

## **Supporting Information**

### **Mesoporous single crystals $\text{Li}_4\text{Ti}_5\text{O}_{12}$ grown on rGO as high-rate anode materials for Lithium-ion Battery**

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#### **Part I: Experimental section**

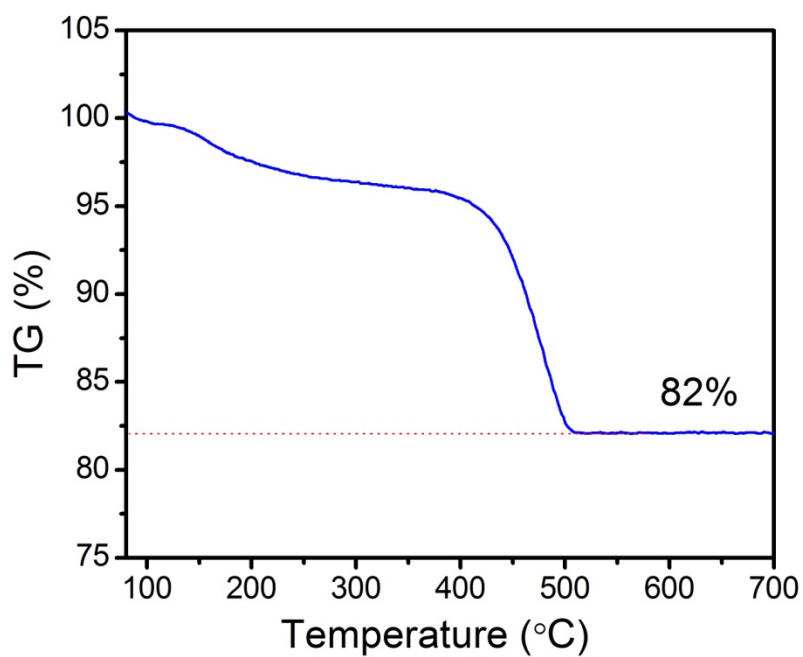
In a typical synthesis of the MSCs-LTO/rGO nanohybrids, all the reactants were purchased and used as received. Graphene oxide (GO) was prepared by Hummers' method. MSCs-LTO/rGO nanohybrids were prepared via hydrothermal reaction and annealing process in Ar atmosphere. First, 60 mg GO was dispersed in 300 ml ethanol through long-time ultrasonication in a sealed flask. Then, the mixture of tetrabutyl titanate (2 g) and ethanol (2 g) was injected into the suspension of GO slowly. After half-hour stir, the mixture of deionized water (2 g) and ethanol (2 g) was injected into the flask the same way as above followed with the reflux reaction at 100 °C for 6 h. Collect the product and wash with ethanol and water for several times. Disperse the as prepared solid in 150 ml deionized water with subsequent hydrothermal reaction at 180 °C for 6 h. After centrifugalization and washing with deionized water, the solid was frozen dry and identified as  $\text{TiO}_2/\text{rGO}$ . Following synthesis, 20 mg  $\text{TiO}_2/\text{rGO}$  was mixed with 0.8 M LiOH solution, and the suspension was transferred into Teflon-lined stainless steel autoclave and kept at 180 °C for 10 h. Still collect the produced

gray powder and wash with water to remove the excess of hydroxide before freezing dry, and finally treated it at 600 °C for 2 h in Ar atmosphere to obtain MSCs-LTO/rGO nanohybrids. For comparison, pure LTO was prepared by the similar process without the addition of GO in the first stage.

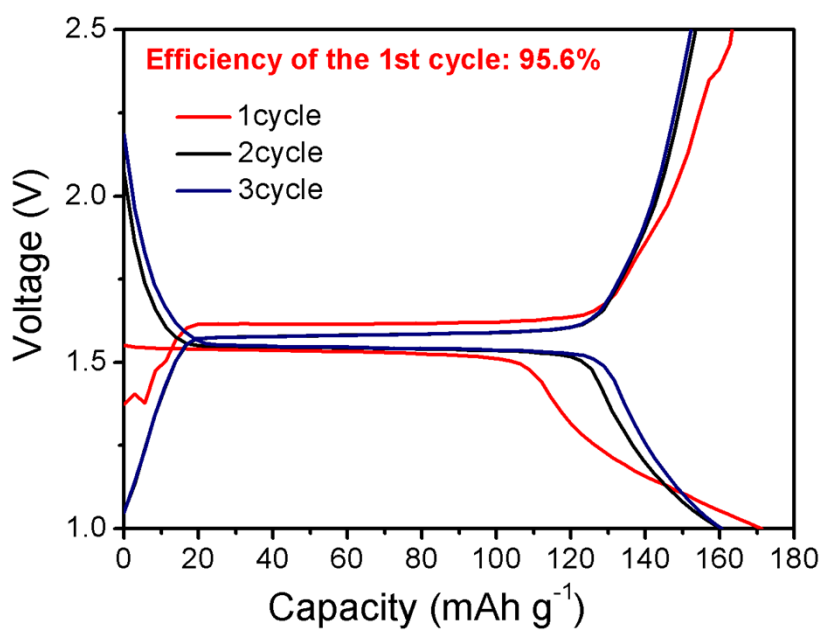
XRD pattern was carried out on a X-ray diffraction (Bruker D2 Phase Table-top Diffractometer) with Cu-K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) at 30 mV and 10 mA. Microstructural properties were determined by transmission electron microscopy (TEM, JEOL JEM-2010). The content of rGO in the sample was obtained using a TG-DSC instrument (NETZSCH STA 449F3). Raman measurement was performed with a Renishaw 2000 system with a 514.5 nm Ar-ion laser and charge-coupled device detector.

Electrochemical measurements were conducted by galvanostatic testing CR2016-type coin cells assembled in an argon filled glove box (Mbraum). To prepare the working electrode, mix the active material, Carbon Black and polyvinyl difluoride (PVDF) in a weight ratio of 80:10:10, and then disperse the mixture in N-methyl-2-pyrrolidinone (NMP) to form uniform slurry which was cast on the Cu foil. The foil loaded with active materials was then dried at 120 °C for 12 h to remove the excess solvent. Pure lithium foil and polypropylene (Celgard 2400) were used as counter electrode and separator, respectively. The electrolyte was composed of 1.0 M LiPF<sub>6</sub> in a mixture of ethylene carbonate and diethyl carbonate (EC-DEC) (volume ratio = 1: 1). The galvanostatic charge-discharge cycling at different current rates was performed on an automatic battery testing system (LAND CT2001A model) in a voltage range of 1.0–2.5 V (vs. Li/Li<sup>+</sup>) at room temperature. The electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) experiments were carried out on a multichannel electrochemical station (Autolab PGSTAT302N). The EIS was tested in the frequency range of 100 kHz to 10 mHz.

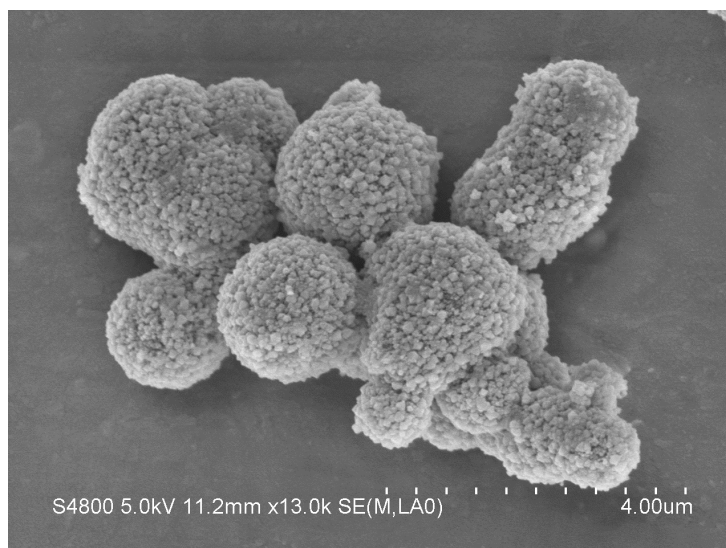
## Part II: Supporting figures



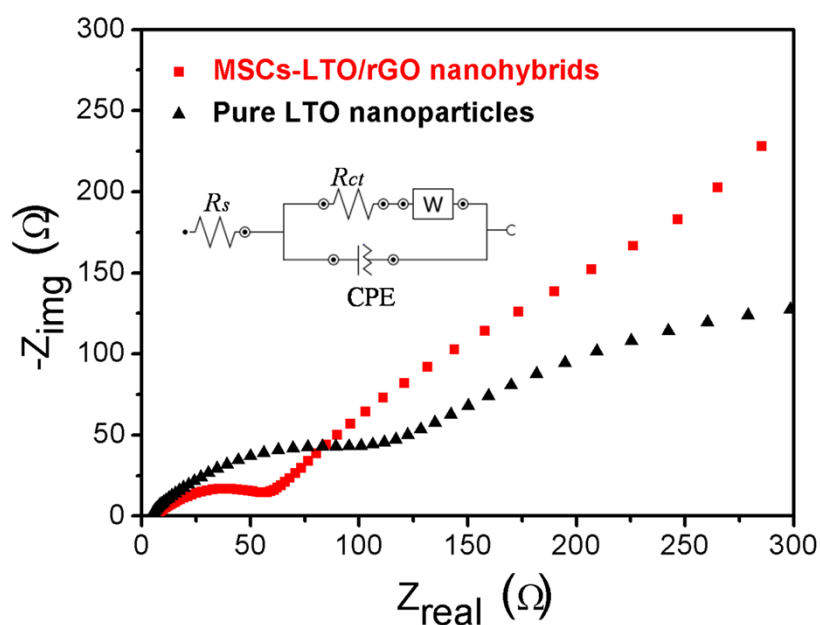
**Fig. S1** TG curve of the MSCs-LTO/rGO nanohybrids.



**Fig. S2** The first three charge/discharge curves of the MSCs-LTO/rGO nanohybrids, showing a high Coulombic efficiency of ~ 95.6% at the first cycle.

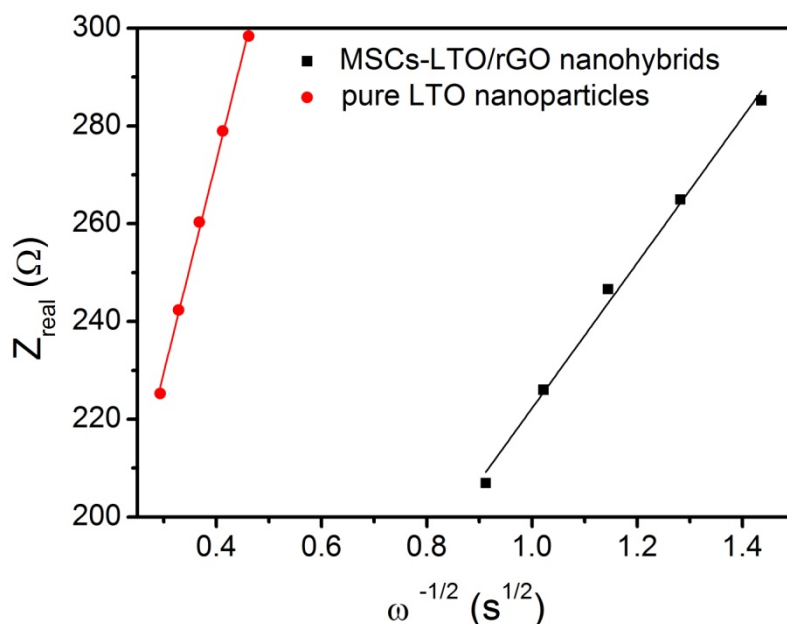


**Fig. S3** SEM image of pure LTO nanoparticles.



**Fig. S4** EIS profiles of the MSCs-LTO/rGO nanohybrids and pure LTO nanoparticles, respectively. The diameter of the semi-circle at high frequencies refers to charge transfer resistance ( $R_{ct}$ ). A lower  $R_{ct}$  of MSCs-LTO/rGO (48.5  $\Omega$ ) than pure LTO (120.0  $\Omega$ ) displayed in Table S1, indicating the remarkably decreased charge-transfer resistance at the electrode/electrolyte interface due to the introduction of rGO. The  $R_s$  of MSCs-LTO/rGO is 6.4  $\Omega$ , which is larger than pure LTO (3.9  $\Omega$ ), suggesting the addition of rGO can increase the

electronic conductivity.<sup>10</sup> The Li ions diffusion coefficient ( $D_{Li}$ ) is also calculated, which proves the faster Li ion diffusion of MSCs-LTO/rGO nano hybrids.



**Fig. S5** Real parts of the complex impedance versus  $\omega^{-1/2}$  of MSCs-LTO/rGO nano hybrids and pure LTO nanoparticles, respectively.

**Table S1** Simulation results of Fig. S4

Sample	$R_s$ (Ω)	$R_{ct}$ (Ω)	$D_{Li}$ (cm <sup>2</sup> s <sup>-1</sup> )
MSCs-LTO/rGO	6.4	48.5	$7.4 \times 10^{-14}$
pure LTO	3.9	120.0	$8.7 \times 10^{-15}$

The lithium ion diffusion coefficient ( $D_{Li}$ ) is calculated according to the following equations:<sup>S1,S2</sup>

$$D_{Li} = \frac{R^2 T^2}{2A^2 n^4 F^4 C^2 \sigma^2} \quad (1)$$

where  $R$  is the gas constant,  $T$  the absolute temperature,  $A$  the surface area,  $F$  the Faraday constant,  $C$  the concentration of lithium ion, and  $\sigma$  the Warburg factor.  $\sigma$  relates to  $Z_{real}$  and can be obtained from the slope of the lines in Fig. S5.

$$Z_{real} = R_D + R_L + \sigma\omega^{1/2} \quad (2)$$

[S1] N. Takami, A. Satoh, M. Hara and T. Ohsaki, *J. Electrochem. Soc.*, 1995, **142**, 371–379.

[S2] S. L. Chou, J. Z. Wang, H. K. Liu and S. X. Dou, *J. Phys. Chem. C*, 2011, **115**, 16220–16227.