ /nanocarbon composite. As shown in figure, the electrochemical properties of the $Li_4Ti_5O_{12}$/RGO nanocomposite prepared by the microwave-assisted alkalization method were similar or better compare to previous studies.[1-8]

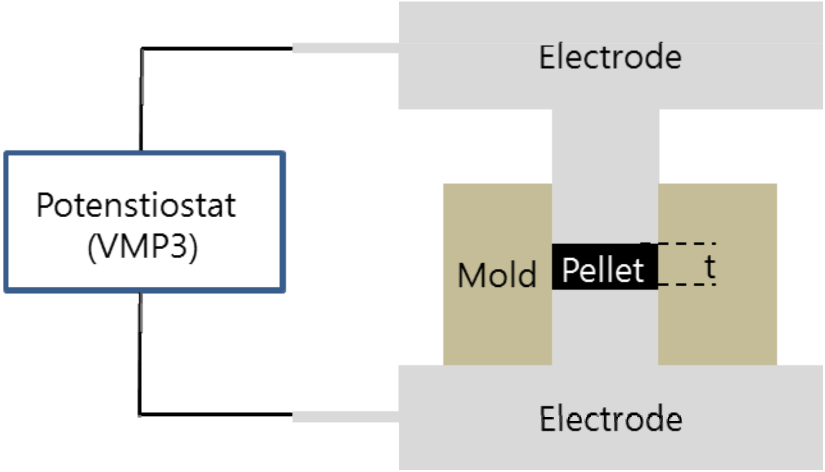

Figure S8. Schematic illustration of the cell and the experimental setup adopted for measuring the electrical conductivity of the nanocomposite by using the two-point probe method. The cell consists of stainless-steel top electrode, fixed bottom electrode, poly(methyl methacrylate) (PMMA) mold, and nanocomposite sample pelletized to desired area *A* and thickness *t* (electrode area $A = 1.33\ \mathrm{cm}^2$). The electrical conductivity of the compressed $Li_4Ti_5O_{12}$/RGO nanocomposite pellet exhibited a much higher value of $0.24\ \mathrm{S\ cm^{-1}}$, compared to the conductivity of $10^{-13}\ \mathrm{S\ cm^{-1}}$ observed in raw $Li_4Ti_5O_{12}$.

< Reference>

(1) X. Li, M. Qu, Y. Huai and Z. Yu, *Electrochim. Acta*, 2010, 55, 2978.

(2) L. Shen, C. Yuan, H. Luo, X. Zhang, K. Xu and F. Zhang, *J. Mater. Chem.*, 2011, 21, 761.

(3) J. Shu, L. Hou, R. Ma, M. Shui, L. Shao, D. Wang, Y. Ren and W. Zheng, *RSC Adv.*, 2012, 2, 10306.

(4) H. K. Kim, S. M. Bak and K. B. Kim, *Electrochem. Commun.*, 2010, 12, 1768.

(5) L. Shen, C. Yuan, H. Luo, X. Zhang, S. Yang and X. Lu, *Nanoscale*, 2011, 3, 572.

(6) H. Xiang, B. Tian, P. Lian, Z. Li and H. Wang, *J. Alloys Comp.*, 2011, 509, 7205.

(7) S. Yi Han, I. Y. Kim, K. Y. Jo and S. Hwang, *J. Phys. Chem. C*, 2012, 116, 7269.

(8) B. Zhang, Y. Yu, Y. Liu, Z. Huang, Y. He and J. Kim, *Nanoscale*, 2013, 5, 2100.