

## Supporting information

# Improving the electrochemical performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode by phosphorus reduction at relatively low temperature

Wenwen Deng<sup>a,†</sup>, Xuyong Feng<sup>b, c,†</sup>, Xiang Li<sup>b, c</sup>, Sean O'Neill<sup>b, c</sup>, Lin Hu<sup>d</sup>, Luyao Liu<sup>e</sup>, Wai-Yeung Wong<sup>f</sup>, Yan-Yan Hu<sup>b, c\*</sup> and Chang Ming Li<sup>a, g\*</sup>

*a* Institute of Materials Science and Devices, Suzhou University of Science and Technology, Suzhou 215000, P. R. China

*b* Department of Chemistry and Biochemistry, Florida State University, Tallahassee, Florida 32306, United States

*c* National High Magnetic Field Laboratory, 1800 East Paul Dirac Drive, Tallahassee, FL 32310 (USA)

*d* Anhui Province Key Laboratory of Condensed Matter Physics at Extreme Conditions, High Magnetic Field Laboratory of Chinese Academy of Sciences, Hefei 230031, P. R. China

*e* College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, China

*f* Department of Applied Biology and Chemical Technology, The Hong Kong Polytechnic University, Hung Hom, Hong Kong, P.R. China

*g* Institute for Clean Energy & Advanced Materials, Southwest University, Chongqing 400715, P. R. China

† These authors contribute the same to this work

Corresponding author: Prof. Changming Li, Email: [ecmli@swu.edu.cn](mailto:ecmli@swu.edu.cn); Prof. Yan-Yan Hu, Email: [hu@chem.fsu.edu](mailto:hu@chem.fsu.edu)

### Experimental:

#### 1. Material preparation

$\text{Li}_4\text{Ti}_5\text{O}_{12}$  was synthesized by hand grinding  $\text{TiO}_2$  and  $\text{LiAc}$  (Li:Ti=4.2:5) for 30 min, then the mixture was calcined at 500 °C for 5h and 800°C for 10h to ensure complete reaction.

Phosphorous reduced  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  was synthesized by hand grinding  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  and 1 wt% phosphorous powder for 30 min, then sintering the mixture at 400°C under vacuum for 2h. The diagram of this synthesis was described in Figure 1. For convenience, the as-prepared  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  was marked as LTO, and the phosphorous treated  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  was marked as LTO/P.

$\text{MoO}_3$  was used as received from Sigma Aldrich.  $\text{MoO}_3/\text{P}$  was synthesized by hand grinding  $\text{MoO}_3$  and 1% phosphorous powder for 30 min, then sintering the mixture at 400°C for 2h under vacuum.

#### 2. Electrochemistry

$\text{Li}_4\text{Ti}_5\text{O}_{12}$ , acetylene black, and polyvinylidene fluoride (pvdf) dissolved in N-methyl-2-pyrrolidinone were mixed together to form a homogenous slurry, which was then cast on a piece of carbon coated copper foil. After drying at 100 °C, the electrode film was punched into discs with a diameter of 12.5 mm. The prepared electrode contains 80 wt%  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ , 10 wt% acetylene black, and 10 wt% Polyvinylidene fluoride (PVDF). Loading of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  on each disc was 2~3 mg. The electrochemical performance of LTO electrodes was measured using CR2032 coin cells with Li metal as the counter electrode. The cells were assembled in an argon-filled dry-box (MBraun) with a microporous membrane (Celgard, K2045) as the separator, and 1 M  $\text{LiPF}_6$  in EC/DMC/DEC (w/w 1:1:1) as the electrolyte. They were cycled on a multi-channel battery test system (LAND) within a voltage range of 1.0 V~2.5 V.

For LTO/P, MoO<sub>3</sub>, and MoO<sub>3</sub>/P electrode, the preparation and testing method is the same.

Cyclic voltammetry (CV) for these batteries was measured at room temperature with a Reference 600 (Gamry Instruments). The AC impedance was measured at room temperature on a Reference 600+ Gamry Instrument, within a frequency range from 0.1 Hz to 5×10<sup>6</sup> Hz.

### 3. Characterization

The crystal structures of these LTO, LTO/P samples were determined by X-ray diffraction (XRD) (X'PERT Pro MPD, Cu K $\alpha$  radiation,  $\lambda=0.15406$  nm). The diffraction patterns were recorded at room temperature in the 2 $\theta$  range from 10 to 80 with a scan rate of 7° min. The X-ray photoelectron spectroscopy (XPS) measurement of LTO and LTO/P powder was carried on VGESCALABMKII. The morphology and particle size of LTO, LTO/P samples were characterized with scanning electron microscopy (SEM, Nova 400 Nano, FEI). Transmission electron microscopy (TEM) was conducted on a JEOL-2010. The electron paramagnetic resonance (EPR) measurement was conducted on an EPR-200 spectrometer using an X band (9.4 GHz) at 140K and room temperature, respectively.

## Results and Discussions:

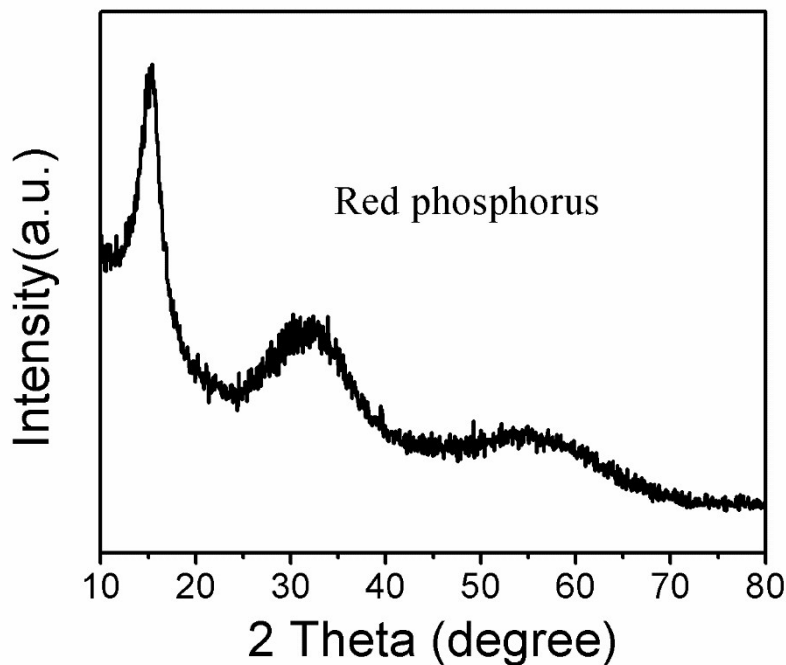


Figure S1 XRD pattern of red phosphorus.

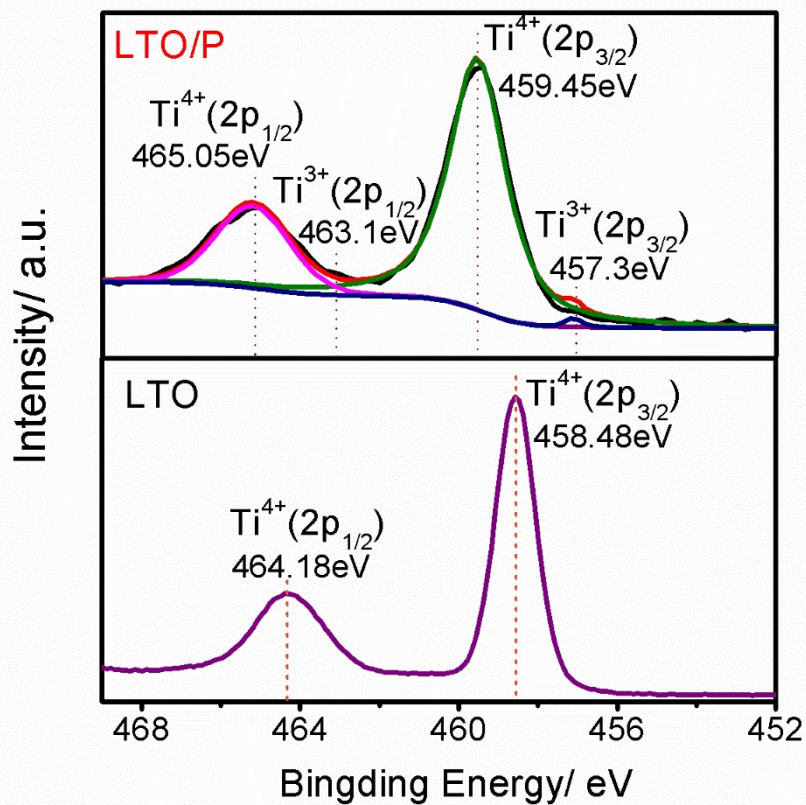


Figure S2 X-ray photoelectron spectroscopy of Ti<sub>2p</sub> in Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> and Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>/P sample.

As can be seen from Figure S2, the two peaks for the LTO sample locate at 464.18 and 458.48 eV are attributed to the Ti 2p<sub>1/2</sub> and Ti 2p<sub>3/2</sub> binding energies of Ti<sup>4+</sup>, respectively. The binding energies for Ti 2p in the LTO/P electrode are located at 465.05 (Ti 2p<sub>1/2</sub>) and 459.45 eV (Ti 2p<sub>3/2</sub>), which are approximately 0.8 and 0.9 eV higher than those in the LTO, respectively, indicating a successful reduction of Ti<sup>4+</sup> to Ti<sup>3+</sup>.<sup>1</sup>

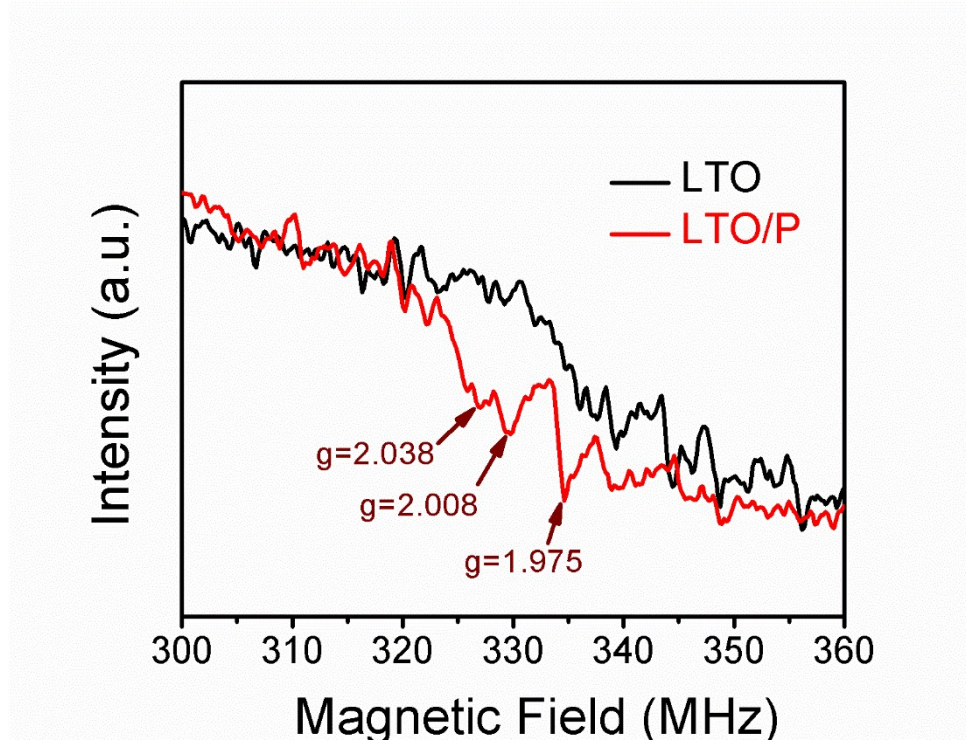


Figure S3 Electron spin resonance spectra for LTO/P sample conducted at room temperature.

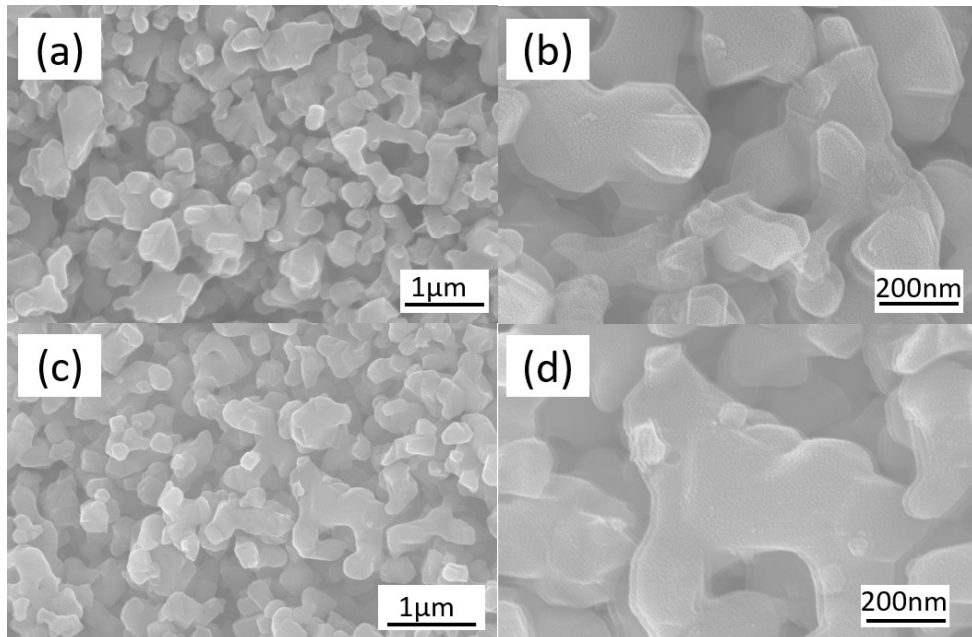


Figure S4 SEM images of LTO (a, b) and LTO/P (c, d) respectively.



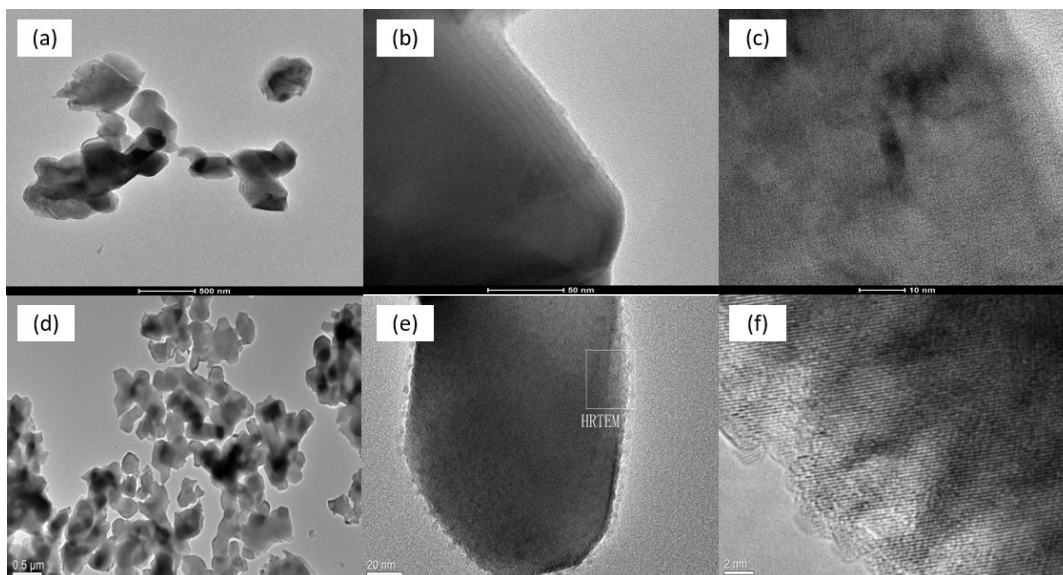


Figure S5 (a) TEM image of the LTO powder; (b, c) HRTEM image of the LTO sample; and (d) TEM image of the LTO/P powder; (e, f) HRTEM image of the LTO/P sample.

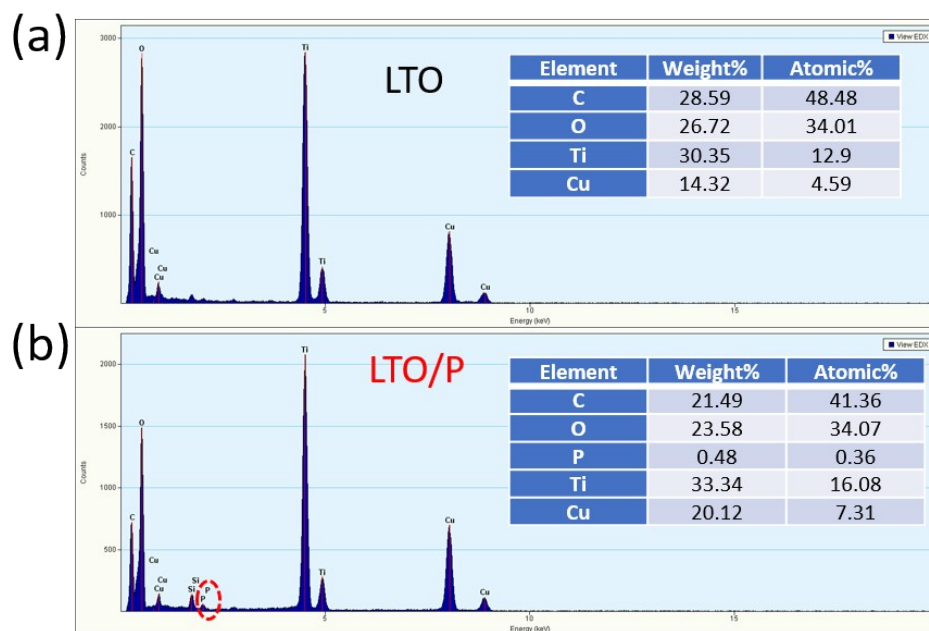


Figure S6 EDS spectrum of the LTO (a) and LTO/P (b). The inset indicates the element content of the mapping area. The Cu (8.05 keV) signal arises from the Cu carrier used for TEM measurement.

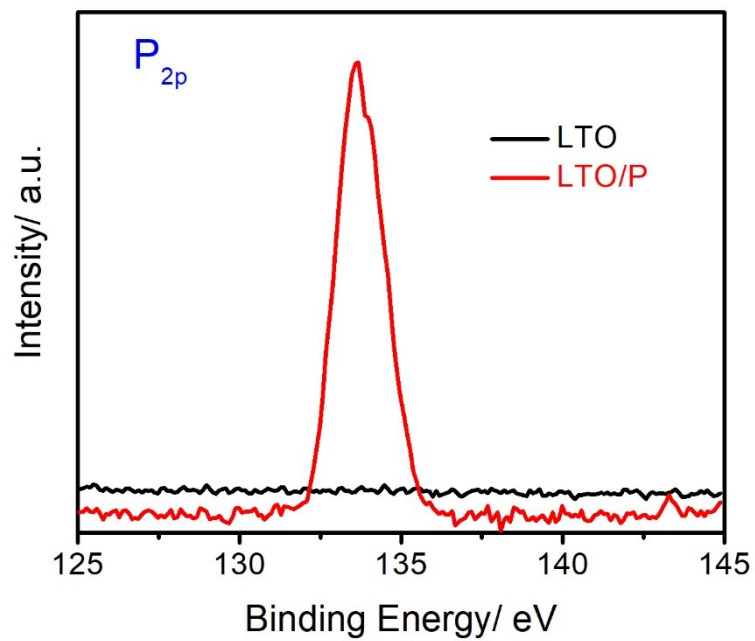


Figure S7 X-ray photoelectron spectroscopy of P<sub>2p</sub> in Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> and Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>/P sample.

References:

- [1] J.-Y. Eom, S.-J. Lim, S.-M. Lee, W.-H. Ryu and H.-S. Kwon, *J. Mater. Chem. A*, 2015, 3, 11183–11188.