

Electronic Supplementary Information (ESI)

Molecular-Layer-Deposited Tincone: a New Hybrid Organic-Inorganic Anode Material for Three-Dimensional Microbatteries

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Experimental

Deposition of tincone by MLD

The deposition of tincone by MLD was performed at 100 °C in a commercial ALD system (GEMStar™ XT Atomic Layer Deposition System, Arradiance, USA) using (tetrakis(dimethylamino)tin (IV), (TDMASn, Strem Chemicals) and Glycerol (GL, Sigma Aldrich) as the precursors. The deposition temperature (100 °C) was chosen based on the MLD window (75-200 °C) for tincone from TDMASn and GL reported previously [1]. The source temperature for both TDMASn and GL was 60 °C. The precursor pipeline was maintained at 100 °C to avoid precursor condensation. Nitrogen gas (99.999%) was used as the carrier gas at a flow rate of 20 sccm. The base pressure in the ALD reactor was sustained at 200 miliTorr. The MLD procedure was set as follows: (1) a 0.5 s supply of TDMASn; (2) a 5 s extended exposure of TDMASn to the substrates; (3) a 10 s purge of oversupplied TDMASn and any by-products; (4) a 1 s supply of GL vapor; (5) a 5 s extended exposure of GL to the substrates; (6) a 30 s purge of unreacted GL and any by-products. Using this reaction sequence, the thickness of tincone

deposited on N-CNTs was controlled by varying the number of MLD cycles. Si wafers, stainless steel (SS) current collectors, and nitrogen-doped carbon nanotubes (N-CNTs) were used as the substrates for tincone deposition. Si wafers and SS were used as received. Nitrogen-doped carbon nanotube (N-CNTs) were synthesized by using a chemical vapor deposition method and using iron (III) nitrate nanohydrate as the catalyst, and the synthesis process was detailed elsewhere [2]. N-CNTs powders were first dispersed in alcohol using an ultrasonic bath and then evenly dripped on an aluminum (Al) foil. After being dried at room temperature, the N-CNTs coated Al foil was cut into pieces and put into the ALD chamber for tincone deposition. After the deposition, tincone/N-CNTs were carefully scraped off the aluminum foil for structural and electrochemical characterizations.

Material characterizations

The thickness of tincone on the Si substrate was obtained by taking an average of five measured data points on a Profilometer. Microstructure of tincone/N-CNTs was characterized using a high-resolution transmission electron microscope (FEI F30). Sn L₃-edge X-ray absorption near edge structures (XANES) measurements was performed at the Soft X-ray Micro-characterization Beamline (SXRMB) of Canadian Light Source (CLS), and data were recorded using surface-sensitive total electron yield (TEY) mode with a probing depth of 1–10 nm. XANES measurements at the C K-edge and the O K-edge were performed at the spherical grating monochromator (SGM) beamline of CLS in a vacuum chamber at 10⁻⁸ torr, and data were recorded using the TEY mode. XANES spectra were first normalized by incident photon flux I₀ and then normalized to the edge jump of unity using Athena software. Tincone deposited on silicon wafers were used for XAFS test. Commercial SnO₂, SnO, and Sn (VWR) were used for comparison with tincone.

Electrochemical measurement

Electrochemical evaluation of tincone deposited on SS and N-CNTs substrates was carried out

in coin cells (CR2032) using lithium metal foils as the counter electrode. Tincone/SS was directly used as the electrode. To prepare the tincone/N-CNTs electrode, tincone/N-CNTs powders, Super P (TIMCAL) and carboxymethyl cellulose (CMC, 5wt% aqueous solution, TIMCAL) with a weight ratio of 7:2:1 were mixed thoroughly in an agate mortar to form an uniform slurry. The slurry was then cast on a copper foil and dried at 60°C in a vacuum oven overnight. The dried electrode was cut into round shapes with a diameter of 1.27 cm. The electrolyte was 1.3M LiPF₆ in ethylene carbonate (EC)/diethylene carbonate (DEC) (3:7 v/v). The cycling performance of the assembled coin cells was evaluated in a voltage range of 0.01-3.0 V on a Neware BTS 4000 battery tester. Cyclic voltammetry (CV) was measured at a sweep rate of 0.2 mV s⁻¹ on a Biologic VSP electrochemical workstation. Electrochemical impedance spectroscopy (EIS) was measured over a frequency range of 100 kHz to 0.01 Hz.

Table SI-1. Summary of deposition condition, post-annealing, and electrochemical activity towards to Li storage for MLD films.

MLD Film (role in LIBs)	Metal precursor	Organic reactant	Deposition T (°C)	Growth per cycle (Å)	Post annealing	Film crystallinity	Electrochemical activity towards Li storage	Ref
LTP (anode)	Li(thd)	TPA	200–240	3.0	As-deposited	Crystalline	~ 10 $\mu\text{Ah cm}^{-2}$ at 0.05C	[3]
Titanicone (anode)	TDMAT	GL	80-160	0.9-0.2	As-deposited	Amorphous	No	[4]
					Air, 500°C	Anatase TiO_2	~ 0.5 $\mu\text{Ah cm}^{-2}$ at 1 μA	
					He, 500°C	Amorphous	~ 0.6 $\mu\text{Ah cm}^{-2}$ at 1 μA	
Vanadicone (cathode)	TEMAV	GL	80-180	1.2-1.5	As-deposited	Amorphous	No	[5]
					Air, 500°C	Crystalline V_2O_5	~1.0 $\mu\text{Ah cm}^{-2}$ at 1C	
					He, 500°C	Amorphous	~1.2 $\mu\text{Ah cm}^{-2}$ at 1C	
Tincone (anode)	TDMASn	GL	100	2.5	As-deposited	Amorphous	450 mAh g^{-1} for tincone/N-CNTs composite at 0.1 Ag^{-1}	Herein

Lithium terephthalate – LTP; Benzene-1,4-dicarboxylic acid – TPA; Tetrakisdimethylaminotitanium – TDMAT; Glycerol – GL; Tetrakisethylmethylaminovanadium – TEMAV; Temperature – T; Benzene-1,4-dicarboxylic acid – TPA; Tetrakis(dimethylamino)tin (IV) – TDMASn.

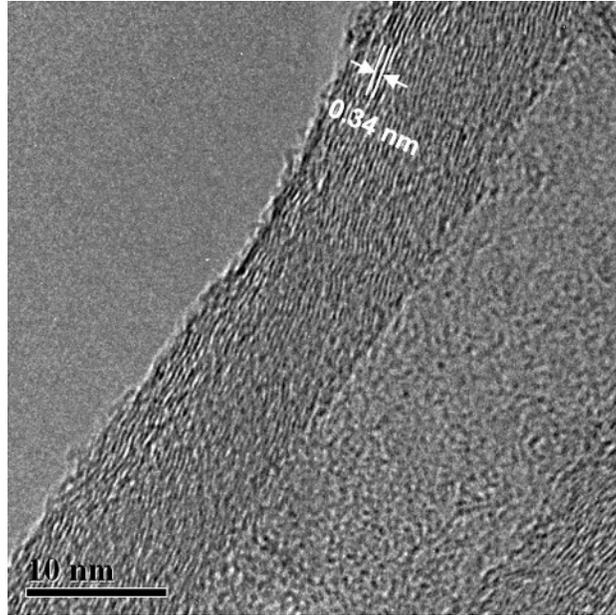


Figure SI-1. HRTEM image of N-CNTs.

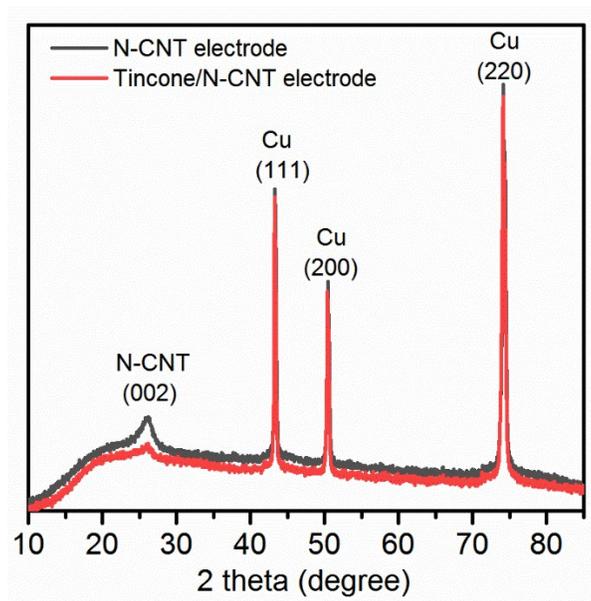


Figure SI-2. XRD patterns of N-CNTs and tincone/N-CNTs electrodes on the Cu current collector.

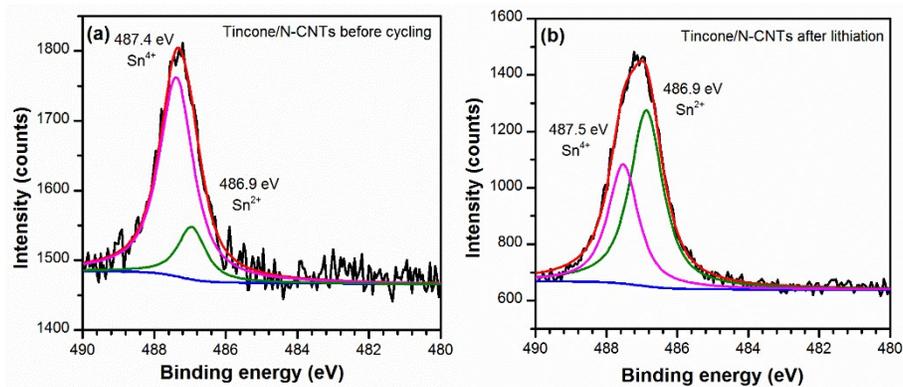


Figure SI-3. XPS spectra at the Sn 3d_{5/2} peak for tincone/N-CNTs (a) before cycling and (b) after lithiation (discharge).

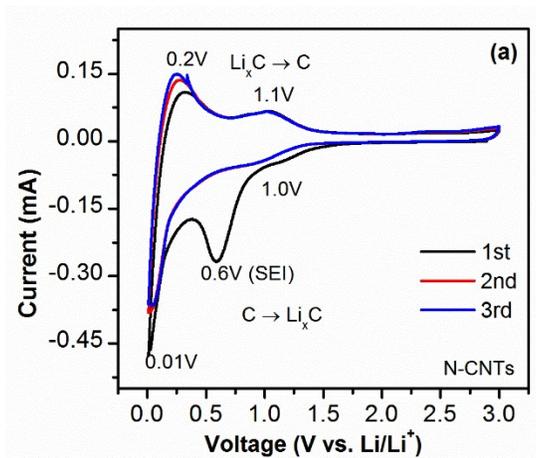


Figure SI-4. CV curves of N-CNTs measured at 0.1 mV s⁻¹ in the first three cycles.

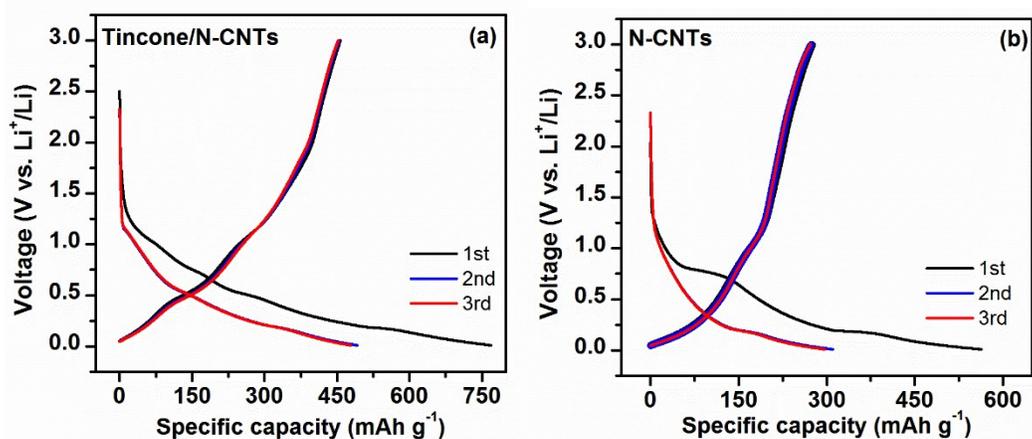


Figure SI-5. Charge-discharge curves of (a) tincone/N-CNTs and (b) of N-CNTs measured at

0.1 A g⁻¹ in the first three cycles.

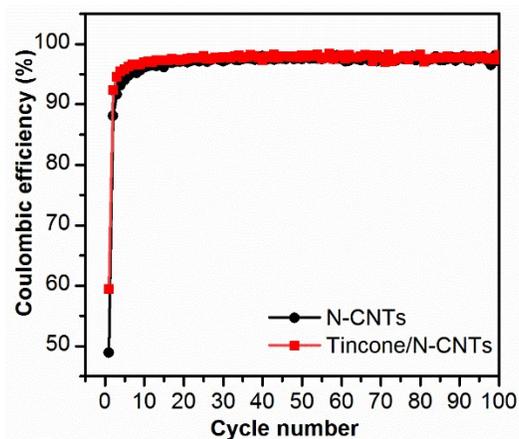


Figure SI-6. Coulombic efficiency (CE) of tincone/N-CNTs and N-CNTs.

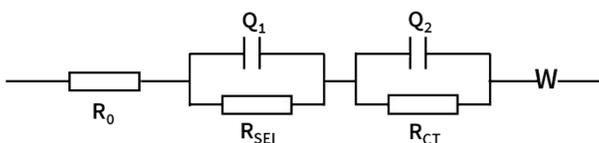


Figure SI-7. Equivalent circuit for fitting EIS data in Figure 4e. R_0 : solution resistance; R_{SEI} : SEI resistance; R_{CT} : charge transfer resistance; W : Warburg impedance.

Table SI-2. Fitting result of EIS test for Tincone/N-CNTs electrode before and after 100 cycles.

	R_0 (Ω)	R_{SEI} (Ω)	R_{CT} (Ω)
Before cycling	2.6	12.5	125.4
After 100 cycles	3.4	24.3	27.6

References

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- [2] M. Arjmand, K. Chizari, B. Krause, P. Pötschke, U. Sundararaja. Effect of synthesis catalyst on structure of nitrogen-doped carbon nanotubes and electrical conductivity and electromagnetic interference shielding of their polymeric nanocomposites. *Carbon*, 2016, 98, 358-372.
- [3] M. Nisula, M. Karppinen, Atomic/Molecular Layer Deposition of Lithium Terephthalate Thin Films as High Rate Capability Li-Ion Battery Anodes. *Nano Lett*, 2016, 16, 1276-1281.
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