Supporting Information for

# Mesoporous Crystalline-Amorphous Oxide Nanocomposite Network for High-Performance Lithium Storage

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## Experimental section

*Material and electrode preparation*:

Pluronic surfactant F127 ($EO_{106}PO_{70}EO_{106}$), citric acid 99.5%, ammonium molybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$) and titanium oxysulfate ($TiOSO_4\cdot xH_2O$) were purchased from Sigma-Aldrich Corp. Carbon black was purchased from Alfa Corp. All chemicals were used as received without any further purification. In a typical synthesis process of TMON, 0.13 g of F127 and 1.00 g of $TiOSO_4\cdot xH_2O$ were dissolved in 10 ml of de-ionized water and kept stirring at 40~50 $^oC$ for 1 h to afford a clear solution A. 0.7 g of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ was dissolved in 10 ml of citric acid aqueous solution under stirring at room temperature (molar ratio of Mo : acid =1:3) to obtain solution B. Then solution B was slowly dropped into the solution A. The mixture was then stirred for 2 h and formed a homogeneously transparent solution (molar ratio of Mo : Ti =1:1.63). Using the aerosol-assisted self-assembly process, solution precursor was atomized to generate droplets which were passed through a heating zone with a $N_2$ flow. In a continuous process, the precursor composite nanoparticles were dried, heated at 450 $^oC$ and collected. Calcination was carried out in a box furnace at temperature of 450°C for 3 h in air to obtain TMON. The heating rate was 1 $^oC\cdot min^{-1}$ below 350°C, kept at 350°C for 3h and heated to 450 $^oC$ at 1 $^oC\cdot min^{-1}$ below 450 $^oC$. Pure $TiO_2$ and $MoO_3$ particles were prepared by the same process with a single salt precursor. Sol-gel synthesis of $TiO_2/MoO_3$ was performed by drying the same precursor solution under stirring and being sintered at same condition as TMON samples.

The electrodes were prepared by mixing 80% active materials, 10% carbon black, and 10% polyvinylidene fluoride (PVDF) dispersed in N-methylpyrrolidinone (NMP) to form slurries. The slurries were stirred for 2 hours and coated on stainless steel foils. After coating, the electrodes were dried at 80 °C for 20 min in vacuum oven to remove the solvent before pressing. The electrodes were pressed at pressure of 2 MPa and then dried in a vacuum oven at 100 °C for another 12 h.

*ALD coating*:

$Al_2O_3$ ALD coating on TMON electrodes were carried out by Cambridge Savanah 100 ALD (Cambridge Nanotech Inc. Savannah 100 & 200). The deposition of alumina from water and trimethylalumiunm (TMA) precursors was used in this experiment. Each cycle produced a maximum of 1.1 Å $A_2O_3$ depending on temperature. The temperature of vacuum chamber was kept at 250 $^oC$.

*Material characterization and electrode measurement:*

X-ray diffraction patterns were recorded on a PANalytical X'Pert Pro X-ray powder diffractometer using copper Kα radiation ($\lambda$ = 1.54 Å). Nitrogen sorption isotherms were measured at 77 K with a Micromeritics ASAP 2020 analyzer. The samples were degassed in vacuum at 180 °C for 3 h before measurements were taken. The specific surface areas were calculated by the Brunauer–Emmett–Teller (BET) method using the adsorption branch in the relative pressure range from 0.04 to 0.25. The pore size distributions *($D_p$)* were derived from the adsorption branch using the Barrett–Joyner–Halenda (BJH) model. Thermogravimetric analysis (TGA) was carried out in a PerkinElmer analyzer from 25 °C to 800 °C with a heating rate of 10 °C $min^{-1}$ and air flow rate of 200 $mL\cdot min^{-1}$. Scanning electron microscopy (SEM) images were taken from a JEOL JSM-6700 FE-SEM. Transmission electron microscopy (TEM) images were obtained using a Philips CM120 microscope operated at 120 kV.

Surface composition was analyzed by XPS. Core level photoemission spectra of C1s and O 1s lines were collected with a PHI 3057 spectrometer using Mg Kα X-rays at 1286.6 eV. All XPS spectra were taken in small area mode with a 78 acceptance angle and 23.5 eV pass energy. The detection angle with respect to the surface normal was 258. All spectra were referenced to the C 1s peak of the graphitic carbon atom at 285.0 eV. The integrated areas of the Ti 2p and Mo 3d photoemission peaks, divided by their sensitivity factors 2.005/1.315 and 1.334/0.665, were used to determine surface atomic percentages.

CV measurements were carried out in an argon-filled glove box between cutoff voltage of 3.5 and 1.0 V. To make 2032 type coin cells, Whatman glass fiber (GF/D) was used as the separator. The charge and discharge measurements were carried out by LAND CT2000 (Wuhan Jinnuo electronics, Ltd., Wuhan, China) at different charge-discharge rates.

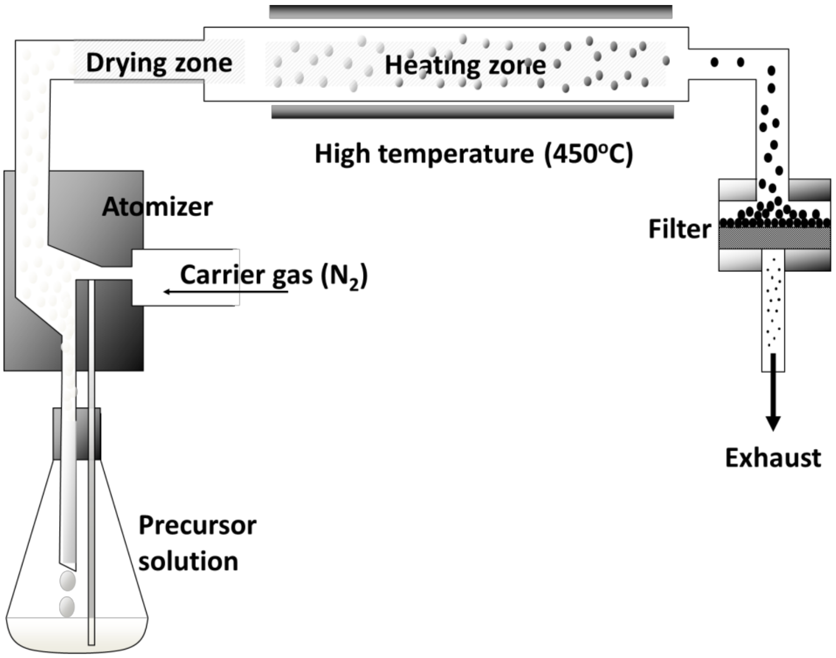

**Figure S1**. Schematic illustration of continuous aerosol-assisted multi-component assembly approach for making TMON nanocomposite particles.

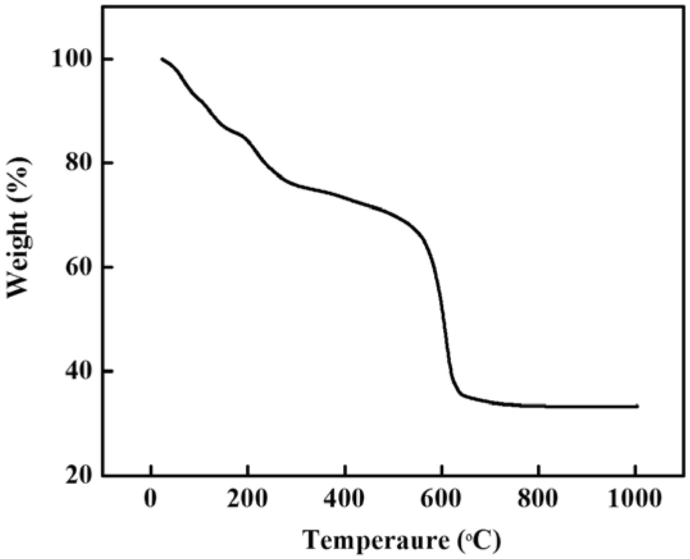

**Figure S2**. TGA curves of $TiOSO_4 \cdot xH_2O$ powder in air (200 mL·min$^{-1}$) using a heating rate of 10

°C·min$^{-1}$.

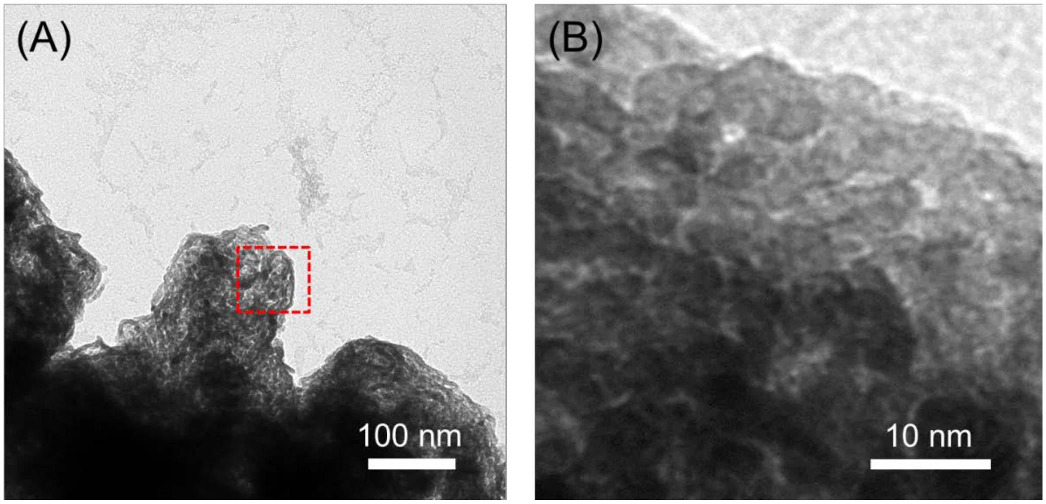

Figure S3

**Figure S3**. TEM images of the TMON-47% with sintering at 450°C for 3h. The nanoporous network composed of ultra-fine crystals can be clearly resolved.

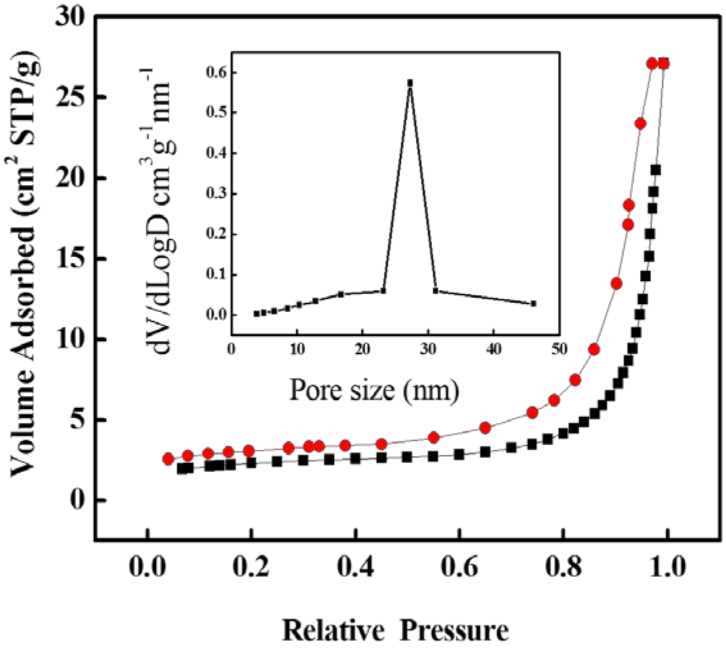

**Figure S4**. Nitrogen sorption isotherms and pore size distributions (inset) of $TiO_2/MoO_3$

composites using sol-gel method.

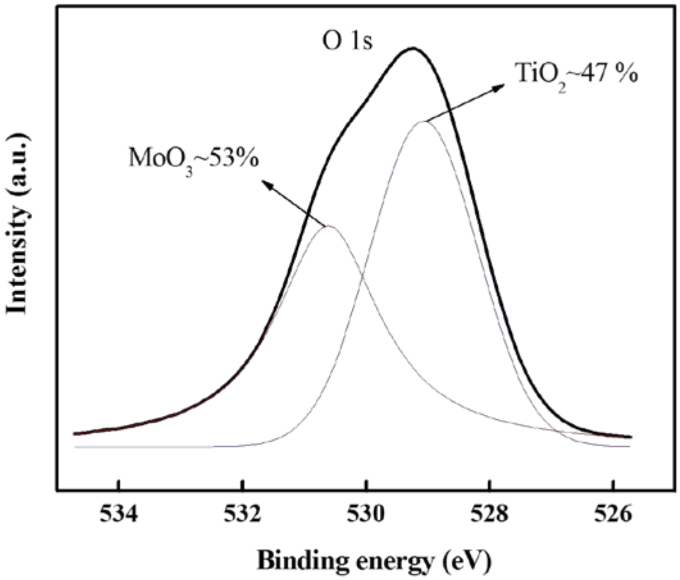

**Figure S5**. XPS curves of O 1s spectra for TMON-47%.

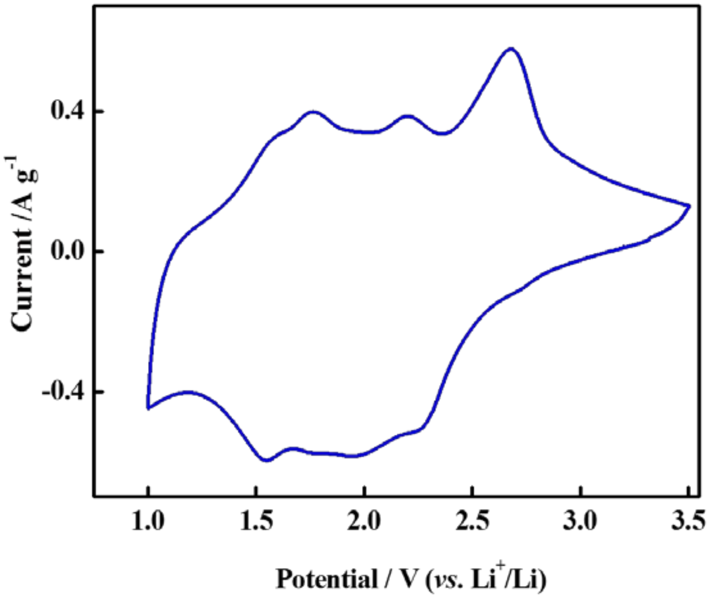

**Figure S6**. CV curve of TMON-47%-ALD electrode at scan rate of 1 mV $s^{-1}$.