

Supplementary Information

Phosphidation of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ Nanoparticles and Their Electrochemical and Biocompatible Superiority for Lithium Rechargeable Batteries

Mi Ru Jo^{†a}, Ki Min Nam^{†b}, YoungMin Lee^a, KyeongSe Song^a, Joon T. Park^{*b}, and Yong-Mook Kang^{*a}

^a Division of Advanced Materials Engineering, Kongju National University, 275 Budae-dong, Cheonan, Chungnam, Republic of Korea

^b Department of Chemistry Korea Advanced Institute of Science and Technology Daejeon, 305-701, Korea

*Corresponding author. E-mail: dake1234@kongju.ac.kr (Y.M.Kang), joontpark@kaist.ac.kr (J.T.Park)

† equal contribution

Experimental

(1) Preparation of phosphidated- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanoparticles

A white powder of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (0.20 g, 99 % Aldrich, pristine- $\text{Li}_4\text{Ti}_5\text{O}_{12}$) and trioctylphosphine (20mL, 90 % Aldrich) were mixed in a 100 mL flask connected to a bubbler under an H_2/Ar (5 %) atmosphere. The reaction mixture was maintained at room temperature for 1h. The resulting white reaction mixture was centrifuged, and the supernatant was removed. The residue was loaded into an alumina boat reactor, which was placed in the tube furnace connected to the gas feed system. After allowing a brief period (30 min) for stabilization of the gas flow (H_2/Ar , 5%), the tube furnace was heated from room temperature to 600 °C at the rate of 4 °C/min, and then maintained for 2 h. Then, the tube furnace was allowed to cool down to room temperature. The resulting gray powder was phosphidated- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ with an average size of 42 ± 12 nm.

(2) Post heat treatment of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanoparticles

The white powder, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (0.20 g, 99 % Aldrich), was loaded into an alumina boat reactor, which was placed in the tube furnace connected to the gas feed system. After allowing a brief period (30 min) for the stabilization of the gas flow (H_2/Ar , 5 %), the tube furnace was heated from room temperature to 600 °C at the rate of 4 °C/min, and then maintain for 2 h. Then, the tube furnace was allowed to cool down to room temperature. The resulting white powder is heat treated- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ with an average size of 42 ± 12 nm.

(3) Characterization

The $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanoparticles were characterized by an XRD (Rigaku D/MAX-RB(12KW) diffractometer, using graphite-monochromatized Cu $K\alpha$ radiation at 40 kV and 100 mA), TEM (low resolution: Omega EM912 operated at 120 kV; high resolution: Philips F20Tecai operated at 200 kV) with a selected area electron diffraction (SAED) pattern and energy disperse analyses of X-ray emission, an X-ray Photoelectron Spectroscopy (XPS) (Mulilab/ESCA 2000) spectrometer using a focused monochromatized Mg $K\alpha$ radiation, and Raman spectroscopy at KBSI and KAIST.

(4) Electrochemical measurements

Electrodes were fabricated by mixing each active material $\text{Li}_4\text{Ti}_5\text{O}_{12}$, acetylene black, and polyvinylidene fluoride (PVDF) with a weight ratio of 80:11:9 using N-methylpyrrolidone (NMP) as a solvent. The resulting slurries were pasted onto Al foils and then dried in a vacuum oven at 120 °C for 5 h. After drying, the electrode foils were pressed and then punched into a rectangular shape. The electrochemical properties of the prepared electrodes were evaluated using CR2016 coin-type cells assembled in an argon-filled glove box. Li metal foil was used as a counter electrode and 1 M solution of LiPF_6 in ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1, v/v) was employed as an electrolyte. The cells were charged and discharged galvanostatically between 1V and 3.0 V at room temperature.

(5) In vitro bio-compatibility test

Pristine or phosphidated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanoparticles were leached with a culture medium composed of DMEM, FBS, peniciline, and streptomycine in an incubator maintained at 37 °C for 24 h. The obtained eluate was mixed with a cell culture medium to grow NiH3T3 fibroblast (mouse embryonic cells) for 24 h. The control corresponds to the tissue culture plate only having a culture medium without any exposure to eluate. After completing the growth of the NiH3T3 fibroblast, the cells were peeled off from tissue culture plate by using Trypsin EDTA solution, and treated thereafter by Trypan blue stain solution (500 μL , 4%, Gibco) and PBS(300 μL) one after the other. The obtained cells were left at room temperature for 10 min before its total cell number and cell viability were measured by a Hemocytometer.

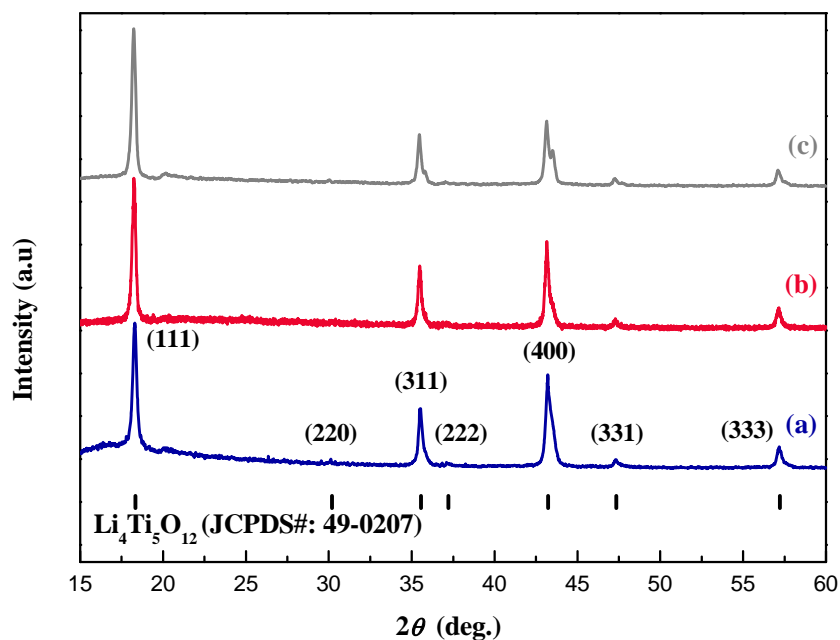


Fig. S1. XRD patterns of (a) pristine- $\text{Li}_4\text{Ti}_5\text{O}_{12}$, (b) phosphidated- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and (c) annealed $\text{Li}_4\text{Ti}_5\text{O}_{12}$ at 600 °C under Ar/ H_2 ambient.

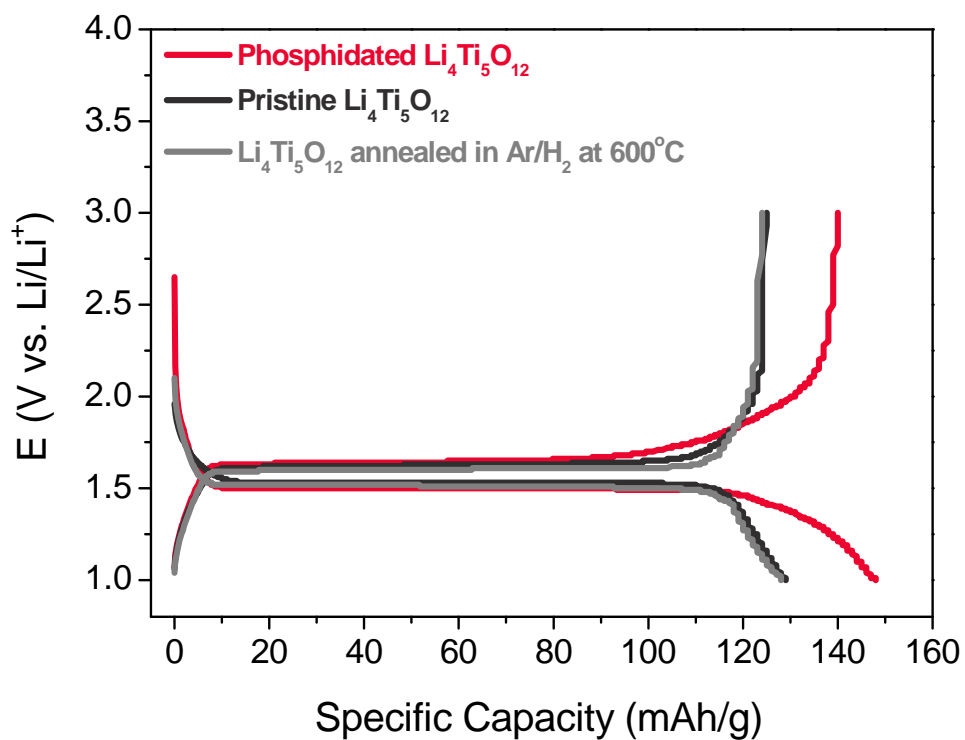


Fig. S2. The initial galvanostate charge/discharge curves of pristine- $\text{Li}_4\text{Ti}_5\text{O}_{12}$, phosphidated- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and annealed $\text{Li}_4\text{Ti}_5\text{O}_{12}$ under Ar/ H_2 ambient at 0.1C

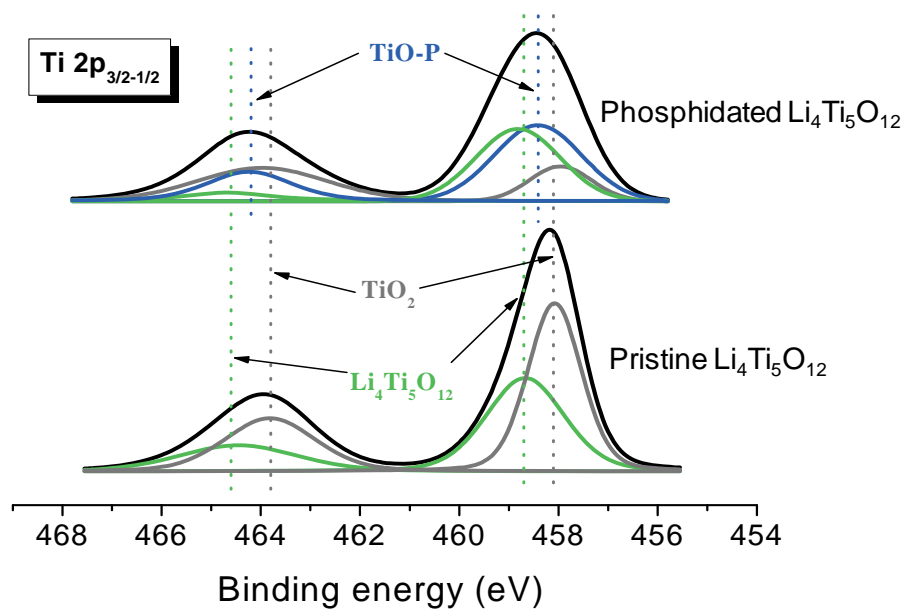


Fig. S3. Titanium 2p X-ray photoelectron spectra of pristine- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and phosphidated- $\text{Li}_4\text{Ti}_5\text{O}_{12}$.

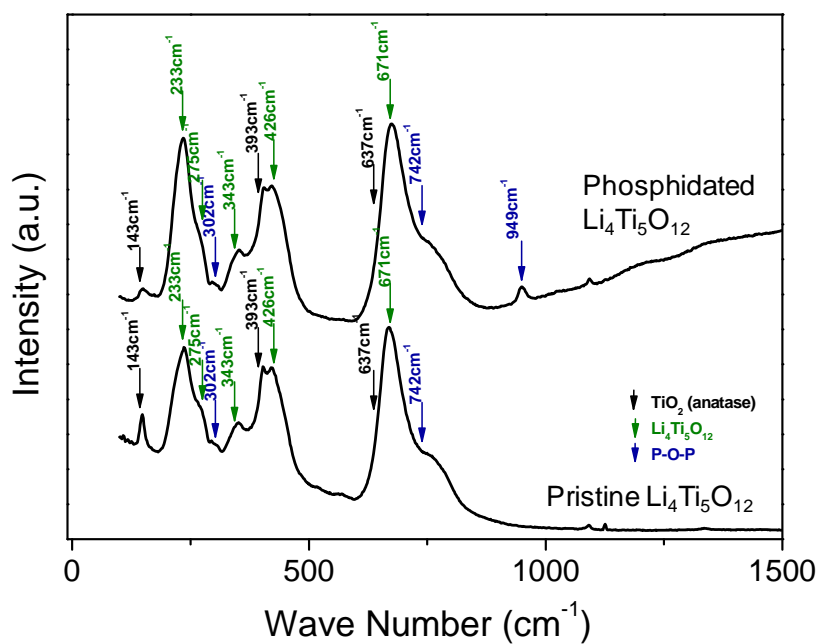


Fig. S4. Raman spectra of pristine- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and phosphidated- $\text{Li}_4\text{Ti}_5\text{O}_{12}$.

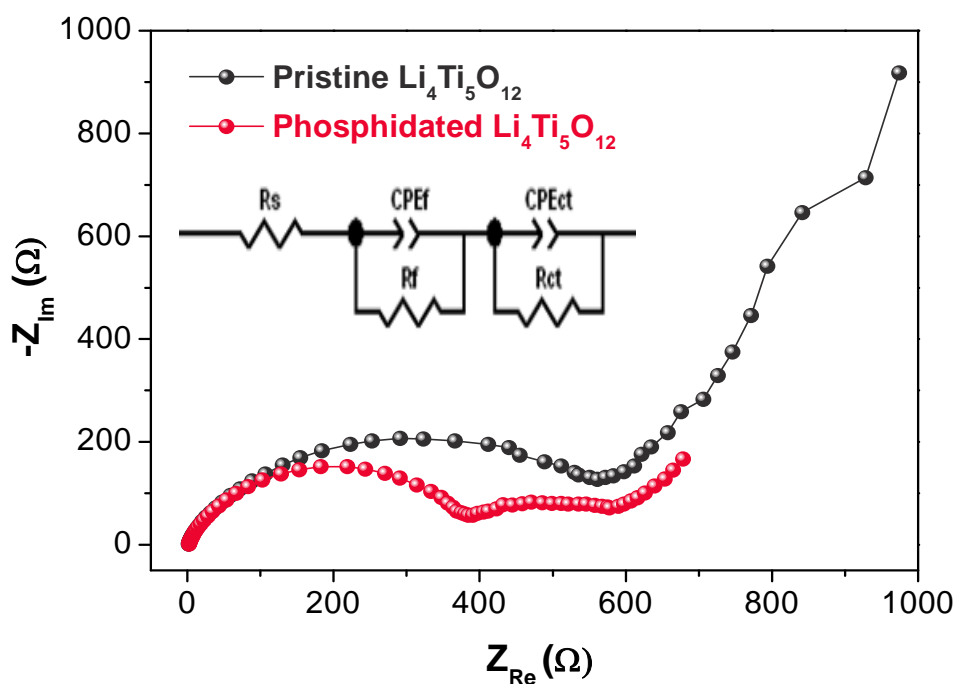


Fig. S5. Nyquist plots of pristine- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and phosphidated- $\text{Li}_4\text{Ti}_5\text{O}_{12}$. The inset figure corresponds to the equivalent circuit used to analyze impedance spectra.

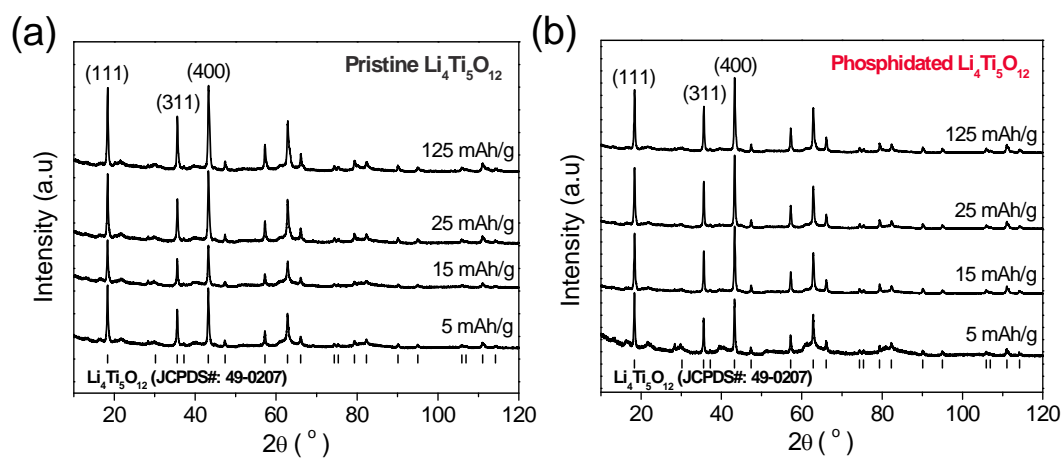


Fig. S6. The ex-situ XRD patterns of $\text{Li}_{4+x}\text{Ti}_5\text{O}_{12}$ structure during the first cycle of $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}$ half cells. (a) pristine- $\text{Li}_4\text{Ti}_5\text{O}_{12}$, and (b) phosphidated- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanoparticles.