Electronic Supplementary Information (ESI)

Crystal to non-crystal transformations in Sn-based MOF anode with long cycle life for lithium storage

*Ruoyu Wang [a], Yao Chen [a], Zaozao Wu [a], Qing Li [a], Hao Wang [a], Dongming Li [a], Zhipeng Yu [a], Jianhua Ding [a,] *, Xiaolan Tong [a] and Jianbo Xiong [a, b,] **

*Email: xiongjianbo1210@163.com.

[a] *Jiangxi Province Key Laboratory of Functional Organic Polymers, East China University of Technology, Nanchang 330013, China.*

[b] *State Key Laboratory of Nuclear Resources and Environment, School of Chemistry and Materials, East China University of Technology, Nanchang 330013, China.*

EXPERIMENTS

Chemicals.

All reagents involved in this study were commercially available and used without further purification. Stannous Chloride Dihydrate ($SnCl_2 \cdot 2H_2O$, RG, ≥99.99%, Adamas), N,N-dimethylformamide ($HCON(CH_3)_2$, AR, ≥99.5%, Xilong scientific), 2,3,6,7,10,11-Hexahydroxytriphenylene (HHTP, RG, ≥99.99%, Adamas), ethanol (EtOH, AR, ≥99.5%, Xilong scientific), acetonitrile (AR, ≥99.5%, Xilong scientific).

Synthesis of Sn(HHTP).

An aqueous solution (5 mL) of HHTP ligand (0.09 mmol, 29.3 mg) was carefully added to a DMF solution (5 mL) of $SnCl_2 \cdot 2H_2O$ (0.1 mmol, 22.6 mg), and the mixture was sonicated for 5 minutes and then heated at 210 ℃ for 72 hours. After cooling, the earthy yellow microcrystalline powder was collected by filtration and washed for three times with water and methanol respectively. To prepare the guest free sample, as-synthesized Sn(HHTP) was immersed in DMF (10 mL for 1d) and anhydrous acetonitrile (10 mL for 3 d), respectively. The acetonitrile solvent was removed at room temperature under vacuum for 24 h to obtain guest free sample.

Synthesis of $Sn_3(HHTP)_2$.

$Sn_3(HHTP)_2$ was synthesized by volatilizing the metal salt ($SnCl_2 \cdot 2H_2O$) and the ligand (HHTP) in a controlled 3:2 feeding ratio at a room temperature.

Material Characterization.

The morphologies and micro-structures of the samples were analyzed using a scanning electron microscope (SEM, Hitachi S4800), X-ray powder diffraction (XRD) was carried out on a X'Pert-Pro MPD diffractometer (PANalytical) with monochromatic Cu Kα radiation (λ = 0.15418 nm, 5°C min^{-1}). The surface chemical properties of samples were investigated by X-ray photoelectron spectroscopy (XPS,Thermo Scientific Escalab 220i-XL, Thermo Scientific, USA). Fourier transformed infrared (FT-IR) spectra were measured on a Bruker ALPHA FT-IR spectrometer.

Electrochemical Measurements.

The working electrodes were prepared by mixing active materials, conducting agent (acetylene black), and PVDF in a weight ratio of 7:1:1 in N-methyl-2-pyrrolidone (NMP) to form the slurry. After being coated on a copper foil, the electrode was dried at 60 °C for 12 h. The CR2032 coin cells were used to evaluate electrochemical performance of half-cells. A polypropylene (PP) microporous membrane served as the separator. The electrolyte was the mixture of ethylene carbonate (EC) and propylene carbonate (PC) with a volume ratio of 1:1 containing 1 M $LiPF_6$. The anodes were punched from copper sheet using a punch die, and the final surface area of each sheet was ~1.13 cm^2 , the thickness of the electrode was ~9μm. Lithium metal foil, Celgard 2400 microporous membrane, and gaskets were used as counter electrode, separator, and fixture, respectively. A LAND multichannel battery tester (CT3002A) was used to perform a constant current charge and discharge test between 0.01 and 3.0 V at various current densities from 0.2 to 2.0 A g^{-1}. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed in the electrochemical workstation (CHI 660D). EIS was performed with ±5 mV amplitude and within the frequency range of 100 kHz−10 mHz.

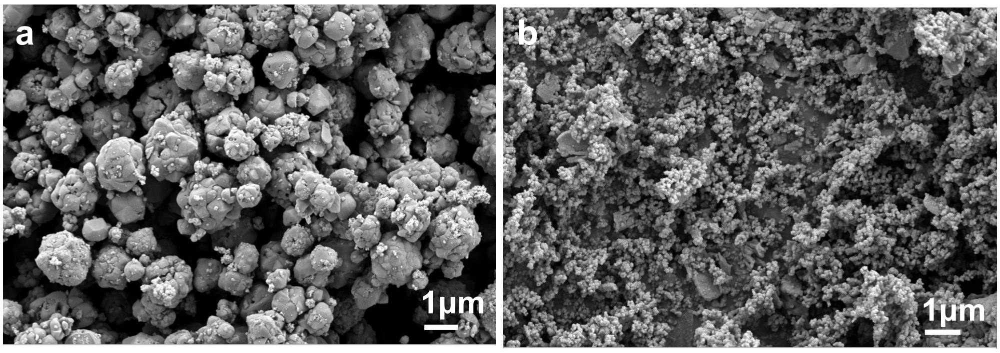

Fig S1. SEM images of Sn-HHTP (a) and $Sn_3(HHTP)_2$ (b).

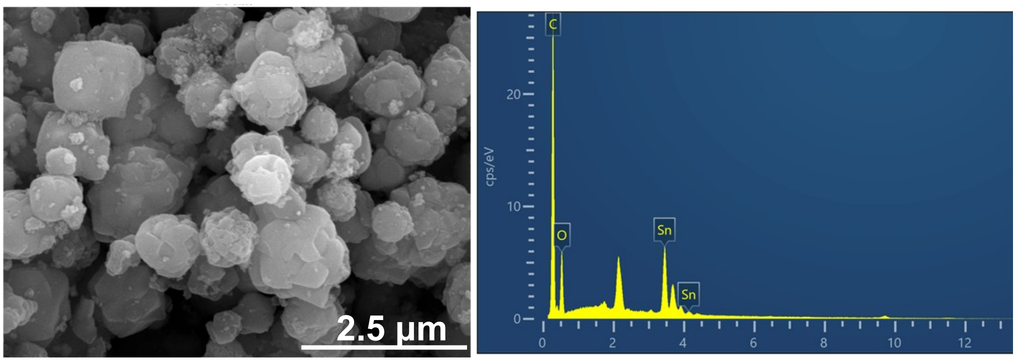

Fig S2. EDS mapping and result of Sn(HHTP).

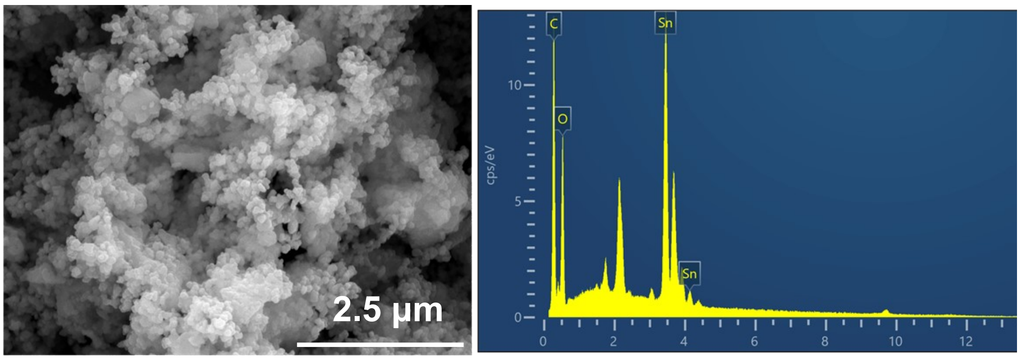

Fig S3. EDS mapping and result of $Sn_3(HHTP)_2$.

Table S1. EDS of elemental content analysis.

Element	Wt %	Wt % sigma	At%
C	56.37	0.26	76.5
O	19.86	0.25	20.24
Sn	23.76	0.21	3.26
Total	100		100

Table S2. EDS of elemental content analysis.

Element	Wt %	Wt % sigma	At%
C	29.28	0.24	56.32
O	23.94	0.26	34.57
Sn	46.77	0.26	9.10
Total	100		100

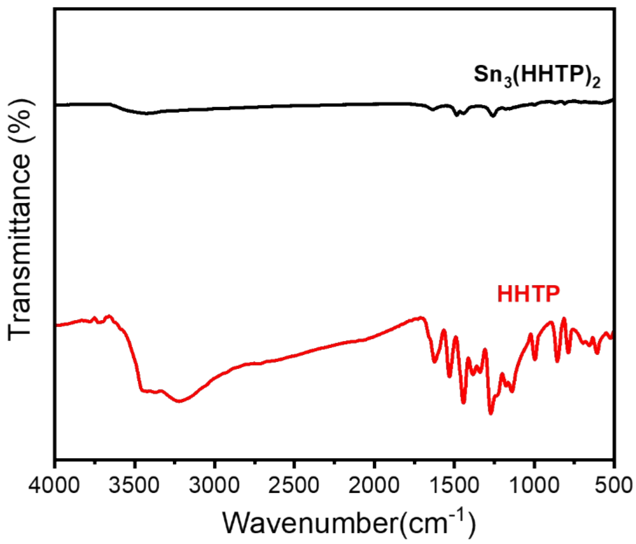

Fig S4. FT-IR spectra of $Sn_3(HHTP)_2$ (black) and HHTP (red).

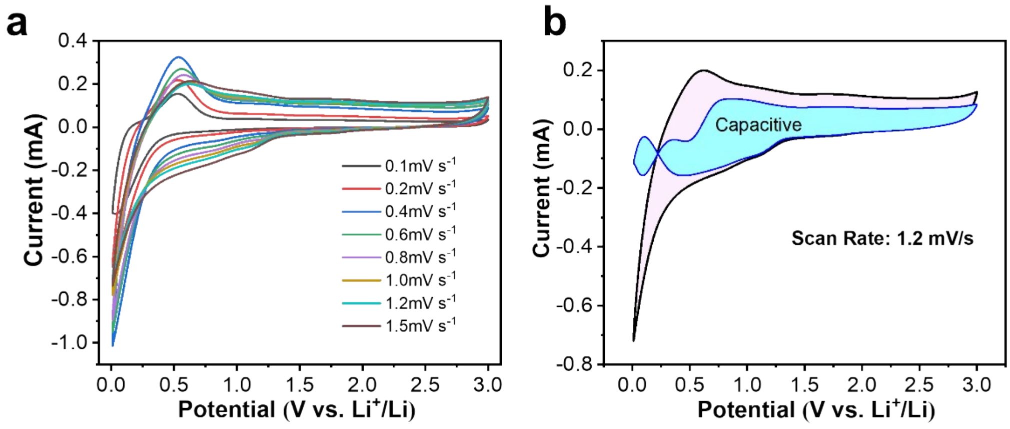

Fig S5. (a) CV curves of $Sn_3(HHTP)_2$ at different scan rates; (b) Proportion of capacitance at 1.2 mV s^{-1}.

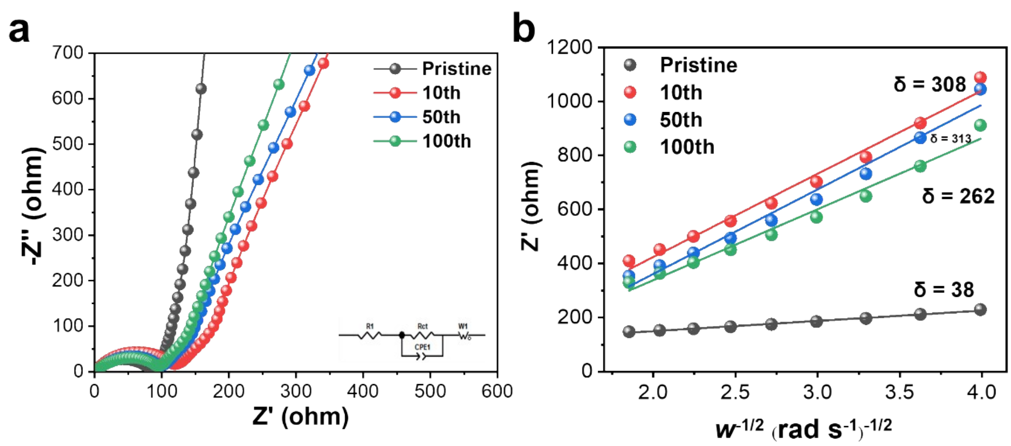

Fig S6. (a)Nyquist plots of $Sn_3(HHTP)_2$. (b) Plots of Z' versus $\omega^{-1/2}$ in the low-frequency region of $Sn_3(HHTP)_2$.