Electronic Supplementary Material (ESI) for ChemComm.

Materials. Lithium titanium oxide ($Li_4Ti_5O_{12}$, LTO) was bought from BTR New Energy Material Ltd. Some physical parameters and SEM image of LTO are exhibited in Table S1 and Figure S1, respectively. Natural graphite flakes were purified by Kansai Coke and Chemicals Co. Ltd, some of the physical characters have been mentioned in our previous work [1]. The lithium metal electrodes were bought from Hefei Kejing Materials Technology Co. Ltd. Activated carbon (AC) employed as quasi-reference electrode material was PW15M13130 bought from Kureha Co. Ltd. Teflonized acetylene black (TBA) employed as binder was bought from Denka Co. Ltd. All the electrolyte salts, including lithium tetrafluoroborate ($LiBF_4$), lithium perchlorate ($LiClO_4$) and lithium hexafluorophosphate ($LiPF_6$) were bought from TCI (Shanghai) Development Co. Ltd., and were used without further purification. Ethylmethyl carbonate (EMC) was bought from TCI (Shanghai) Development Co. Ltd., and was dried by molecular sieves before use.

Cell fabrications. The active material (LTO, graphite and AC) was mixed with carboxymethyl cellulose (M.W. 700000, Aladdin Chemistry co., Ltd.) and acetylene black (Hefei Kejing Materials Technology Co. Ltd) at a mass ratio of 20: 1: 2 in water to form a homogeneous slurry. The slurry was coated on the current collector (copper foil for LTO electrode, aluminum foil for both graphite and AC electrodes) and cut into a round disk (ϕ=14 mm), the mass of active material was ~5 mg per electrode. All electrodes and separators were dried under vacuum at 130 °C for over 3 hours before use. All the electrochemical cells were assembled in a glove box filled with Ar—atmosphere.

Electrochemical measurements. The cutoff voltages of galvanostatic charge-discharge cycling for Li/LTO and Li/graphite cells (CR2302 two-electrode coin cells) were 2~1 V and 3~5 V respectively. The cutoff voltages of LTO/graphite three-electrode cells (3ESTC15, Hefei Kejing Materials Technology Co. Ltd.) were 0~3.5 V. The quasi-reference electrode employed in a three-electrode cell was a heavy AC electrode. Electrochemical impedance spectroscopic (EIS) measurements were performed at amplitude of 5 mV in the frequency range of 100 kHz to 0.005 Hz using PARSTAT-2273 advanced electrochemical system. The LTO electrodes were discharged to the half capacity (~70 mAh g^{-1}) in Li/LTO cells before they were used in symmetric cells for EIS measurements.

Unless otherwise mentioned, the current density was 0.05 A g^{-1} and all correlative measurements were carried out at about 27 ℃.

Data availability. The data that support the findings of this study are available from the corresponding authors on request.

Figure S1. SEM image of $Li_4Ti_5O_{12}$.

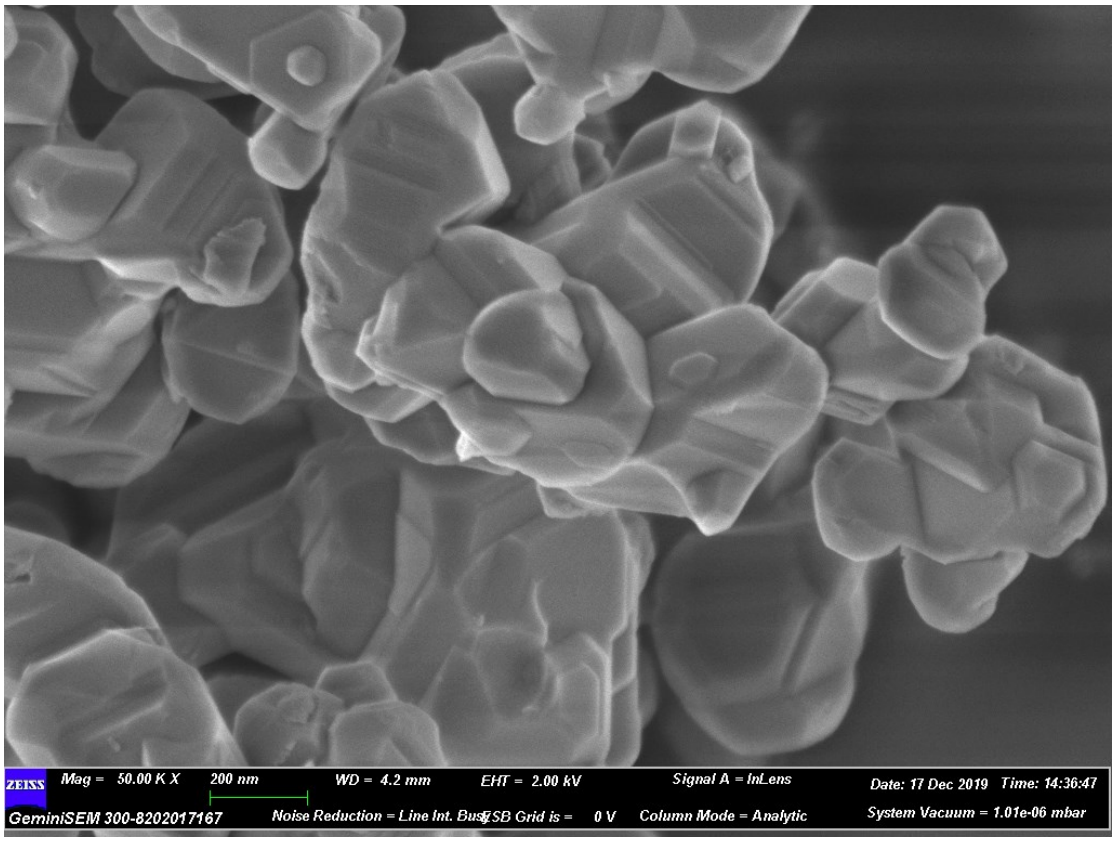

Table S1. Physical parameters of $Li_4Ti_5O_{12}$.

BET Specific Area / $m^2\ g^{-1}$	Tap Density / $g\ mL^{-1}$	Particle Size Distribution		
		D(0.1) / μm	D(0.5) / μm	D(0.9) / μm
3.5352	0.774	1.729	2.834	5.166

1. Y. Huang, J. Li and H. Wang, *ACS Applied Energy Materials*, 2019, **2**, 4544-4550.