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Electronic Supplementary Information (ESI)

Novel template-free solvothermal synthesis of mesoporous $\text{Li}_4\text{Ti}_5\text{O}_{12}$ -C microspheres for high power lithium ion batteries

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Experimental

1. Preparation of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ -C microspheres and pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$:

In a typical synthesis, 1.2 ml tetrabutyl titanate (TBT, 98%), 1.0 ml furfural and 2.5 g $\text{CH}_3\text{COOLi}\cdot 2\text{H}_2\text{O}$ were dissolved in 60 ml ethanol with stirring. The resulting solution was then transferred into a Teflon-lined autoclave and kept at 180 °C for 24 h. The resulting brown precipitate was separated by filtration, washed several times with deionized water to remove the excess hydroxides before drying at 80 °C for 6 h. Subsequently, the brown powder was calcinated at 550 °C for 2 h in a nitrogen atmosphere to obtain $\text{Li}_4\text{Ti}_5\text{O}_{12}$ -C microspheres. The pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was prepared in a similar manner to the preparation of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ -C microspheres, except for the absence of furfural in the process.

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 transmission electron microscopy (TEM) (TEM, FEI, Tecnai-20, USA), energy-dispersive X-ray spectroscopy (EDX, Phoenix), high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2010), and field-emission scanning electron microscopy (FESEM, LEO 1430VP, Germany). The N_2

adsorption/desorption determined by Brunauer Emmett-Teller (BET) measurements using an ASAP-2010 surface area analyzer. Thermogravimetric (TG) analyses were performed on a TG instrument (NETZSCH STA 409 PC) using a heating rate of 10 °C min⁻¹ in air atmosphere from 30 °C to 600 °C.

3. Electrochemical experiments:

The electrochemical characterization was carried out by galvanostatic cycling in a CR2016-type coin cell. The working electrodes were prepared by a slurry coating procedure. In brief, the slurry consisted of 80 wt.% active material, 10 wt.% acetylene black and 10 wt.% polyvinylidene fluoride (PVDF) dissolved in N-methyl pyrrolidinone (NMP), and was spread uniformly on an aluminium foil current collector. Finally, the electrode was dried under vacuum at 110 °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 LiPF₆ solution in a 1 : 1 (V : V) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) was used as electrolyte. The cells were galvanostatically charged and discharged under 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 ~ 10⁶ Hz.

Sample Characterizations

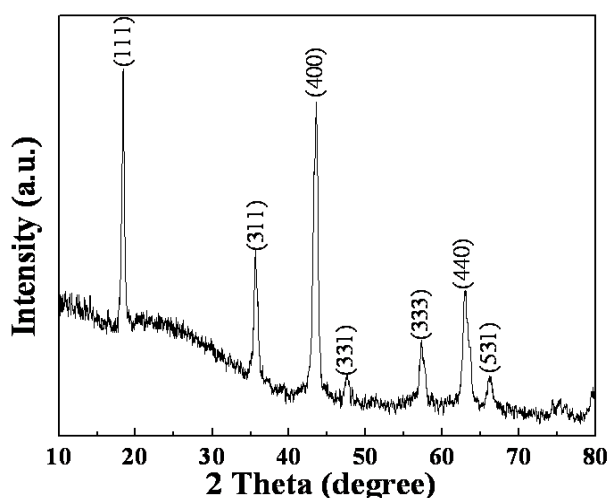


Fig. S1 X-ray diffraction patterns of pure Li₄Ti₅O₁₂

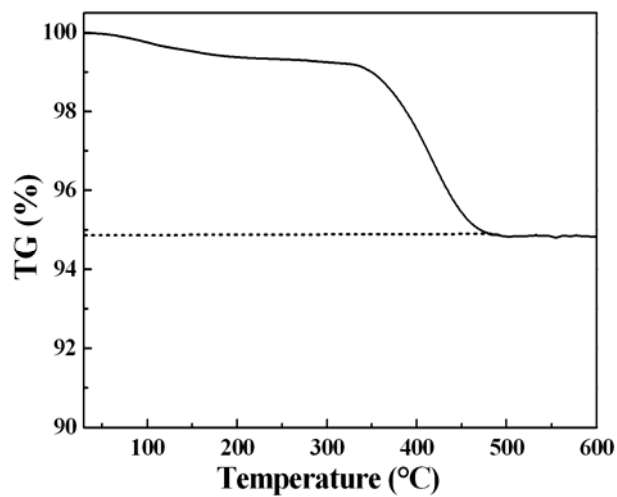


Fig. S2 TG curve of the mesoporous $\text{Li}_4\text{Ti}_5\text{O}_{12}\text{-C}$ microspheres at $10\text{ }^\circ\text{C min}^{-1}$ under air. The residual weight ratio corresponds to the content of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ in the hybrid materials.

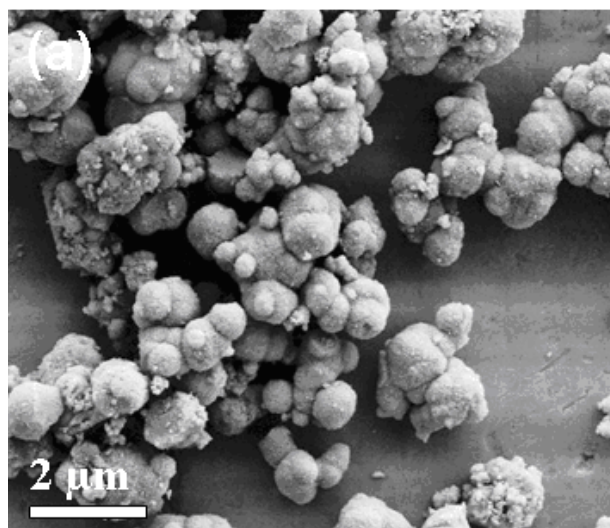


Fig. S3 FESEM image of pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$.

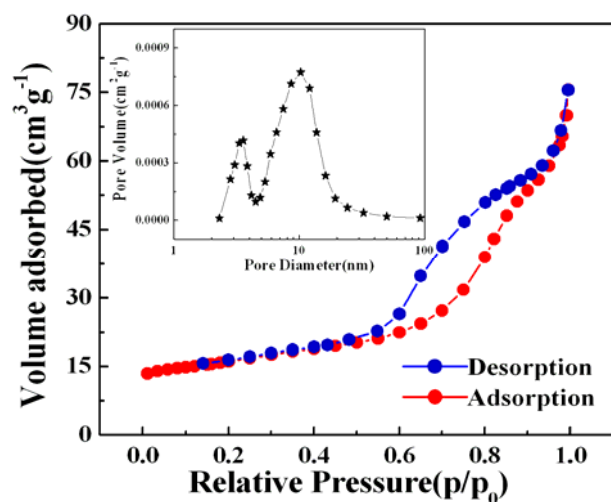


Fig. S4 N₂ adsorption/desorption isotherm of the as-prepared Li₄Ti₅O₁₂. The inset shows the pore size distributions calculated using the BJH method.

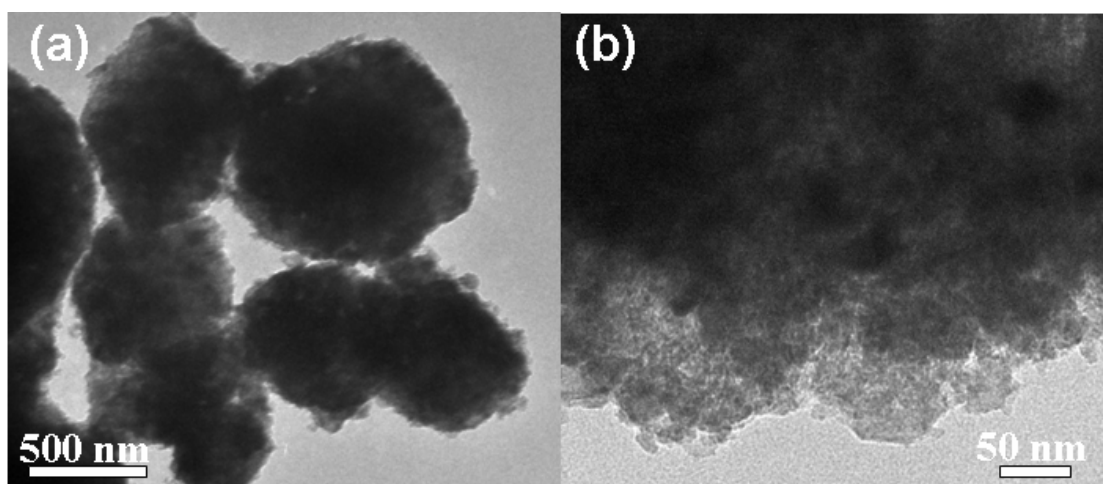


Fig. S5 TEM images of pure Li₄Ti₅O₁₂.

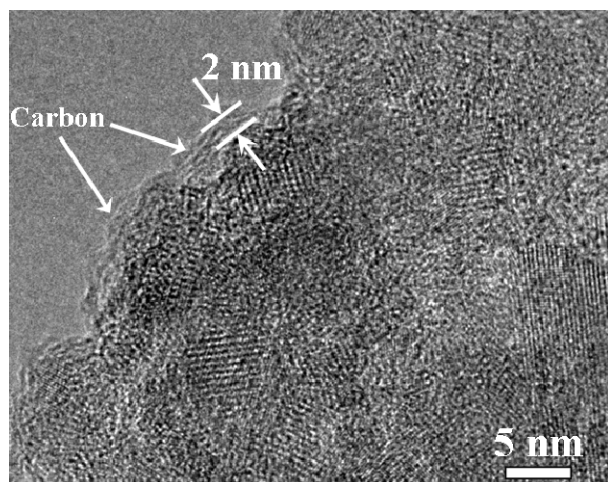


Fig. S6 HRTEM image of mesoporous Li₄Ti₅O₁₂-C microspheres.

Table 1 Impedance parameters of the pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and mesoporous $\text{Li}_4\text{Ti}_5\text{O}_{12}\text{-C}$ microspheres electrodes.

Samples	R_s (Ω)	R_{ct} (Ω)	i^0 (mA cm^{-2})
$\text{Li}_4\text{Ti}_5\text{O}_{12}$	4.2	138.7	0.19
$\text{Li}_4\text{Ti}_5\text{O}_{12}\text{-C}$	2.1	49.3	0.52