Regulating π-Type Interactions between O 2p and TM t2g Orbitals via Ti Doping and Surface Dielectric Coatings for Li-Rich Cathode

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1. EXPERIMENTAL SECTION

1.1 Synthesis of Materials

The precursor of LLOs($Li_{1.2}Mn_{0.54}Ni_{0.13}Co_{0.13}O_2$) was first prepared by co-precipitatio. The synthesis conditions were nitrogen atmosphere, PH 12, and reaction temperature of 60 °C. The prepared precursor was mixed with $LiOH{\cdot}H_2O$(5% excess) and then held at 450 °C for 5 h and 900 °C for 18 h to obtain LLOs. To obtain the modified materials, niobium ethanolate and tetrabutyl titanate were dissolved in 50 ml of ethanol at a molar ratio of 2:1 and stirred for 1 h. Subsequently, 1 g of LLOs was added and evaporated with stirring at 80 °C in an oil bath. After the solution was evaporated, the powder was scooped out with a medicine spoon and put into a muffle furnace at 700 °C for 6 h. The modified materials were obtained by cooling the furnace to room temperature. The mass fractions of the coating layer were 1 wt%, 2 wt%, and 4 wt%, which were recorded as 1% TN, 2% TN, and 4% TN, respectively.

1.2 Material characterizations

The crystal structure and physical phases were determined by X-ray diffraction (XRD) (PANalytical, PW 3040-X'Pert Pro). Scanning electron microscopy (Zeiss SUPRATM55) and transmission electron microscopy (JEOL-JEM 2100) were used to visualize particle morphology and fine structure. Elemental valence states were detected by X-ray photoelectron spectroscopy (XPS) (Thermo Scientific ESCALAB 250Xi).

1.3 Electrochemical Measurements

Electrode sheets were prepared by a coating method. The mass ratio of cathode

material, conductive agent (Super P) and PVDF (dissolved in NMP as a binder) was 75:15:10. The half-cells were assembled in a glove box with an electrolyte composition of 1M LiPF6/EC: DMC (1:1). Constant-current charge/discharge tests were performed on a blue power tester (LANHE CT2001A) with a voltage range of 2.0-4.7 V. The current density is denoted by C, and 1C = 250 mA g^{-1}. Electrochemical alternating current impedance (EIS) tests were performed on a VMP2 electrochemical workstation (Princeton Applied Research VersaSTAT3). The frequency range was 100 kHz to 10 mHz with a voltage perturbation of 5 mV. The constant current intermittent titration technique (GITT) measurements were performed by charging/discharging at a constant current of 0.1C for 10 min, followed by a 40 min rest in the open circuit.

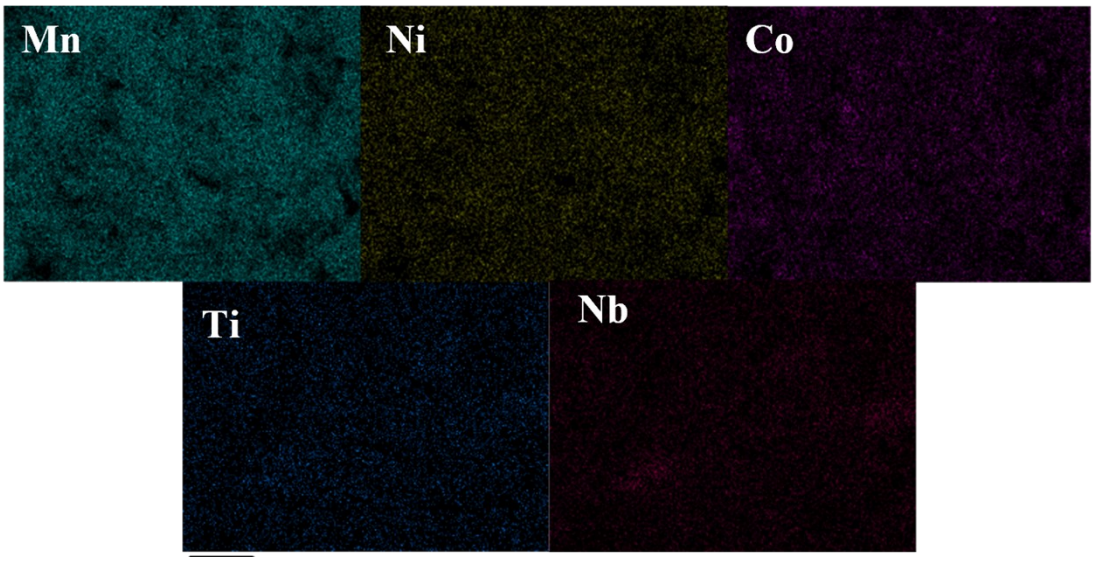

Fig. S1. EDS energy spectra of 2% TN.

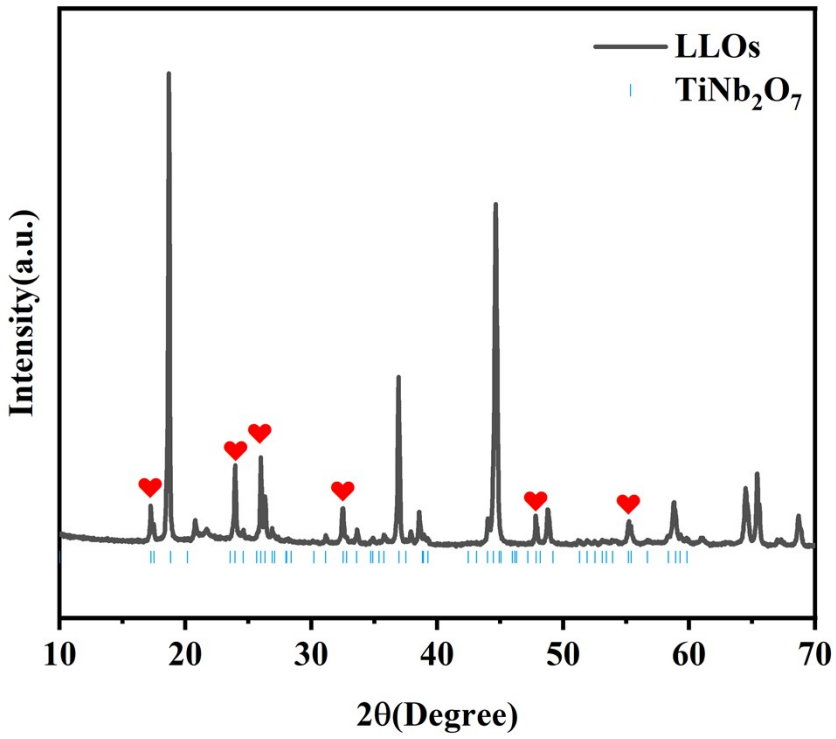

Fig.S2. XRD pattern of LLOs coated with 20 wt% $TiNb_2O_7$.

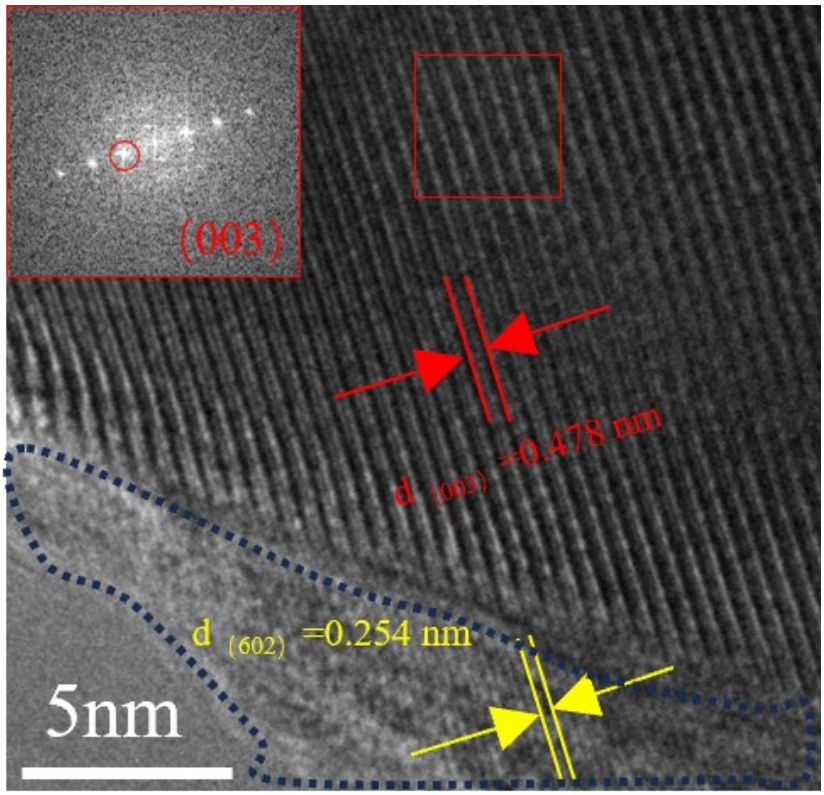

Fig.S3. Localized TEM of 2% TN samples.

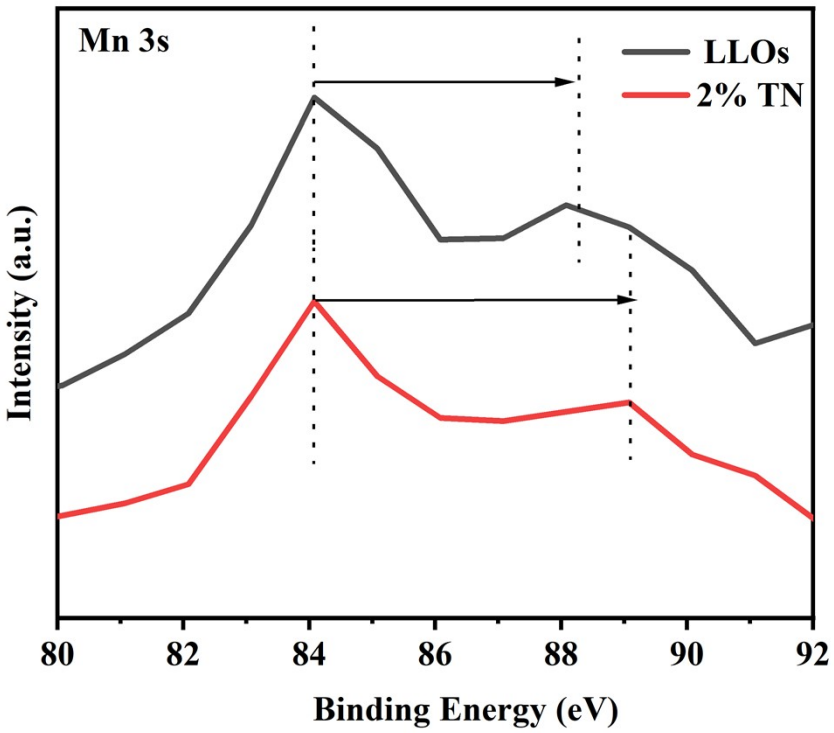

Fig. S4. Mn 3s orbital XPS results for LLOs and 2% TN.

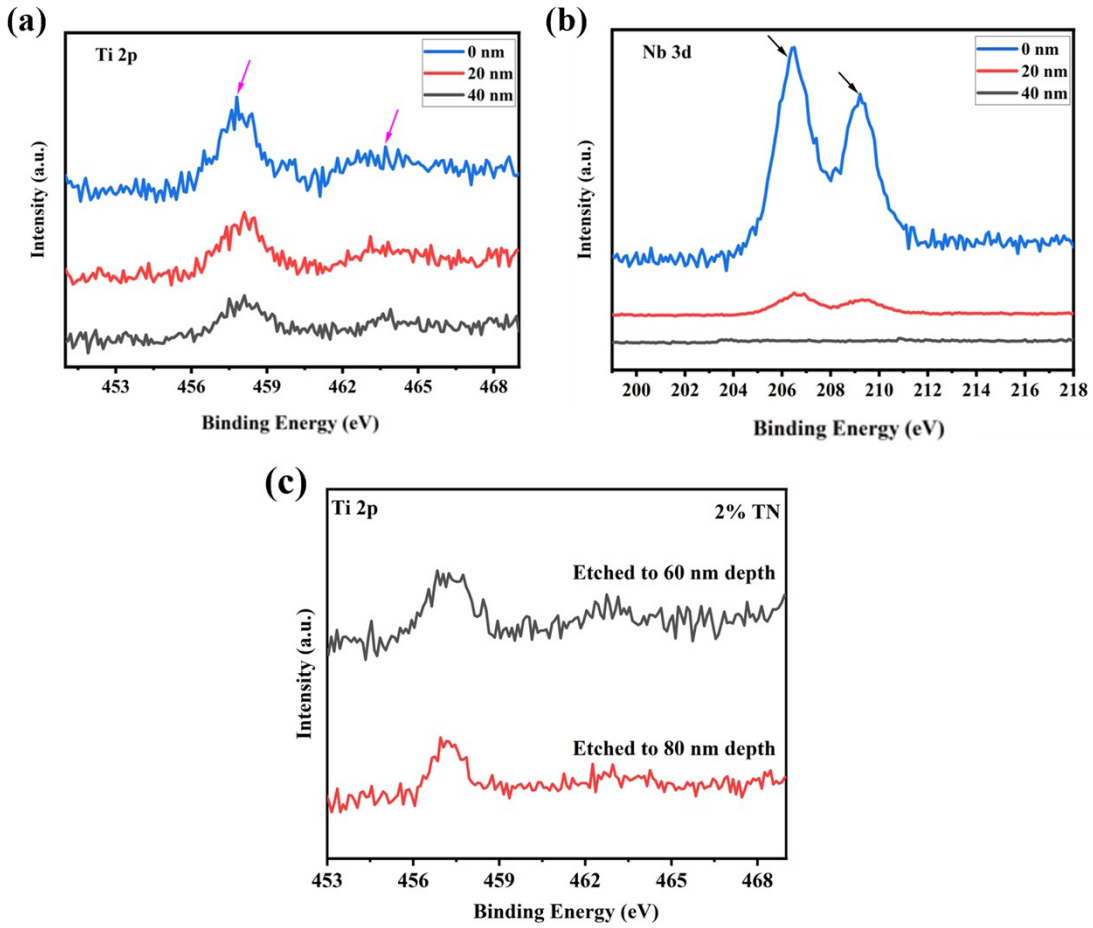

Fig. S5. Results of xps etching of Ti/Nb elements at different depths.

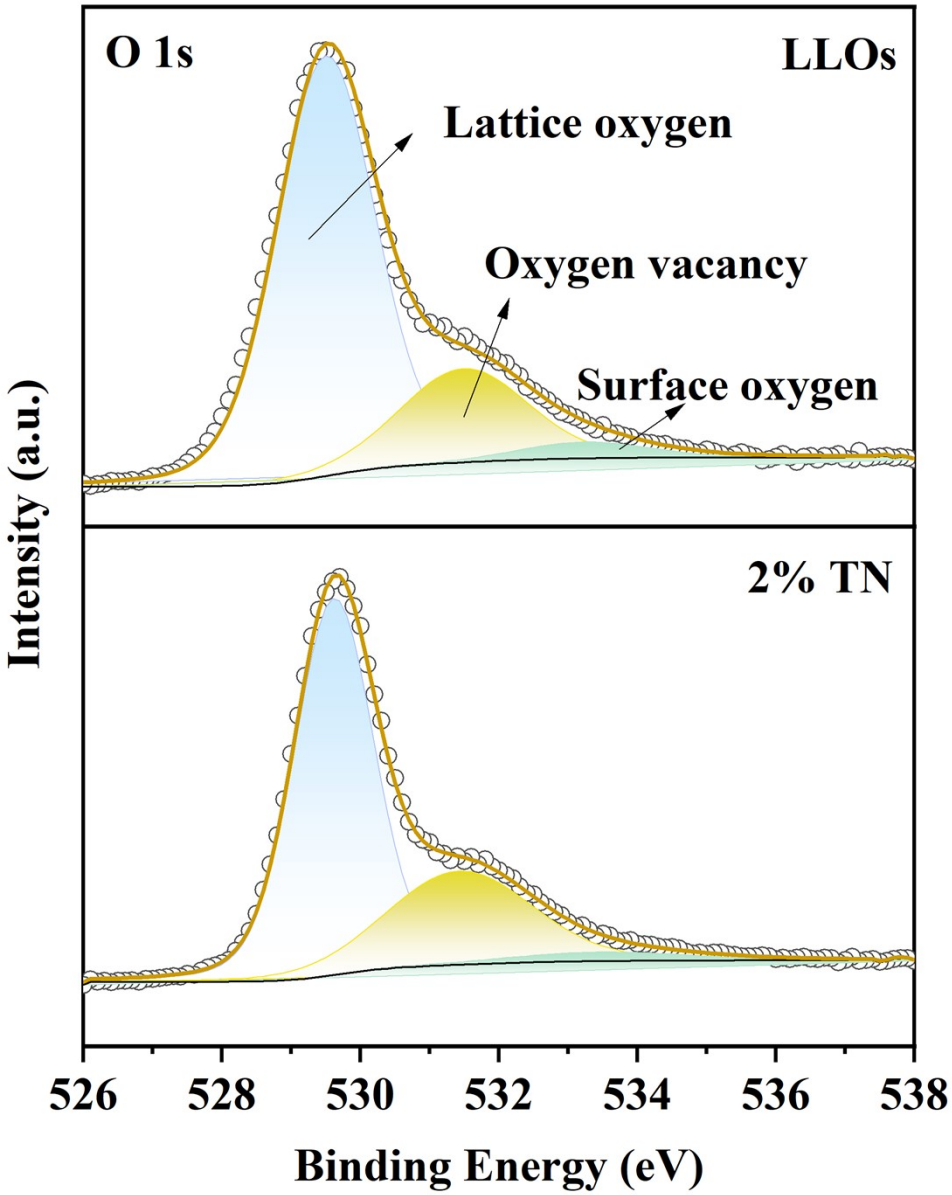

Fig. S6. O1S fitting results for LLOs and 2% TN samples

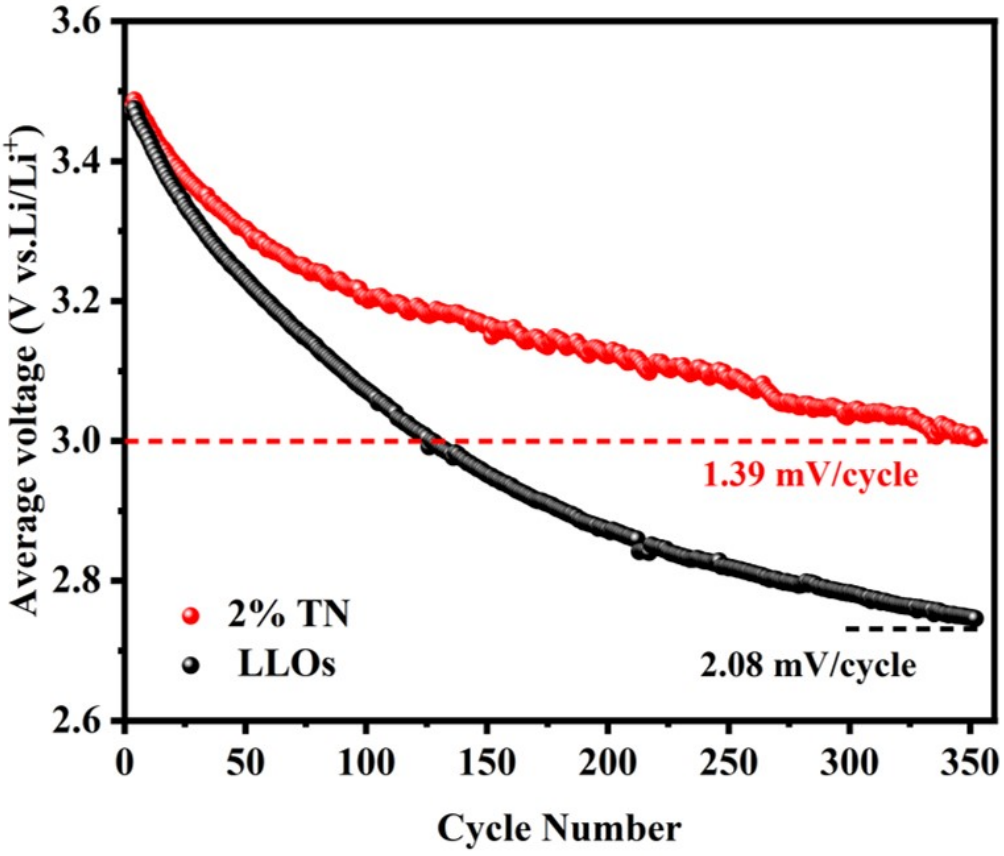

Fig. S7. Voltage decay curves for LLOs and 2% TN samples undergoing 350 cycles

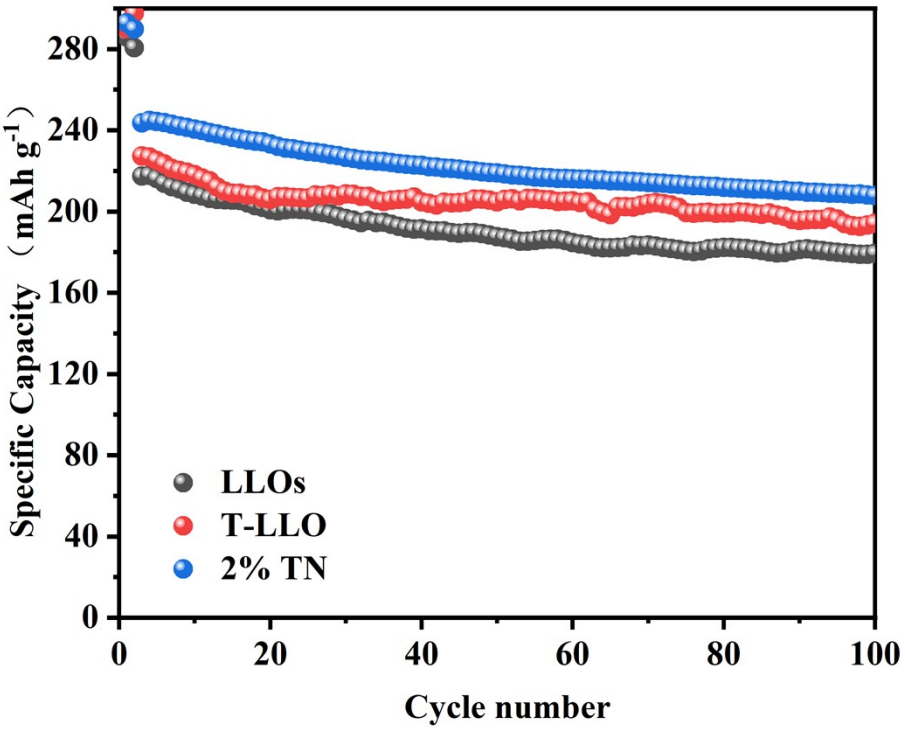

Fig. S8. Cycling performance of individual samples of 1C within 2-4.7 V.

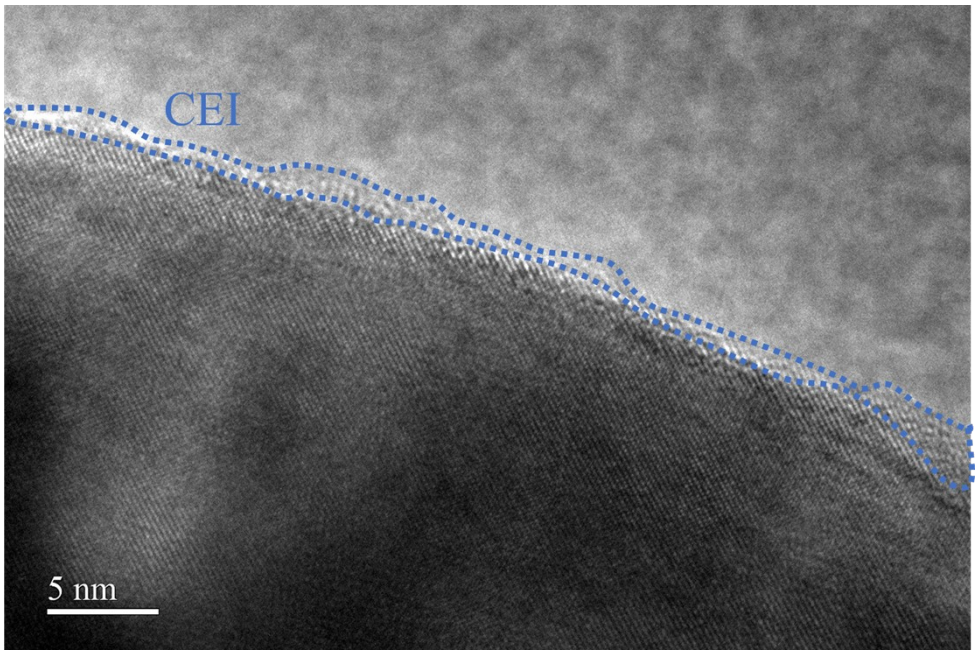

Fig. S9. TEM image of T-LLO after 100 cycles.

Table S1 Data of electrochemical properties of materials.

Sample	Charge specific capacity ($mAh\ g^{-1}$)	Discharge specific capacity ($mAh\ g^{-1}$)	Coulomb efficiency (%)
LLOs	340.4	282.7	83.05
1% TN	330.7	289.5	87.54
2% TN	330.4	289.8	87.71
4% TN	337.2	280.7	83.26

Table S2 Impedance fits for all samples before and after cycling.

	Sample	LLOs	2% TN
1st	R_{ct} (Ω)	119.6	98.4
500th	R_{sf} (Ω)	171.8	91.87
	R_{ct} (Ω)	1116	221