

Electronic Supplementary Information

for

Effect of lithium incorporation on tweaking the electrocatalytic behavior of tantalum-based oxides

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Supporting Information

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Experimental Procedure

Chemicals

Tantalum ethoxide ($\text{Ta}(\text{OC}_2\text{H}_5)_5$), lithium nitrate (LiNO_3), 1-butanol (anhydrous, 99.8%), poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol) (PEG-PPG-PEG, Pluronic P123), concentrated nitric acid (HNO_3 , 68-70%), isopropanol ($(\text{CH}_3)_2\text{CHOH}$), Nafion[®] perfluorinated resin solution (5 wt. % in mixture of lower aliphatic alcohols and water), potassium chloride (KCl, ACS reagent grade), ascorbic acid ($\text{C}_6\text{H}_6\text{O}_6$), and commercial tantalum oxide ($\text{c-Ta}_2\text{O}_5$) were purchased from Sigma-Aldrich. All chemicals were directly used as received without further purification.

Materials Synthesis

Lithium-incorporated tantalum oxides were synthesized by the modification of a previously reported mesoporous metal oxide synthesis route discovered by the University of Connecticut known as the UCT method.⁽¹⁾ In the adopted synthesis method 10 g of $\text{Ta}(\text{OC}_2\text{H}_5)_5$ was dissolved in 20 mL of anhydrous 1-butanol under argon environment. The obtained solution was sealed and stirred under argon for 12 hours. About 2.0 mL of the tantalum precursor prepared with the above method was then withdrawn from the sealed flask and mixed with 1.0 g of P123 (1). The mixture was stirred for 30 minutes under N_2 until the completion of inverse micellization. A solution of HNO_3 (1.5 g, 68-70%), 1-butanol (2.0 ml), and LiNO_3 prepared separately was added dropwise to the micelle solution. To promote a slow hydrolysis the obtained sol was then dried at room temperature by adopting the evaporation induced self-assembly (EISA) method (2). A transparent gel was obtained after 2 days. To remove the soft template (P123) and condense the tantalum oxide-based material, the dried gel was thermally treated in a tube furnace at 250°C for 12 hours and 550°C for 1 hour, respectively. To minimize the pore structure collapse, the initial calcination step at 250°C was done at the rate of 1°C/min. However, the second phase of the heat treatment at 550°C was done at 10°C/min to complete the sintering process. Four different materials were synthesized by varying the Li:Ta mole ratio (0.5:1, 1:1, 2:1, and 3:1) and labeled as LTO-0.5, LTO-1, LTO-2, and LTO-3.

Material Characterizations

Powder X-ray diffraction (PXRD) was performed on a Rigaku Ultima IV diffractometer possessing Copper K- α x-ray ($\lambda=0.15406$ nm) as the energy source. Transmission electron microscopy (TEM), high-resolution electron microscopy (HR-TEM), and selected area electron diffraction (SAED) images were captured with a Titan Themis ACEM operating at 300 kV. The nitrogen adsorption-desorption analysis was done using a Quantachrome Autosorb iQ₂ surface analysis instrument. The microstructures and morphologies of the metal oxides were investigated using FEI Nova Nano SEM 450 FESEM with an accelerating voltage of 2 kV and a beam current of 1 mA. X-ray photoelectron spectroscopy (XPS) was done with a Physical Electronics PHI 590 spectrometer equipped with an Al K- α X-ray anode for exciting the photoemission. Binding energies of Li 1s, O 1s, and Ta 4f were measured based on the ionization energy of the adventitious C 1s, C-C peak at 284.8 eV. Electrical tests were all performed on a CHI Model 600E series analyzer/workstation. Secondary-ion mass spectroscopy (SIMS) was conducted by the Hiden Compact SIMS tool.

Electrode Preparation

The electrocatalysts inks were prepared by mixing 5 mg of the tantalum-based oxides with 300 μL isopropanol, 600 μL water, and 80 μL of Nafion[®] solution. The mixture was then sonicated for 60 minutes to obtain a uniform suspension. A 25 μL aliquot of the prepared suspension was dropcast onto glassy carbon electrodes (GCE) then air dried at room temperature within 60 minutes. The fabrication of the commercial tantalum oxide electrode was also done through the same procedure. All coated GCE electrodes were utilized as working electrodes while an Ag/AgCl (with 1 M KCl solution) and a platinum electrode was used as the reference and counter electrodes, respectively. The electrochemical measurements were carried out using a CHI600 E potentiostat (CH Instrument, Texas).

Supporting Figures

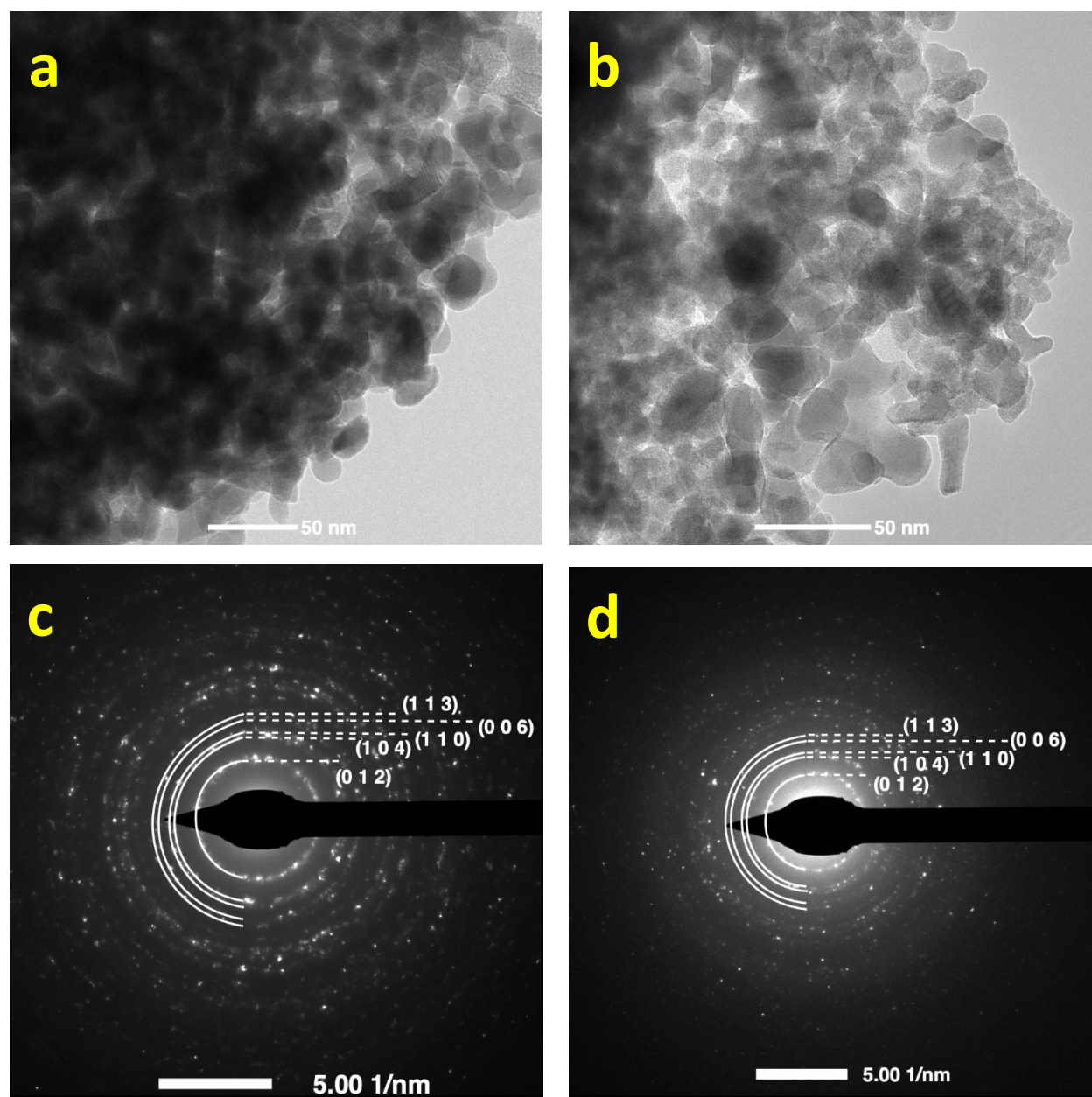


Fig. S1 Low resolution TEM image of; (a) LTO-1 (b) LTO-2. Selected area electron diffraction (SAED) of; (c) LTO-1 (d) LTO-2.

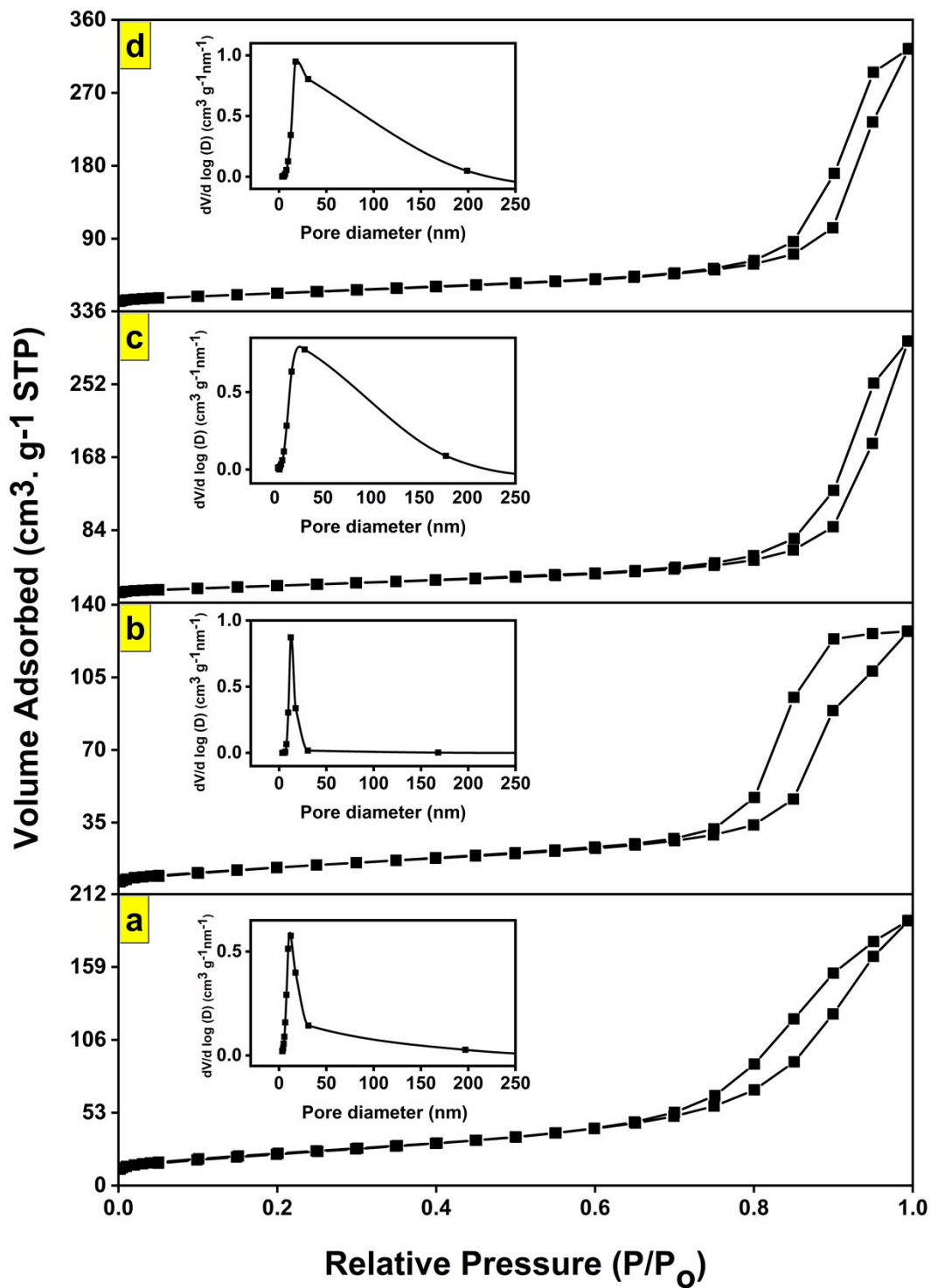


Fig. S2 Nitrogen adsorption-desorption isotherms of LTO samples. Insets show the pore size distributions.

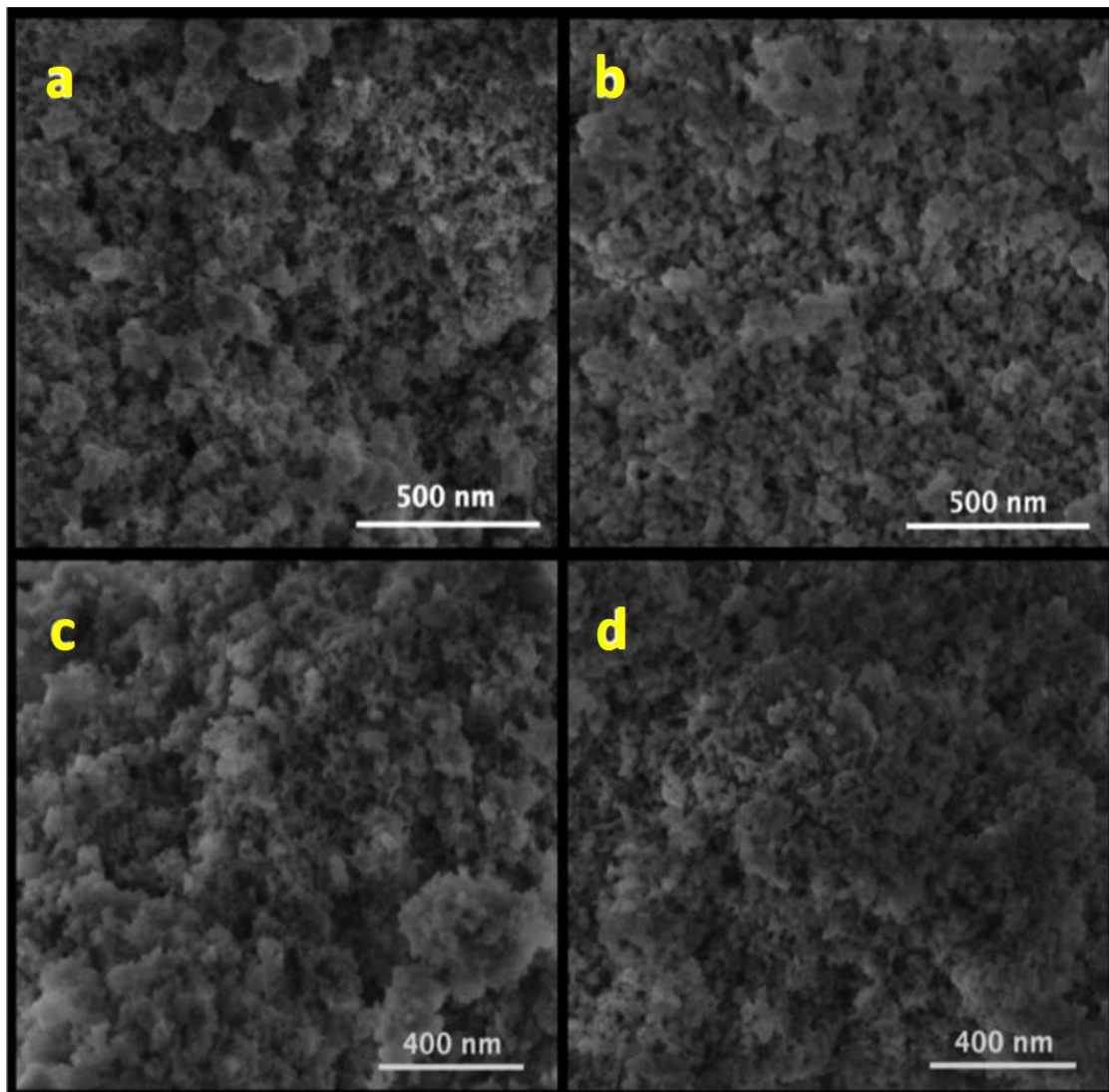


Fig. S3 SEM images of LTO samples microstructures a) LTO-0.5 b) LTO-1 c) LTO-2 d) LTO-3.

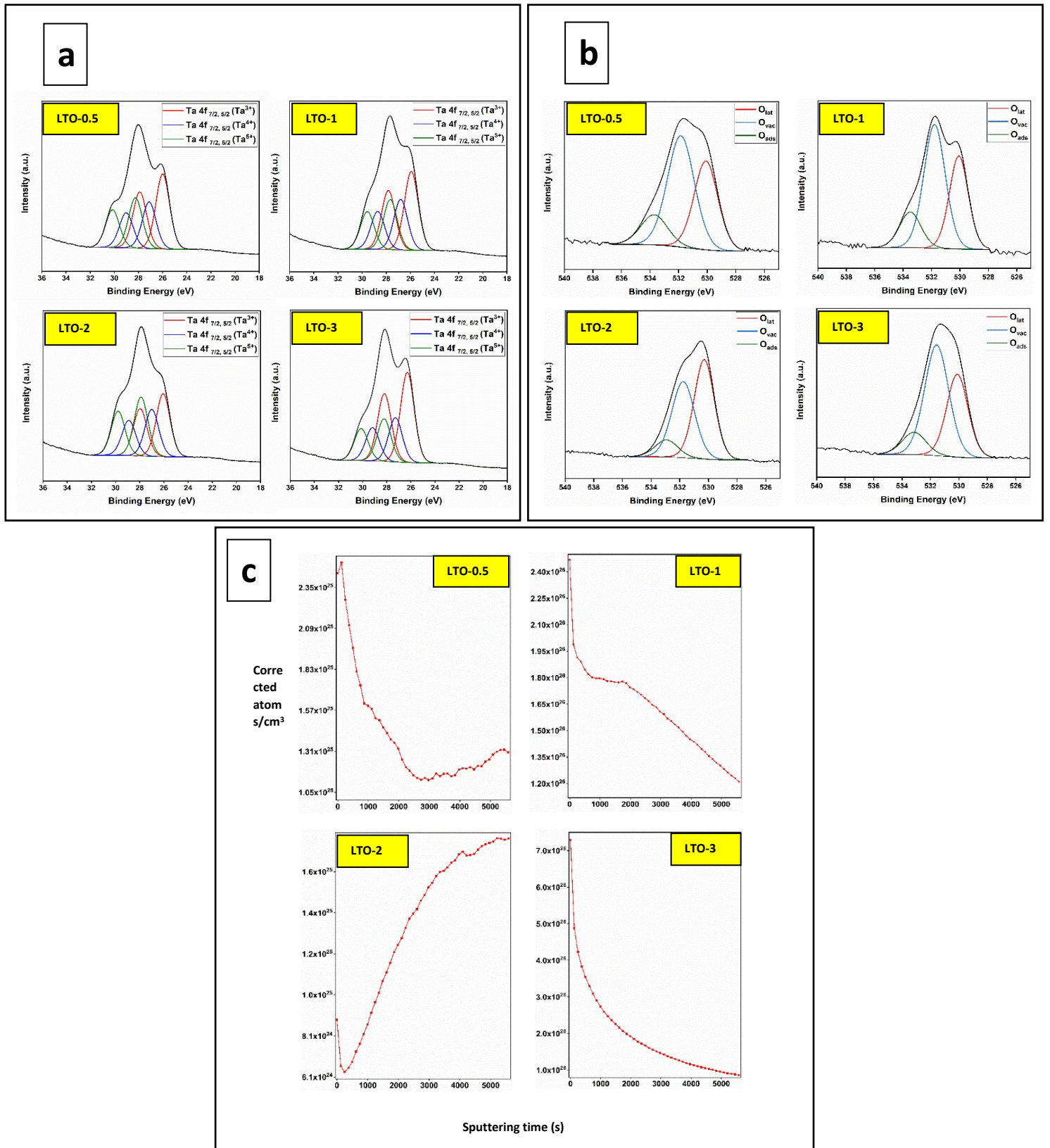


Fig. S4 High-resolution XPS spectra of; (a) Ta 4f peaks (b) O 1s peaks of LTO samples. (c) SIMS depth profile of Li in LTO samples.

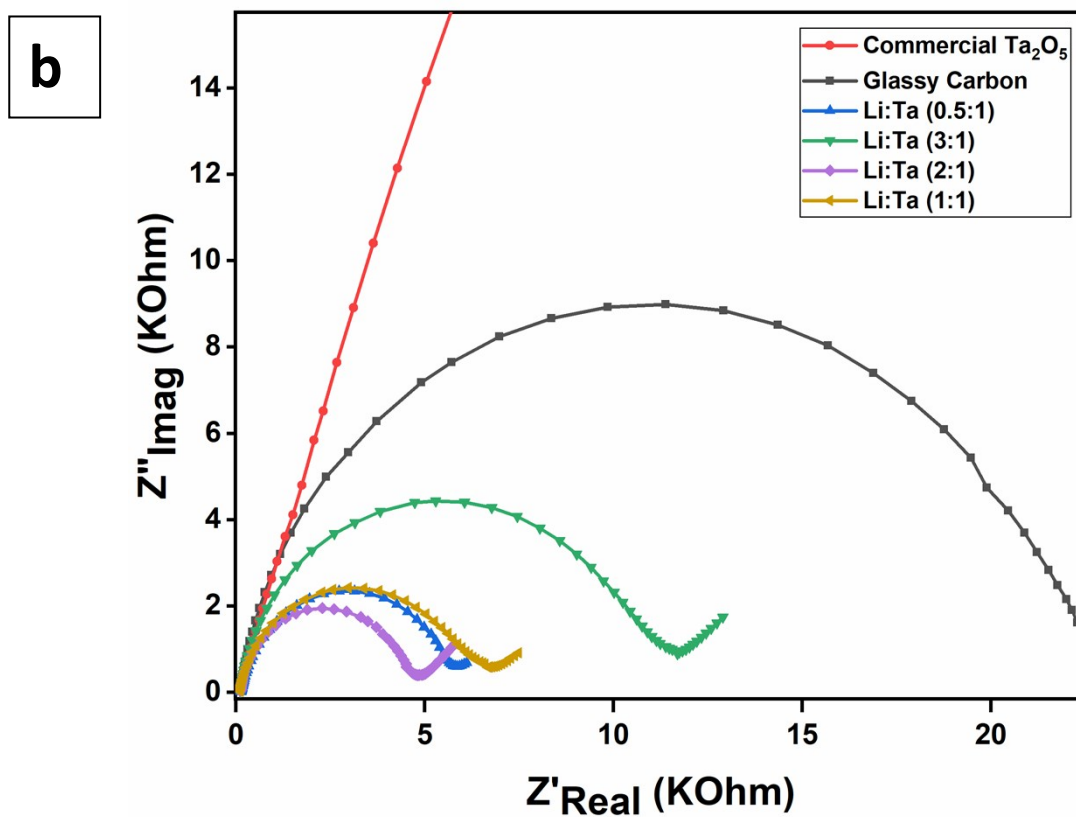
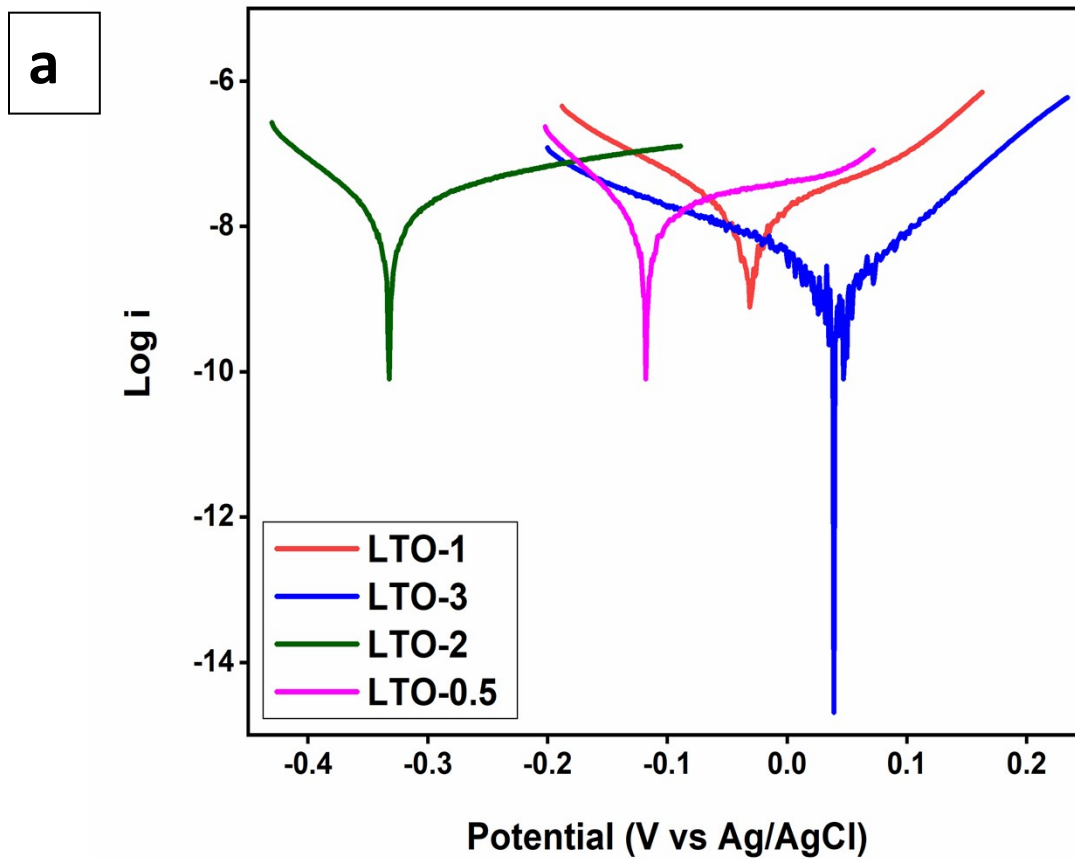


Fig. S5 (a) Potentiodynamic polarization (b) EIS spectra of LTO electrodes in ascorbic acid solution at the frequency range of 1-10⁵.

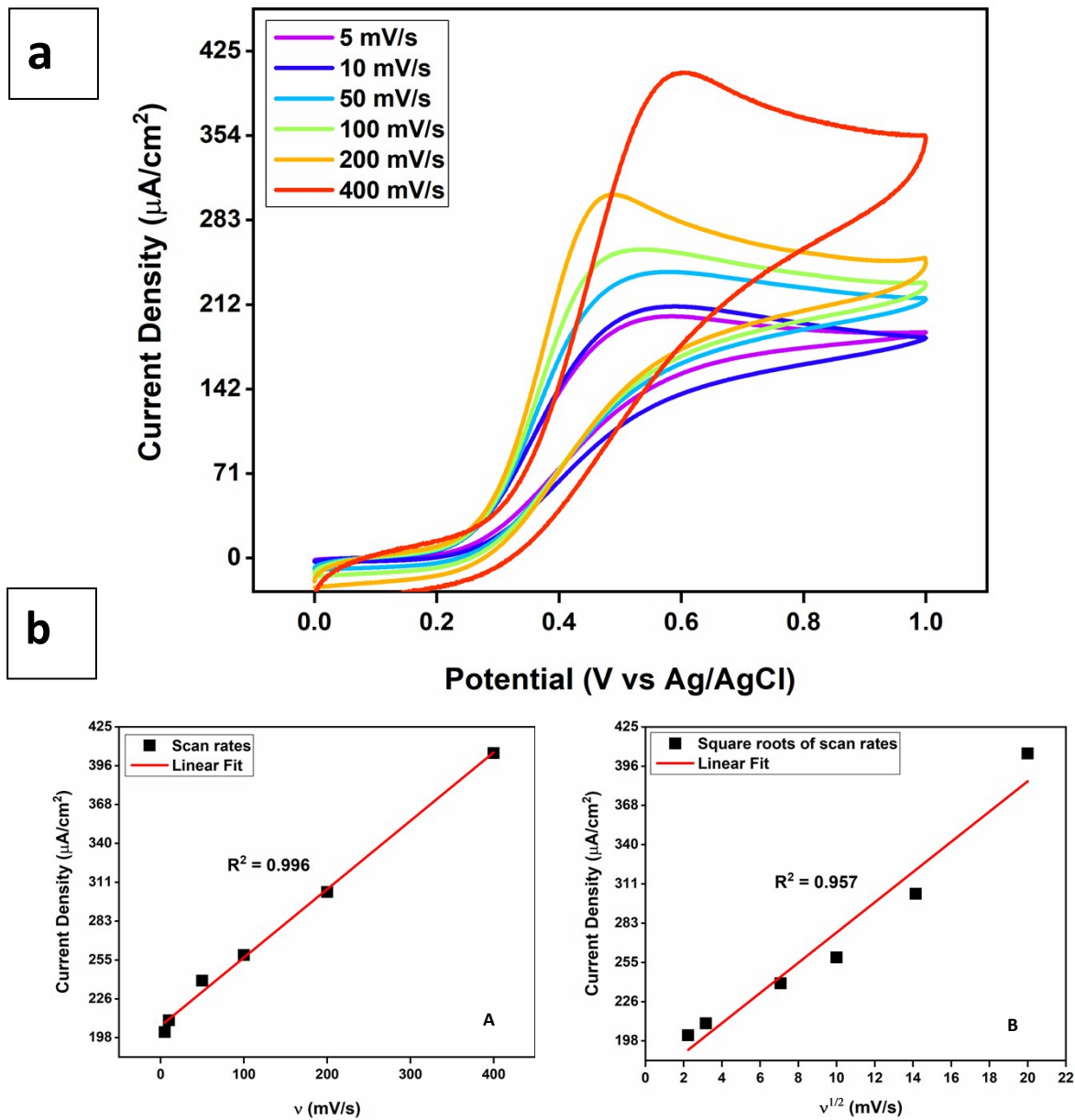


Fig. S6 (a) CVs of LTO-2 in AA solution at scan rates of 5 mVs⁻¹, 10 mVs⁻¹, 50 mVs⁻¹, 100 mVs⁻¹, 200 mVs⁻¹, and 400 mVs⁻¹. (b) I vs. ν (A) and I vs. $\nu^{1/2}$ (B) plots.

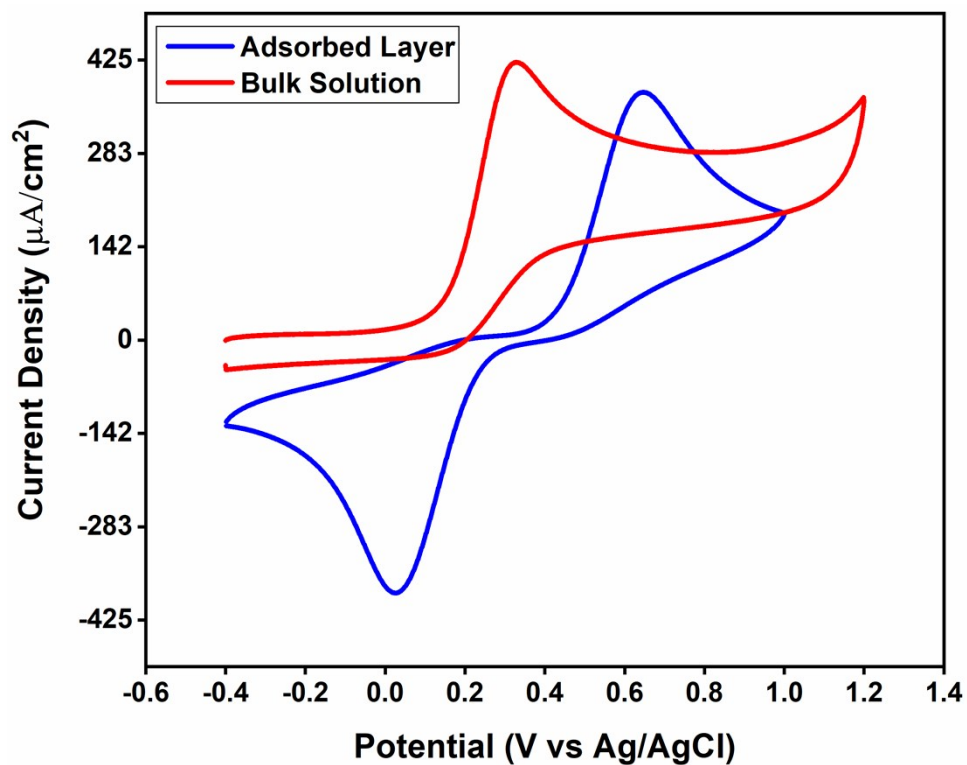


Fig. S7 Cyclic voltammograms of electrooxidation of ascorbic acid as an adsorbed layer on LTO-2 electrode and in the electrolyte solution.

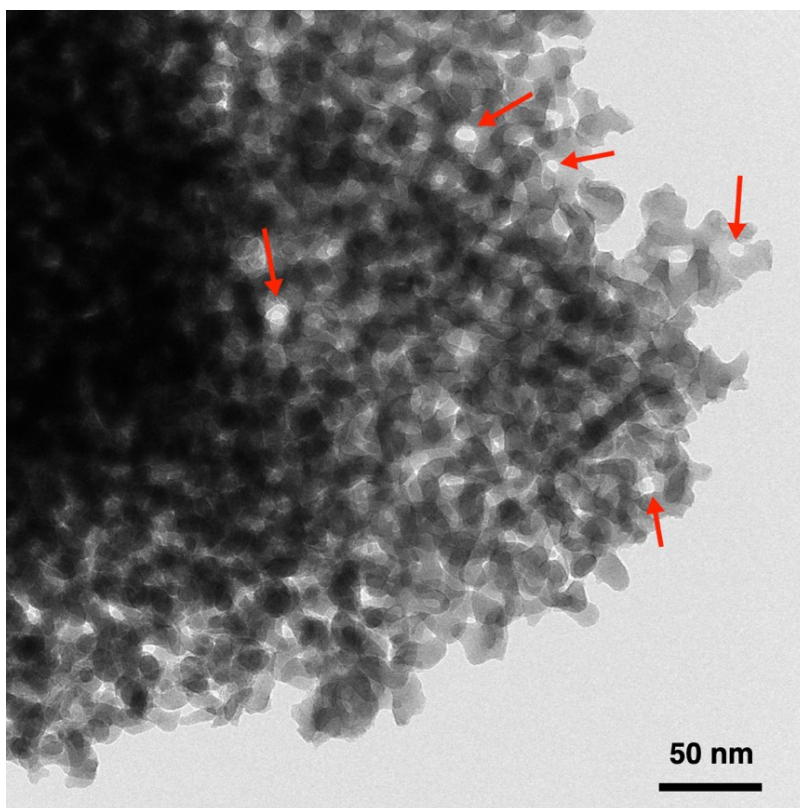


Fig. S8 TEM image of LTO-1 sample. Some of the pores are indicated by red arrows.

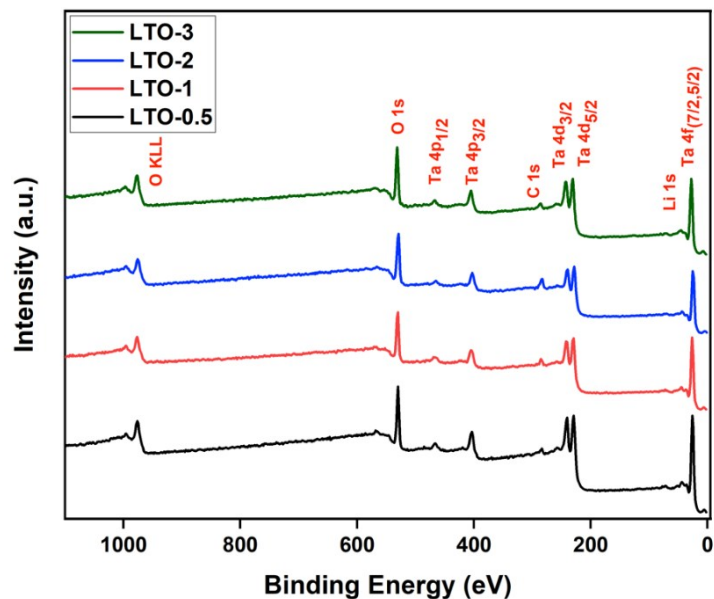


Fig. S9 XPS survey spectra of LTO samples.

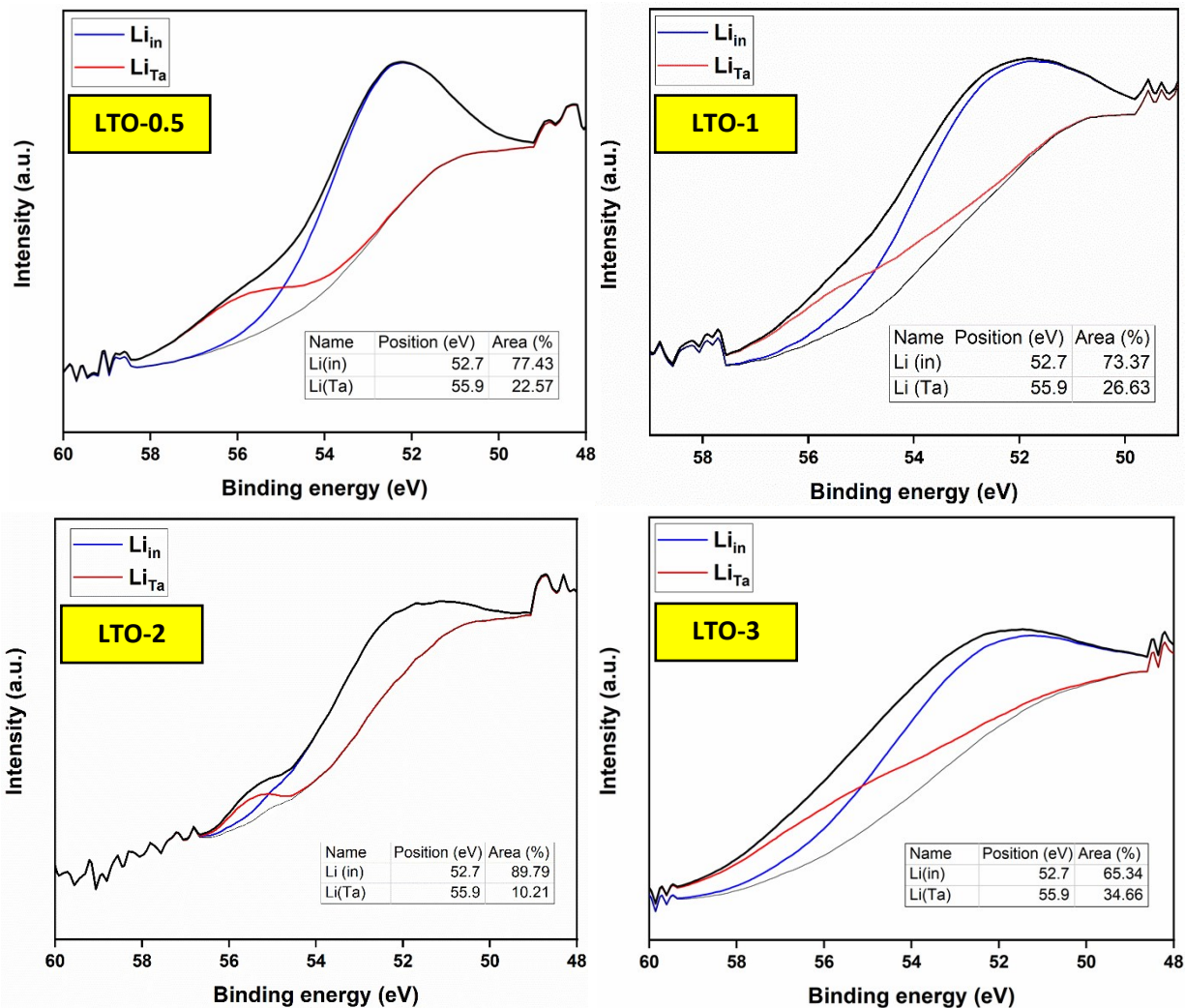


Fig. S10 XPS high-resolution spectra of Li in LTO samples. Li 1s spectra are deconvoluted by two Lorentzian/Gaussian peaks located at 52.7 and 55.9 eV. The embedded tables show the area under two synthetic peaks in different LTO samples.

References

1. Poyraz AS, Kuo CH, Biswas S, King'Ondu CK, Suib SL. A general approach to crystalline and monomodal pore size mesoporous materials. *Nat Commun.* 2013;4:1–10.
2. Guo L, Hagiwara H, Ida S, Daio T, Ishihara T. One-pot soft-templating method to synthesize crystalline mesoporous tantalum oxide and its photocatalytic activity for overall water splitting. *ACS Appl Mater Interfaces.* 2013;5(21):11080–6.