Electronic Supplementary Information (ESI) for:

Oxidation-Reduction Assisted Exfoliation of $LiCoO_2$ into Nanosheets and Reassembly into Functional Li-ion Battery Cathodes

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Materials Characterization

XRD characterization was performed with monochromatic Cu Kα radiation (λ = 1.5405 Å, Panalytical X'pert Pro). Field emission scanning electron microscopy (SEM, XL30) was used to examine the morphology of reassembled LCO particles.

Multiple-collector inductively coupled plasma mass spectrometry (iCaP Q ICP-MS, Thermo Scientific) was used to analyze the composition of the LCO after charging (sample II in Scheme 1), after exfoliation in TEA solution (sample IV), after electrophoresis (sample VI), and after reassembly (sample VII). different LCO samples. To obtain sample IV, the solution containing LCO suspended in TEA was centrifuged at 5000 rpm to remove the unexfoliated LCO particles, followed by vacuum-filteration through a 0.22 μm PVDF filter membrane (Sigma-Aldrich, Durapore) to obtain only nanosheets. All of the samples were digested with 70% nitric acid (trace metal grade) at 160 ^{o}C and 300 psi using a microwave hydrothermal reactor (Discover-SP, 909150).

For thermal gravimetric analysis, the LCO nanosheets were recovered from the TEA solution using centrifugation and the sample was dried in air at 105 ^{o}C overnight. The sample (9.82 mg) was placed in a silicon crucible that was suspended from the arm of a microbalance. The crucible was then heated in a vertical tube furnace (Setaram TG 92) to 1000 ^{o}C with a ramp rate of 0.15 ^{o}C/sec in oxygen and the change in mass was recorded.

For Raman spectroscopy, the nanosheets were recovered from the TEA solution using centrifugation (>14,000 rpm for half an hour) and dried at 50 ^{o}C. Raman spectra were collected with a 532 nm laser and a triple-grating monochromator (SpectraPro 300i, Action Research). The laser beam was focused onto the sample through a Mitutoyo M Plan Apo 50X objective with 0.42 N.A. Measuring powers at the samples were 230 μW and 47 μW for bulk LCO and LCO nanosheets respectively, and all spectra were collected with an exposure times of 60 s and 20 scans.

To prepare samples for TEM characterization, the nanosheet dispersion was centrifuged at 5000 rpm to remove the unexfoliated particles first. Then, the LCO nanosheets were separated from the aqueous TEA solutions using centrifugation at 14,000 rpm (Microfuge, I8) and collected from the decanted phase. The recovered LCO nanosheets were re-dispersed in isopropanol (LCO IPA dispersion) by sonicating with a tip probe sonicator (CPX 600, 660W) for 10 min and dropped onto a Cu grid for TEM characterization (JEOL 2010F) under 200 keV.

For AFM characterization, the LCO IPA dispersion was drop cast onto clean silicon substrates using spin coating at 600 rpm. The silicon substrate was sonicated in DI water, ethanol, and acetone for 30 minutes separately to clean the surface. AFM measurements were performed using an Asylum Research (MFP 3D, classic) microscope with tapping mode.

Electrochemical Testing

Cyclic voltammetry (CV): The as-prepared TEA-nanosheet dispersion was washed using dialysis in DI water first, then centrifuged at 14000 rpm to separate the nanosheets. This sample was then re-dispersed in *N*-methyl-2-pyrrolidone (NMP, Sigma Aldrich). Nanosheets collected from the anode after electrophoresis were re-dispersed in NMP directly. Polyvinylidene difluoride (PVDF, Sigma Aldrich) and graphite (C-Nergy, KS-6) were added into the nanosheet/NMP slurries with a ratio of 7:2:1 by weight. The slurry was coated onto Al foil using a doctor blade, then heated at 110 ^{o}C for at least 12 hours until completely dry. The acquired electrode was assembled into a pouch cell with Li metal as the counter electrode. 1 M $LiPF_6$ in EC/DMC/DEC (4:2:4) was used as the electrolyte (MTI Corp) and the separator was monoPE from Celgard. The CV measurements were performed using a potentiostat (Biologic MPG2) with a scan rate of 1 mV/s.

Galvanostatic cycling: The LCO active material was mixed with graphite and PVDF with a weight ratio of 8:1:1. The electrode and pouch cells were prepared as described before. Galvanostatic cycling was performed using a 0.2 C rate (25 mA/g) from 4.3 to 3 V vs. Li/Li^+ (MPG2, Biologic). Differential capacity analysis was performed using the EC-lab software from Biologic.

Supporting Tables

Table S1. The redox potential for OH^-/O_2 in the different concentrations of TEA-OH solution, showing the feasibility of OH^- oxidation by the LCO electrode after it was charged to 4.3 V vs. Li/Li^+.

TEA: V_{Li^+}	Concentration of TEA-OH (mM)	Solution pH	Redox potential of OH^-/O_2	
			V vs. NHE	V vs. Li/Li^+
10	166.2	13.65	0.42	3.46
5	83.1	13.40	0.44	3.48
2	33.2	13.09	0.46	3.50
1	16.6	12.83	0.47	3.51
0.5	8.3	12.55	0.49	3.53

Supporting Figures

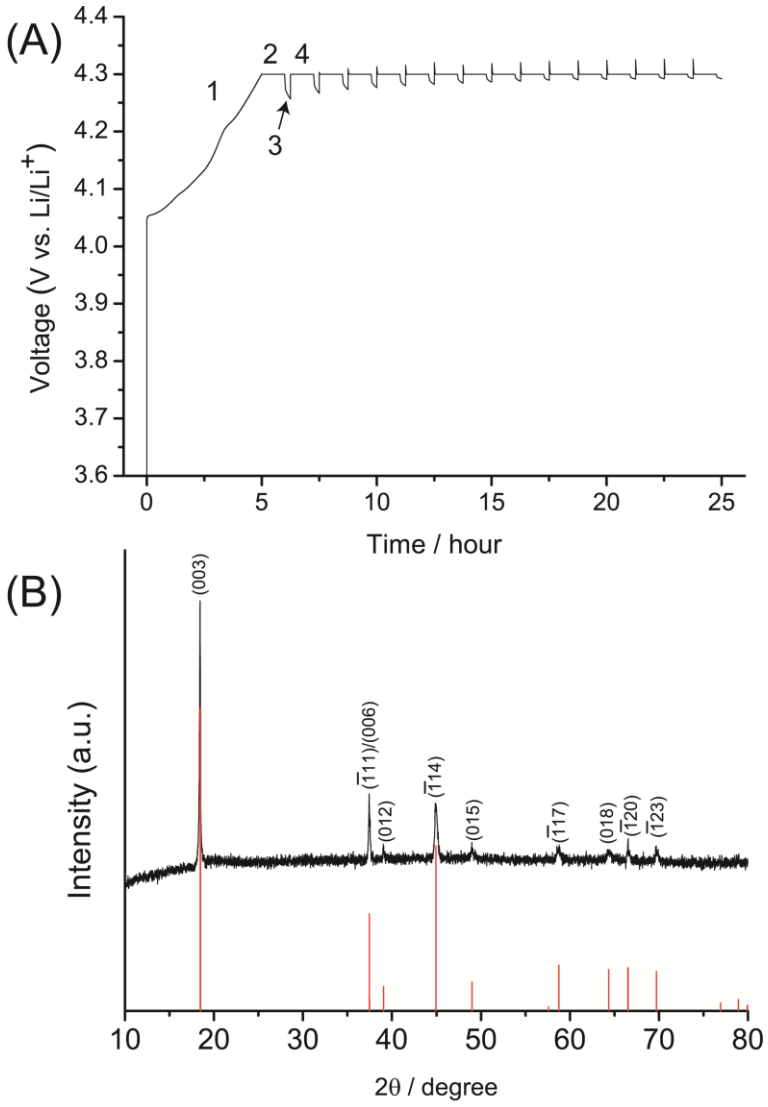

Figure S1. (A) Voltage vs. time plot of the charging process used to oxidize $LiCoO_2$. In region 1, the electrode was charged galvanostatically at 0.05 C until 4.3 V vs. Li/Li^+. Then the electrode was held at 4.3 V for 1 hour (region 2), followed by a 15 minute rest at open circuit (region 3) and another 1 hour hold at 4.3 V (region 4) if the open circuit voltage was less than 4.29 V. This was repeated for approximately 1 day until the open circuit voltage was higher than 4.29 V. (B) XRD pattern of the delithiated $Li_{1-x}CoO_2$ particles, matching the reference pattern for $Li_{0.5}CoO_2$ (from ref. 20 in the manuscript).

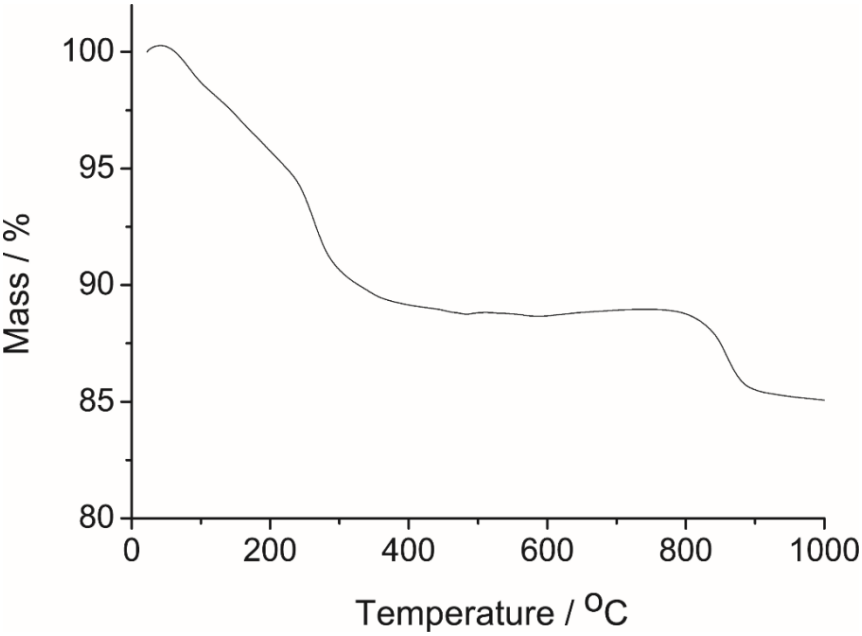

Figure S2. Thermal gravimetric analysis of the LCO nanosheets that were recovered from the TEA solution (TEA: V_{Li^+} = 1) using centrifugation. At 500 ^{o}C the mass loss was 11.2%.

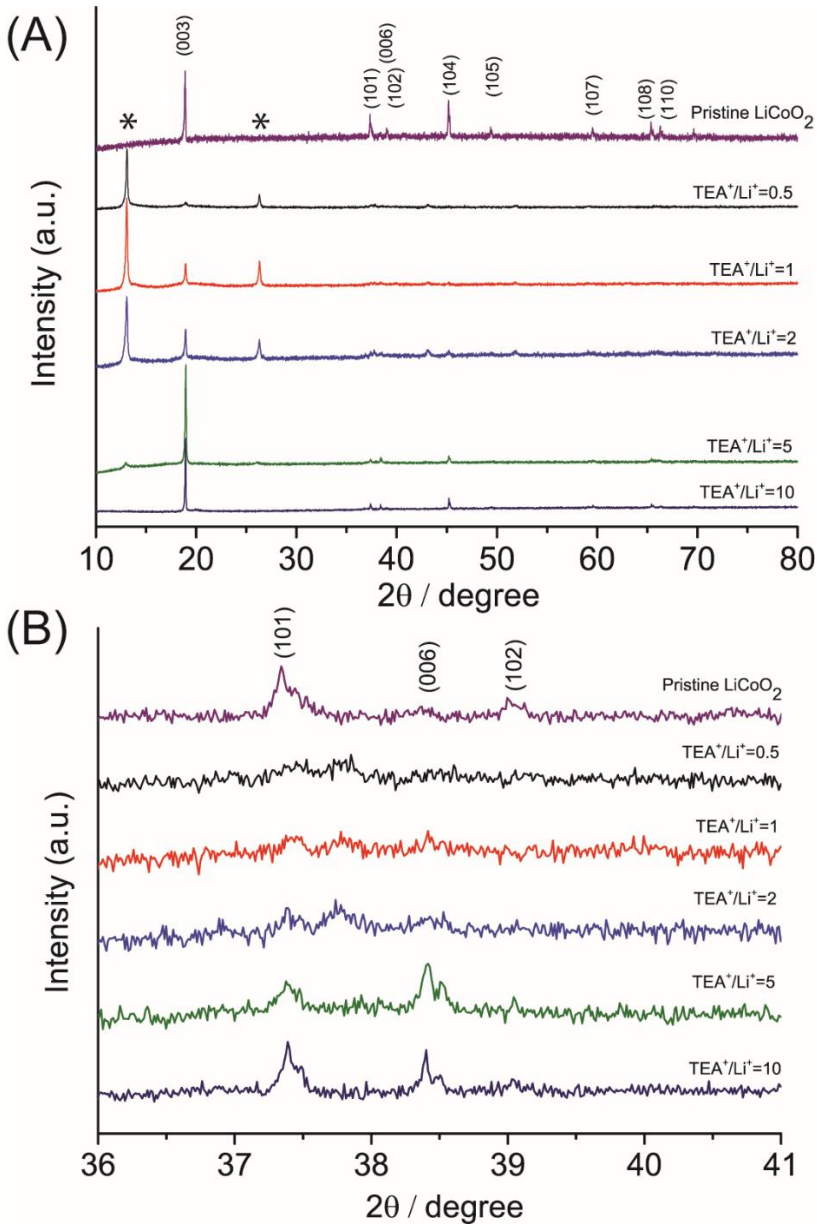

Figure S3. (A) XRD of pristine LCO (O3-type) and unexfoliated LCO obtained after sonication and centrifugation in different TEA^+:V_{Li^+} of 0.5, 1, 2, 5, and 10. Planes from O3-LCO are labelled and asterisks indicate peaks for the LCO intercalated with TEA^+; (B) Zoom-in of XRD patterns from $35^o < 2\theta < 40^o$.

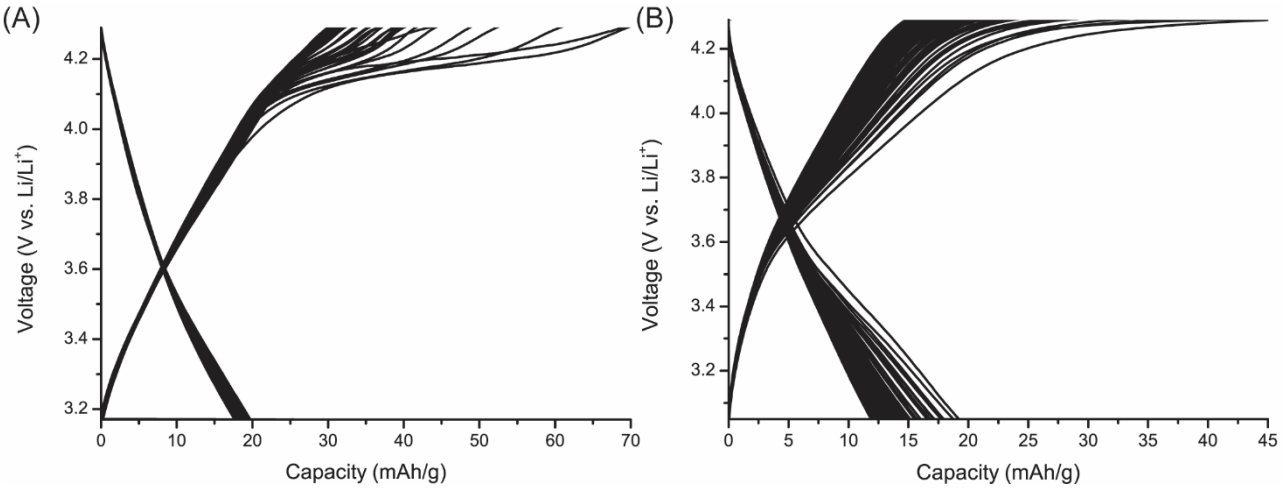

Figure S4. Galvanostatic cycling data of nanosheets (A) after dialysis in DI water, (B) after restacking through dialysis in 1M $LiNO_3$. Fifty charge/discharge cycles are shown for both materials.

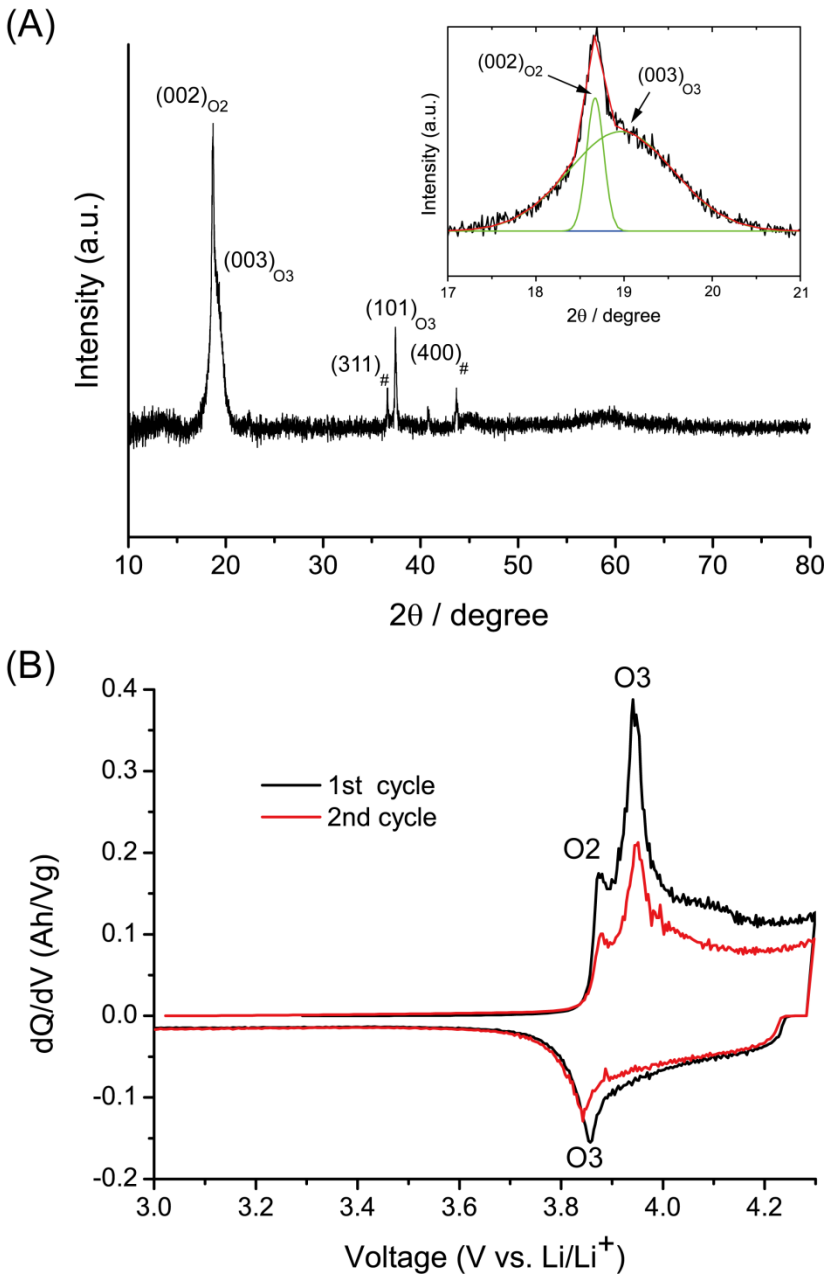

Figure S5. Characterization of LCO particles reassembled after electrophoresis and microwave hydrothermal treatment in LiOH without annealing. (A) XRD with inset showing fitting results to O2 and O3-LCO reflections; #: Co_3O_4. (B) Differential capacity vs. potential plot obtained from galvanostatic measurement showing delithiation from O2 and O3-LCO.

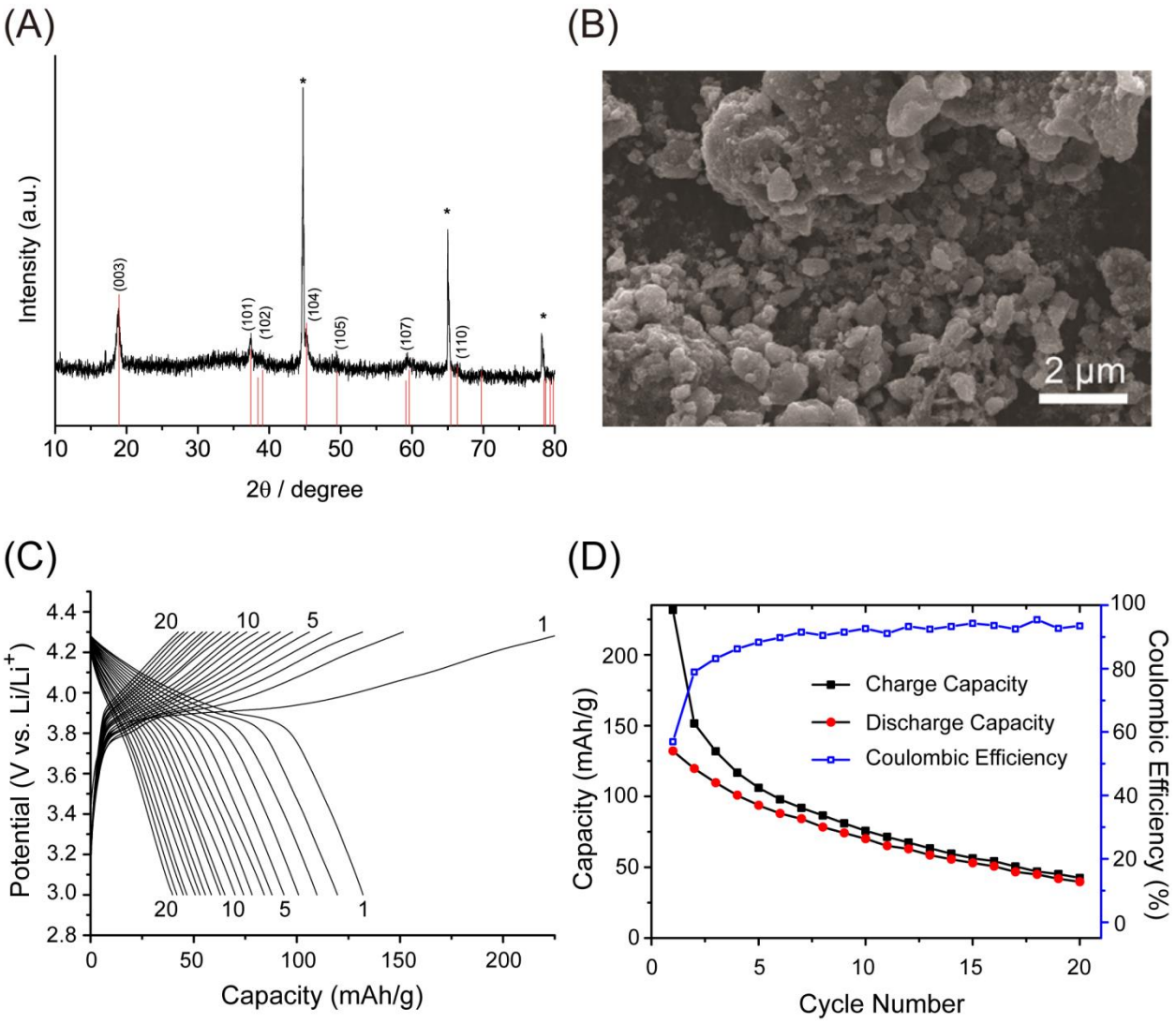

Figure S6. Characterization of reassembled LCO particles obtained after purification by electrophoresis, microwave hydrothermal treatment, and annealing at 500 ^{o}C for 2 hours. (A) XRD pattern matching O3-LCO; * indicate peaks from Al foil substrate. (B) SEM images. (C) Galvanostatic cycling data between 3.0 - 4.3 V vs. Li/Li^{+}. (B) Coulombic efficiency and charge/discharge capacity for each cycle.

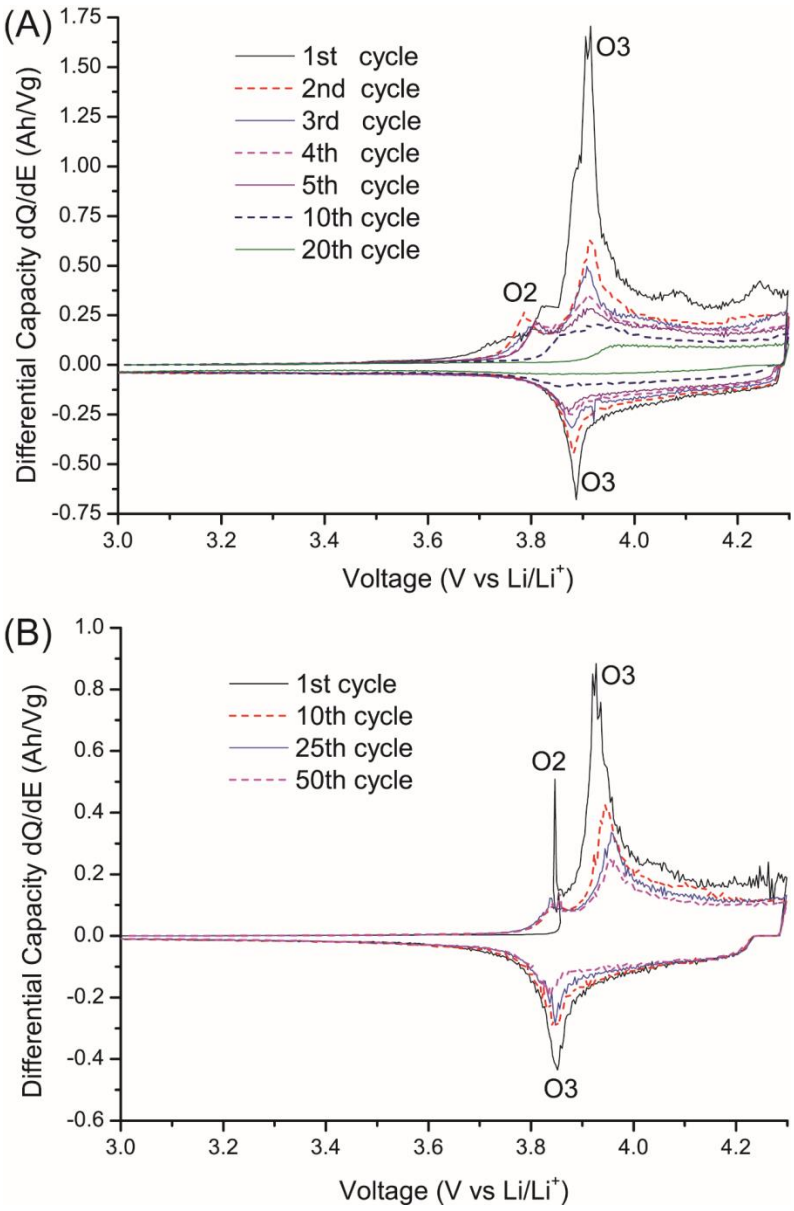

Figure S7. Differential capacity vs. voltage plot of LCO reassembled particles (A) without ALD coating and (B) with Al_2O_3 ALD coating.