

Electronic Supplementary Information (ESI)

***In situ* synthesis of high-loading Li₄Ti₅O₁₂-graphene hybrid nanostructures for high rate lithium ion batteries**

Laifa Shen,^a Changzhou Yuan,^b Hongjun Luo,^a Xiaogang Zhang,^{*a} Sudong Yang^a and Xiangjun Lu^a

^a College of Material Science & Engineering, Nanjing University of Aeronautics and Astronautics, Nanjing, 210016, P.R. China.

^b School of materials Science and Engineering, Anhui University of technology, Ma`anshan, 243002, P.R. China.

E-mail: azhangxg@163.com

Experimental

1. Preparation of Li₄Ti₅O₁₂/GNS nanocomposites:

All the reagents were of analytical grade purity and used as received. Graphite oxide (GO) was synthesized from natural graphite powders (SP-1, Sinopharm Chemical Reagent Co., Ltd, China) by a modified Hummers method originally reported by Kovtyukhova *et al.*,¹ in which pre-oxidation of graphite is followed by oxidation with Hummers' method. In a typical synthesis, 250 mg GO was dissolved into 200 mL ethanol with sonicating for 4 h. Then 2.5 ml tetrabutyl titanate was added drop-by-drop into the suspension and the mixture was magnetically stirred for 30 min followed by the addition of 2.5 ml H₂O. After being further stirred for 30 min, the mixture was refluxed at 90 °C for 8 h. After the reaction, the suspension and precipitate were separated by centrifugation, washed with deionized water and ethanol and dried at 60 °C for 12 h. Following synthesis, an amount of 0.4 g TiO₂/GO was dispersed in a 2.5 M LiOH aqueous solution, the hydrazine hydrate (85 %) as reductant was added in the above solution and stirred for 5 min. The suspension was transferred into Teflon-lined stainless steel autoclave and kept at 100 °C for 10 h. The precipitate was separated by filtration, washed with deionized water several times to remove an excess of hydroxides before drying at 60 °C for 12 h. Subsequently, the as-prepared Li₄Ti₅O₁₂-precursor anchored on GNS was calcined at 600 °C under N₂ for 2 h to obtain crystalline Li₄Ti₅O₁₂/GNS. The process for preparing pure Li₄Ti₅O₁₂ was similar to that of Li₄Ti₅O₁₂/GNS preparation, except without the GO in the first stage.

2. Sample characterization:

The crystal structure of the obtained samples was characterized by X-ray diffraction (XRD) (Bruker D8 advance) with Cu K α radiation. Microstructural properties were obtained using a transmission electron microscopy (TEM, FEI, Tecnai-20) and high-resolution transmission electron microscopic (HRTEM, JEOL JEM-2010), and

field emission scanning electron microscopy (FESEM LEO 1430VP), and atomic force microscopy (AFM, Seiko Instrument, SPA-300HV). TG was performed on a TG-DSC instrument (NETZSCH STA 409 PC) using a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ in air atmosphere from 40 to $900\text{ }^{\circ}\text{C}$. Raman spectra were collected using a Renishaw 2000 system with an argon ion laser (514.5 nm) and charge-coupled device detector. The electronic conductivities of the samples were measured by a four-point probe method (SDY-5 Four-Point probe meter).

3. Electrochemical experiments:

The electrochemical characterization was carried out by galvanostatic cycling in a CR2016-type coin cell. The raw $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrode was prepared by mixing 76 wt.% active material, 14 wt.% carbon black, and 10 wt.% polyvinylidene fluoride (PVDF) in *N*-methyl pyrrolidinone (NMP). While the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /GNS electrode was prepared by mixing 90 wt.% composite and 10 wt.% PVDF in NMP in order to match the carbon content of the raw $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrodes (The content of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ in the composite electrode is 76 %). Then the slurry was spread uniformly on aluminium foil current collector. Finally, the electrode was dried under vacuum at $110\text{ }^{\circ}\text{C}$ for 12 h. Test cells were assembled in an argon-filled glove box using Li foil as the counter electrode and polypropylene (PP) film as the separator. 1 mol L^{-1} LiPF_6 solution in a 1 : 1 (V : V) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) was used as electrolyte. The coin cells were galvanostatically charged- discharged at different current densities between 1.0 and 2.5 V (vs. Li/Li^+) using a CT2001A cell test instrument (LAND Electronic Co.). The AC impedance spectrum was measured by using a Solatron 1260 Impedance Analyzer in the frequency range 10^{-2} - 10^6 Hz.

Sample Characterizations

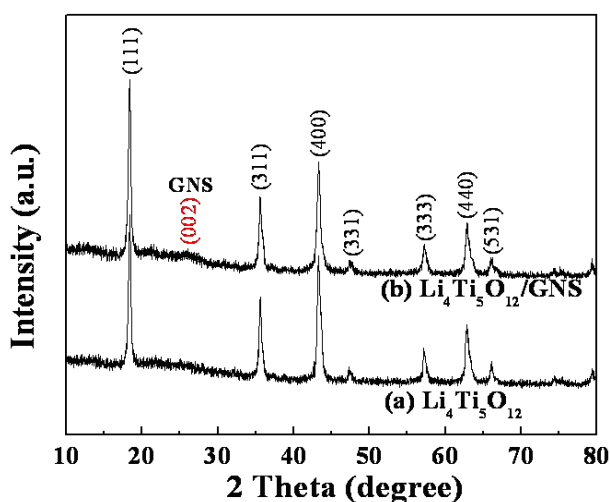


Fig. S1 XRD patterns of (a) the pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$ prepared without the presence of GNS and (b) $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /GNS nanocomposites.

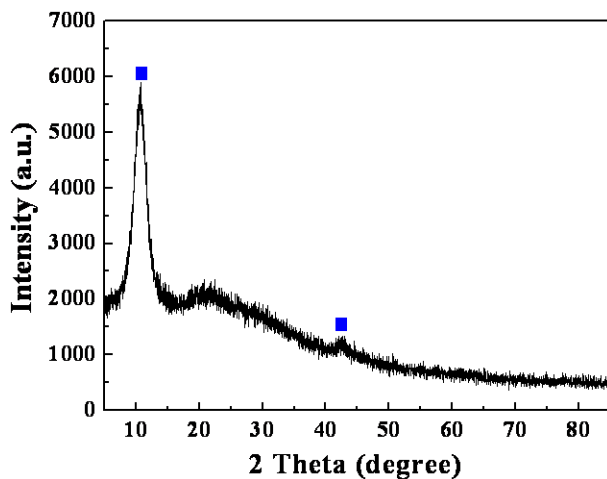


Fig. S2 XRD pattern of graphite oxide

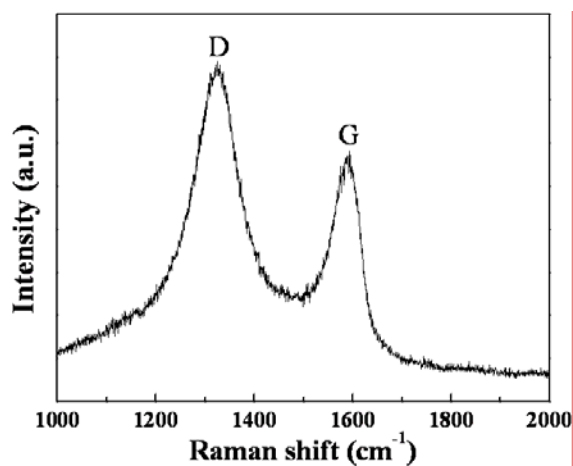


Fig. S3 Raman spectra of the $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{GNS}$ nanocomposites.

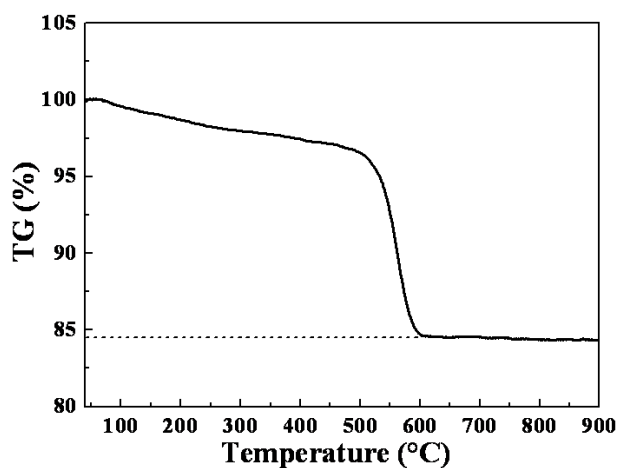


Fig. S4 TG curve of the $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{GNS}$ nanocomposites at 10 °C min^{-1} under air. The residual weight ratio corresponds to the content of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ in the hybrid materials.

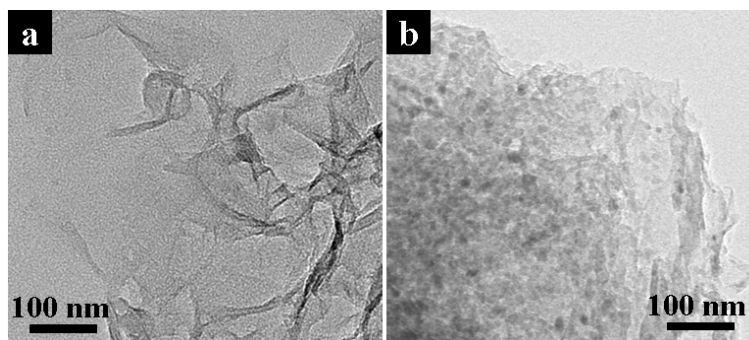


Fig. S5 TEM images of (a) GNS and (b) TiO₂/GO

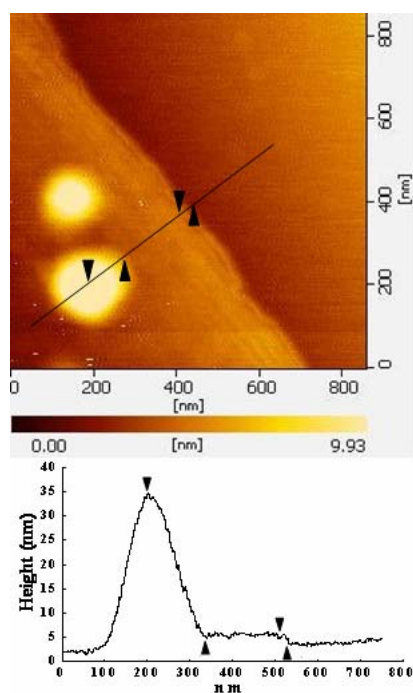


Fig. S6 AFM image of Li₄Ti₅O₁₂ NPs anchored on GNS. The line scan shows the peaks arising from Li₄Ti₅O₁₂ NPs and the height of GNS.

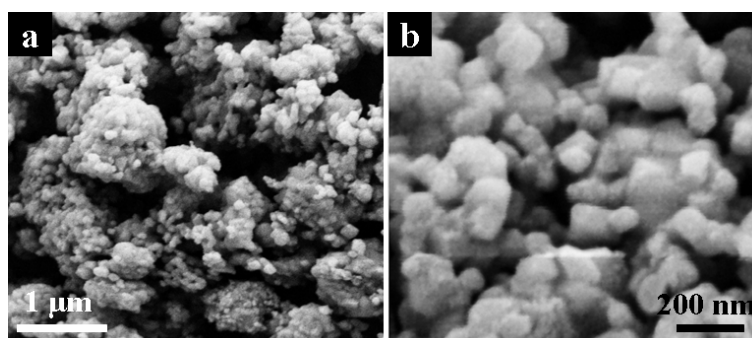


Fig. S7 Typical FESEM images of Li₄Ti₅O₁₂ sample synthesized under the control experiment in the absence of graphene sheets.

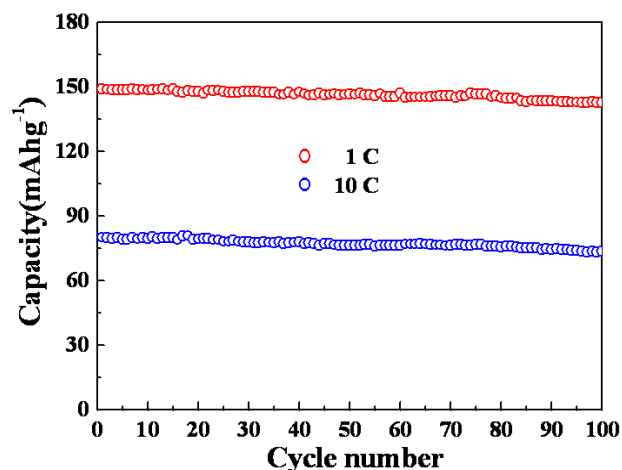


Fig. S8 Cycle performance of the pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrode under different current densities.

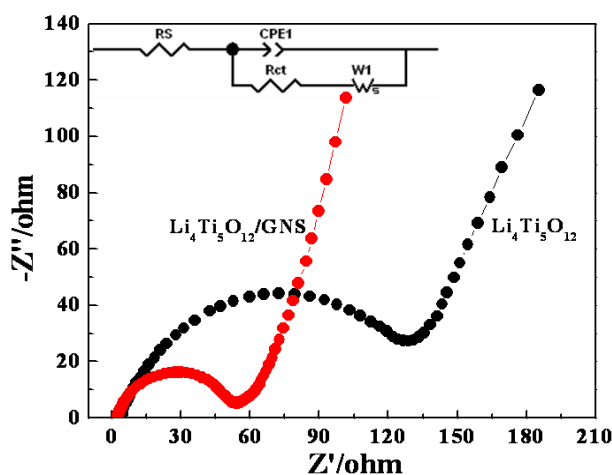


Fig. S9 Electrochemical impedance spectra of the pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{GNS}$ nanocomposites electrodes at the voltage of 1.55 V.

Table 1 Impedance parameters of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{GNS}$ nanocomposites electrodes.

Samples	R_s (Ω)	R_{ct} (Ω)	i^0 (mA cm^{-2})
$\text{Li}_4\text{Ti}_5\text{O}_{12}$	4.1	126.1	0.20
$\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{GNS}$	2.6	52.9	0.49

References

1. N. I. Kovtyukhova, P. J. Ollivier, B. R. Martin, T. E. Mallouk, S. A. Chizhik, E. V. Buzaneva and A. D. Gorchinskiy, *Chem. Mater.*, 1999, 11, 771-778.