### **Electronic Supplementary Information**

# Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> hollow mesoporous microspheres assembled by nanoparticles for high rate lithium-ion battery anodes

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### 1. X-ray diffraction (XRD) analysis of the products after hydrothermal process



(PAHP) and  $\rm Li_4Ti_5O_{12}$  calcinated at different temperatures.

Fig. S1 The XRD patterns of the PAHP and  $Li_4Ti_5O_{12}$  calcinated at different temperatures.

# 2. Thermal analysis data.



Fig. S2 TG-DSC test of the PAHP.

Fig. S2 shows a weight loss of ~ 13% and the flat plateau around 400 °C implies the formation of  $Li_4Ti_5O_{12}$ .

3. The morphologies of the PAHP and  $Li_4Ti_5O_{12}$  calcinated at different temperatures.



Fig. S3 The SEM images of the PAHP (a) and  $Li_4Ti_5O_{12}$  calcinated at different temperatures 300 °C (b); 600 °C (c); 900 °C (d);



4. The HRTEM image of the Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> calcinated at 400 °C.

Fig. S4 HRTEM image of the  $\rm Li_4Ti_5O_{12}$  calcinated at 400  $^\circ C$ 

## 5. The formation mechanism of the hollow structured $\rm Li_4Ti_5O_{12}$ .



Scheme 1 The formation mechanism of the hollow structured  $Li_4Ti_5O_{12}$ .

On the basis of SEM, crystal structure and chemical composition analysis, the

dissolution-etch-crystallization mechanism was put forward to illustrate the formation of hollow structured  $Li_4Ti_5O_{12}$  (presented in Scheme S1, Electronic Supplementary Information). During the hydrothermal treatment of TiO<sub>2</sub> powder in LiOH solution, OH<sup>-</sup> and H<sub>2</sub>O would enter into the TiO<sub>2</sub> particles and interact with the titanium ions and/or lattice oxygen to form titanium hydroxyl species (probably HTiO<sub>3</sub><sup>-</sup>) <sup>49</sup>. Then, Li<sup>+</sup> was attracted by HTiO<sub>3</sub><sup>-</sup> and reacted with it to form supersaturating Li-Ti-O particles, whose particle volume is smaller than HTiO<sub>3</sub><sup>-</sup> particles. The volume shrinkage of the Li-Ti-O formation could cause the repack of many HTiO<sub>3</sub><sup>-</sup> particles. Meanwhile, a large number OH<sup>-</sup> could enter into the HTiO<sub>3</sub><sup>-</sup> microspheres leading to the etch of HTiO<sub>3</sub><sup>-</sup> microspheres. The presence of abundant OH<sup>-</sup> would promote the etch and the fast formation of hollow structured Li-Ti-O microspheres. With further hydrothermal treatment for 48 h, the hollow structured LiTiO<sub>2</sub> microspheres were formed. Finally, the Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> hollow microspheres were obtained by a short thermal treatment of the LiTiO<sub>2</sub> microspheres.

6. Coulombic efficiency of the  $Li_4Ti_5O_{12}$  hollow mesoporous microsphere electrodes.



Fig. S5 Coulombic efficiency for the 500 cycles at the rates of 10 C, 20 C and 40 C.

### 7. The rate properties of three samples annealed at 300 (LTO - 300), 400 (LTO -



400) and 600 °C (LTO - 600).

Fig. S6 The rate properties of LTO - 300, LTO - 400 and LTO - 600.

The much lower discharge capacity of LTO - 300 and LTO - 600 compared to LTO - 400 may be because of the difference in active material contents. Spinel  $Li_4Ti_5O_{12}$  was the major phase of the LTO - 600. However, the major constituent of the LTO - 300 was LiTiO<sub>2</sub>, which possesses very poor electrochemical performance.