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Novel Preparation of Core-shell Electrode Materials via Evaporation-Induced Self-Assembly of Nanoparticles for Advanced Li-Ion Batteries

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Experimental Section

1.1 Synthesis of core Li-excess Li[Li$_{0.2}$Mn$_{0.54}$Ni$_{0.13}$Co$_{0.13}$]O$_2$ nanoparticles.

Li-excess Li[Li$_{0.2}$Mn$_{0.54}$Ni$_{0.13}$Co$_{0.13}$]O$_2$ nanoparticles were synthesized using surfactant-assisted dispersion in a sol-gel method. We first prepared three precursor solutions: 5.4 mmol F127 (EO$_{106}$PO$_{70}$EO$_{106}$) in 50 mL ethanol, 0.08 mol transition metal acetate tetrahydrates (a molar ratio of Mn^{2+}:Ni^{2+}:Co^{2+}=0.54:0.13:0.13) in 50 mL ethanol, and 0.12 mol lithium hydroxide in 20 mL DI water. The molar ratio of F127/Mn^{2+} was 0.01. The transition metal precursor solution was added dropwise into the F127/ethanol solution under continuous stirring at 40°C, and then the lithium precursor solution was added. The mixed solution was heated at 80°C until the solvent was completely evaporated. Afterwards, the mixture was dried in air at 120°C for 12 h. The heat treatment of the dried mixture was carried out in air at 300°C for 3 h, followed by sintering at 900°C for 12 h. Li[Li$_{0.2}$Mn$_{0.54}$Ni$_{0.13}$Co$_{0.13}$]O$_2$ nanoparticles were collected after cooling to room temperature.

1.2 Synthesis of shell layered-spinel integrated $Li_4Mn_{4.5}Ni_{0.5}O_{12}$ material.

The layered-spinel integrated $Li_4Mn_{4.5}Ni_{0.5}O_{12}$ was synthesized by a facile sol-gel method. Two precursor solutions were first prepared: 20 mmol transition metal (II) acetate tetrahydrates (a molar ratio of $Mn^{2+}:Ni^{2+}=9:1$) in 50 mL distilled water, and 16 mmol lithium hydroxide in 15 mL distilled water. The transition metal precursor solution was added dropwise into the lithium precursor solution under continuous stirring. The mixed solution was then heated at 80°C until the solvent was completely evaporated. Afterwards, the mixture was dried in air at 120°C for 12 h. The heat treatment of the dried mixture was carried out in air at 500°C for 5 h, followed by sintering at 900°C for 3h. The as-prepared particles were collected after cooling to room temperature.

1.3 Preparation of core-shell composite materials.

Ten mg $Li_4Mn_{4.5}Ni_{0.5}O_{12}$ was first dispersed in 20 mL ethanol in a sealed vial using an one-step sonication treatment in a VWR B2500A-BTH ultrasonication water bath, operating at 210 W and 40 kHz for 2 h. 90 mg $Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$ powders were then added into the as-prepared suspension of $Li_4Mn_{4.5}Ni_{0.5}O_{12}$, followed by continuously stirring at 80°C until the solvent was completely evaporated. The composite materials were dried in air at 120°C for 12 h. The heat treatment of the dried powders was carried out in air at 500°C for 3 h and collected after cooling to room temperature.

1.4 Material characterizations

The crystal structure of the obtained powders was investigated by x-ray diffraction (XRD) using a Rigaku MiniFlex X-ray diffractometer with Cu Kα radiation. XRD Data was collected in the range of $10° \leq 2\theta \leq 80°$ at a scan rate of 2º/min at room temperature. The Morphology of the samples was observed using field emission scanning electron microscopy (FE-SEM) on a FEI Quanta 3D FEG FIB/SEM dual beam system. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were captured to investigate the crystal structure and core-shell structure of samples using a JEM-2010 instrument microscope at an acceleration voltage of 200 kV.

1.5 Electrochemical Measurements

Electrochemical properties of the synthesized cathode materials were evaluated using 2032-type coin cells. Typically, the cathodes were prepared by uniformly coating a homogeneous slurry of 80 wt % active material powders, 10 wt % acetylene black (conductive carbon, Alfa Aesar, 99.5%), and 10 wt % polyvinylidene fluoride (PVDF, Alfa Aesar) binder in 1-methyl-3-pyrrolidone (NMP) solvent on aluminum foils and then dried in vacuum at 120˚C for 24 h. Coin cells were assembled in an argon-filled glove box. The electrolyte was 1 M $LiPF_6$ dissolved in ethylene carbonate (EC), dimethyl carbonate

(DMC) and diethyl carbonate (DEC) at a volumetric ratio of 1:1:1. The electrochemical performance was tested at various C-rate regimes in the voltage range of 2.0-4.99 V by using an 8-channel battery analyzer (MTI Corporation). 1C rate was defined as 250 mAh/g. Cyclic voltammetric (CV) measurement was carried out on a CHI605C electrochemical analyzer at a scanning rate of 0.1 mV/s between 2.0 V and 4.99 V vs. Li/Li$^+$. All electrochemical measurements were performed at room temperature.
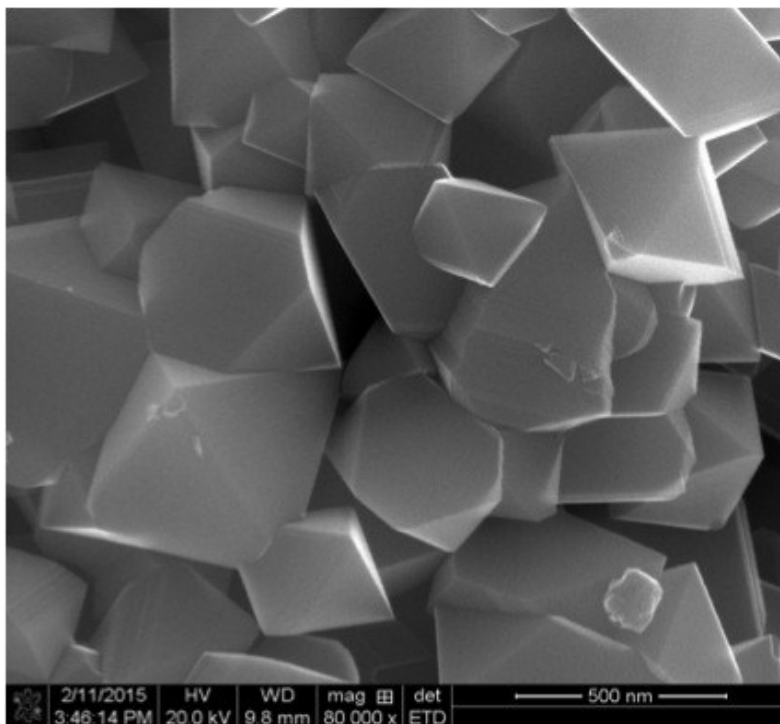
Fig. S1. SEM image of spinel $Li_4Mn_{4.5}Ni_{0.5}O_{12}$.

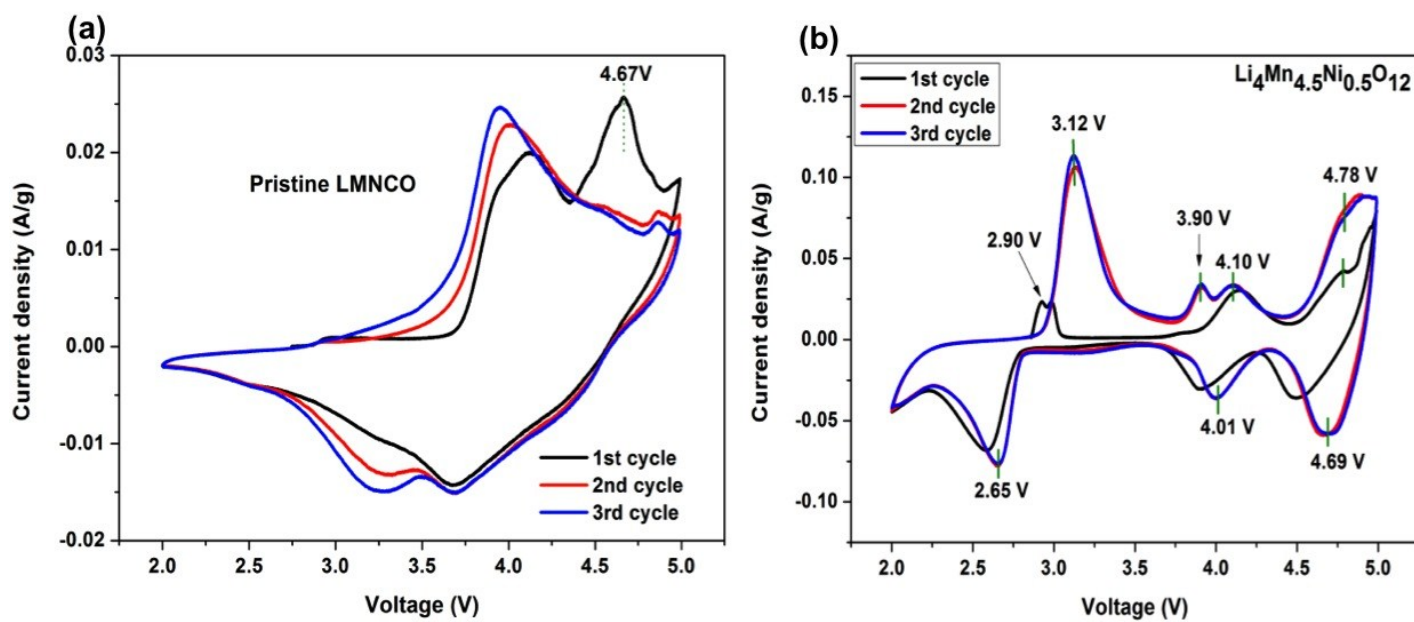**Fig. S2.** Cyclic voltammograms of (a) pristine LMNCO, (b) spinel $Li_4Mn_{4.5}Ni_{0.5}O_{12}$ cathodes in the first three cycles at a scan rate of 0.1 mV/s in a voltage range of 2.0 - 4.99 V *vs*. Li/Li$^+$.