# **Supporting Information**

## Construction of Cu<sub>3</sub>Mo<sub>2</sub>O<sub>9</sub> Nanoplates with Excellent Lithium Storage Properties Based on a pH-Dependent Dimensional Change

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Received: May 1st, 2015

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### **Experimental section**

*Materials*: Ammonium molybdate tetrahydrate (AMT), copper acetate dihydrate (CAD), hydrochloric acid (HCl) were obtained from Shanghai Chemical Reagent. All the chemicals were of general-purpose reagent grade unless otherwise stated.

**Preparation of**  $(NH_4)_2Cu(MoO_4)_2$  (ACM-1 and ACM-2): First, 0.88 g (0.72 mmol) AMT and 0.50 g (2.50 mmol) CAD were dissolved in 40 mL deionized water and stirred at room temperature for 20 min to form a green suspension solution. Subsequently, the solution was transferred into a Teflon-lined stainless steel autoclave (50 mL). It was sealed, maintained at 383 K for 30 min, and then cooled naturally to room temperature. Finally, a yellow product (ACM-1) was collected *via* centrifugation at 9000 rpm for 10 min, further washed with deionized water and ethanol for several times, and dried at vacuum at 333 K for 12 h. The ACM-2 was obtained using the same hydrothermal conditions but with different initial molar ratio of AMT (0.12 g, 0.10 mmol) to CAD (0.01 g, 0.05 mmol).

*Preparation of*  $Cu_3(OH)_2(MoO_4)_2$  (*CMOHs*): First, 0.05 g ACM-1 was gradually added to an aqueous solution (50 ml) with a pH value of 2.5 and stirred at 373 K for 5 min to form a suspension solution. Then the solution was transferred and cooled naturally to room temperature. Finally, a green product (CMOH-1) was collected *via* centrifugation at 9000 rpm for 10 min, further washed with deionized water and ethanol for several times, and dried at vacuum at 333 K for 12 h. The CMOH-2 and CMOH-3 were prepared using the similar method as CMOH-1 but with the pH values of 3.0 and 3.5, respectively. The CMOH-4 was prepared as the similar method as CMOH-1 but using ACM-2 as precursor.

*Preparation of two Cu*<sub>3</sub>*Mo*<sub>2</sub>*O*<sub>9</sub> (*CM-1 and CM-2*): The CM-1 and CM-2 were obtained by sintering the precursors CMOH-1 and CMOH-2 at 773 K for 3 h in a muffle furnace.

*Characterization*: XRD measurements were recorded on a Philips X'Pert Pro X-ray diffractometer using a monochromatized Cu K $\alpha$  radiation source (40 kV, 40 mA) with a wavelength of 0.1542 nm and analyzed in the range  $10^{\circ} \le 2\theta \le 70^{\circ}$ . Field emission scanning electron microscope (FE-SEM) images were obtained on a Supra 40 operated at 5 kV. The composition of the sample was obtained by X-ray energy dispersive spectrometry (EDS) analysis attached to the FE-SEM instrument. Transmission electron microscopy (TEM), high-resolution TEM (HR-TEM) images and selected area electron diffraction (SAED) pattern were obtained with a JEF 2100F field-emission transmission electron microscope using an accelerating voltage of 200 kV, and the materials were dispersed in ethanol by ultra-sonication for 20 minutes in an ultrasonic bath.

X-ray photoelectron spectroscopy (XPS) analysis was carried out in a ESCALAB 250 electron spectrometer with a VG Scienta R3000 electron energy analyzer, using Al K $\alpha$  radiation (1486.6 eV) in ultra-high vacuum (2.00 × 10<sup>-9</sup> torr) at room temperature. The energy resolution of the instrument is 0.16 eV. The C1s peak (284.8 eV) was used as the internal standard for binding-energy calibration. N<sub>2</sub> adsorption measurements were determined by an ASAP 2020 accelerated surface area and porosimetry instrument (Micromeritics), equipped with automated surface area, at 77 K using Barrett-Emmett-Teller (BET) calculations for the surface area. Wavelength dispersive X-ray fluorescence (WDXRF) spectrum of the CM-2 nanoplate sample was carried out using a Shimadzu XRF-1800 spectrometer equipped with a rhodium target X-ray tube.

*Electrochemical tests:* Electrodes for electrochemical studies were prepared by mixing 70 wt% the as-obtained CM-1 or CM-2, 20 wt% conducting acetylene black, and 10 wt% polyvinylidene fluoride in *N*-methylpyrrolidone. The slurry was pasted on a clean copper foil, and dried in vacuo at 373 K for 12 h. Subsequently, the coated foil was roll-pressed and cut into a round slice. Test cells were assembled in an argon-filled glove box using lithium foil as the counter electrode and the reference electrode, Celgard 2400 as the separator, and a mixed solution of LiPF<sub>6</sub> (1 mol·dm<sup>-3</sup>) with ethylene carbonate, ethyl methyl carbonate and dimethyl carbonate (1:1:1, v/v/v) as electrolyte. The cells were charged and discharged from 0.01 to 3.00 V at the current density of 100 mA·g<sup>-1</sup> with a LAND CT2001A cell test instrument.



Figure S1. XRD patterns of the ACMs.



Figure S2. XRD patterns of the CMOHs.



**Figure S3.** XRD patterns of the materials obtained by treating the ACM-1 with aqueous solutions with the pH values of 4.0 (a) and 5.0 (b).



**Figure S4.** The photograph revealing the dissolution of CMOH at the pH value of 1.0.



Figure S5. The XRD pattern and FE-SEM image of the CM-1.



**Figure S5'.** FE-SEM images of the CM-1 nanorods (a), CM-2 nanoplates (b) and CM-3 nanoparticles (c).



Figure S5". The XRD pattern of the CM-3.



Figure S6. The EDS spectrum of the CM-2 nanoplates.



Figure S7. The WDXRF spectrum of the CM-2 nanoplates.



**Figure S8.** The XPS survey spectrum of the CM-2 nanoplates (a), XPS spectra of Cu 2p (b), Mo 3d (c) and O 1s peaks (d) of the CM-2 material.



**Figure S9.** (a) Charge-discharge voltage profiles of the CM-1 electrode at the first, second, third, tenth and fiftieth cycles and (b) cycling performance of the electrode at a current density of 100 mA·g<sup>-1</sup>; (c) Charge-discharge voltage profiles of the CM-3 electrode at the first, second, third, tenth and fiftieth cycles and (d) cycling performance of the electrode at a current density of 100 mA·g<sup>-1</sup>.



**Figure S10.**  $N_2$  adsorption-desorption isotherms and pore size distributions of the CM-1 (A), CM-2 (B) and CM-3 (C).

# **Table 1.** Comparison of electrochemical performances of transitionmetal molybdates.

Molybdates	Reversible capacity (mAh·g <sup>-1</sup> )	Current density (mA·g <sup>-1</sup> )	Coulombic efficiency in 1 <sup>th</sup>	References
Cu <sub>3</sub> Mo <sub>2</sub> O <sub>9</sub> nanoplates	754/80 <sup>th</sup> cycle	100	91.7%	This work
Cu <sub>3</sub> Mo <sub>2</sub> O <sub>9</sub> nanorods	301/80 <sup>th</sup> cycle	100	63.4%	This work
$CaMoO_4$ nanocrystallites	398/20 <sup>th</sup> cycle	60	62.4%	5c
CoMoO <sub>4</sub> nanoplates	560/50 <sup>th</sup> cycle	100	70.3%	8
Co <sub>2</sub> Mo <sub>3</sub> O <sub>8</sub> particles	$425/40^{\text{th}}$ cycle	60	28.3%	9
Cu <sub>3</sub> Mo <sub>2</sub> O <sub>9</sub> micropompons	129/100 <sup>th</sup> cycle	100	35.3%	10
NiMoO <sub>4</sub> nanorods	120/50 <sup>th</sup> cycle	50	77.7%	20
CoMoO <sub>4</sub> nanorods	120/50 <sup>th</sup> cycle	50	51.2%	20
Mn <sub>2</sub> Mo <sub>3</sub> O <sub>8</sub> microspheres	390/25 <sup>th</sup> cycle	200	74.7%	24
Mn <sub>2</sub> Mo <sub>3</sub> O <sub>8</sub> particles	205/50 <sup>th</sup> cycle	30	79.6%	25a
Ni <sub>x</sub> Co <sub>1-x</sub> MoO <sub>4</sub> nanowires	520/20 <sup>th</sup> cycle	196	74.3%	25b