# Electronic supplementary Information (ESI)

Fresh $MoO_2$ as a better electrode for pseudocapacitive sodium-ion storage

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## Experimental section

### Synthesis:

$MoO_2$ was obtained via a solvothermal reaction. Briefly, 0.3 g commercial Molybdenum trioxide ($MoO_3$, Alading) was dispersed into water and ethylene glycol (EG, Alfa-Aesar, > 99 %) at room temperature under stirring for 1 h. After that, the mixture was transferred into a 100 mL Teflon stainless steel autoclave, sealed and maintained at 200 $^oC$ for 24 h. After cooling down to room temperature, the solution with powders was filtered and washed with absolute ethanol three times (Sinopharm, 99 %) and dried at 70 $^oC$ in vacuum for 6 h. As-obtained sample was denoted as fresh $MoO_2$ (F-$MoO_2$). Annealed $MoO_2$ (A-$MoO_2$) was obtained after Ar-treatment at 300 $^oC$ for 1 h.

### Structure:

*X-ray diffraction (XRD)*: PANalytical multipurpose diffractometer with an X'celerator detector (PANalytical X' Pert Pro); *Scanning electron microscopy (SEM)*: FEI Helios Nanolab 600-i; *Transmission electron microscopy (TEM)*: FEI Tecnai G2 F-20 at 200 kV; *X-ray photoelectron spectroscopy (XPS)*: Thermo Fisher Scientific ESCALAB 250 Xi using Al Kα radiation. All XPS signals were calibrated using C-1s at 284.8 eV before deconvolution.

### Electrochemistry:

All the tests are performed at room temperature. Cu foil was first cleaned by oxalic acid and pure ethanol to get rid of possible organic contaminations. The working electrode was prepared by mixing the active materials (80 *wt* %), carbon black (Super-P) (10 *wt* %), and poly-(vinylidene fluoride) (PVDF) (10 *wt*

%) in N-methyl-2-pyrrolidone (NMP), and then pasted on one piece of clean Cu foil using doctor blade, followed by drying at 80 °C under vacuum overnight. Glass-fiber (Whatman, GF-D) and Na-metal were used as separator and counter/reference electrode. Electrolyte was 1 M $NaClO_4$ in ethylene carbonate/diethyl carbonate/ fluoroethylene carbonate (EC/DEC/FEC, 1:1:0.05, vol *%,* home-made). The cells were assembled in an Ar-filled glove box with $O_2$ and $H_2O$ lower than 0.5 ppm. The fresh cells were aged overnight before the measurements to ensure full percolation of the electrolyte. Cyclic voltammetry (CV) curves were recorded on a CHI 630 B electrochemical workstation. Galvanostatic charge-discharge tests were performed on a LAND CT-2100A battery testing system (5 V/2 mA).

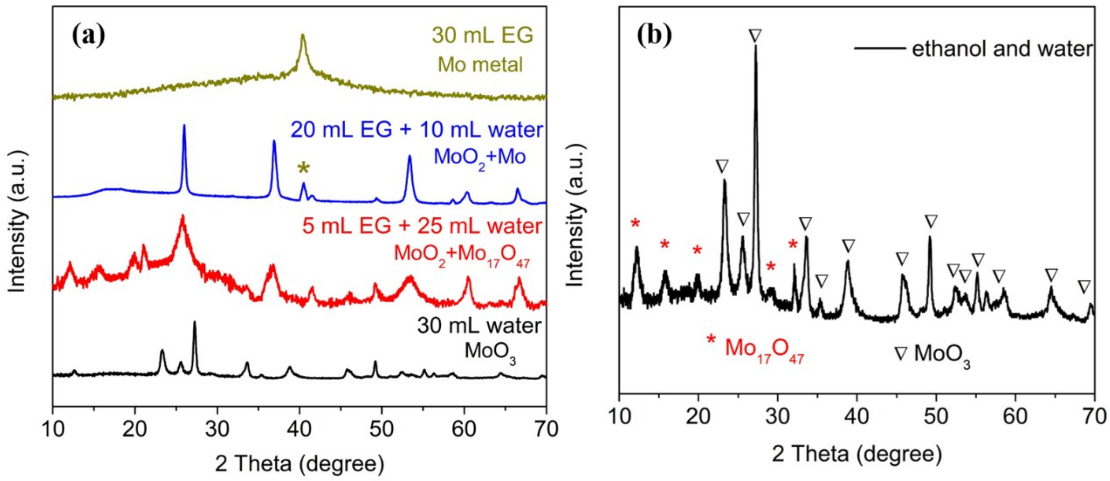

**Figure S1**. XRD patters of products

(a) different EG/water ratio; (b) ethanol and water without EG

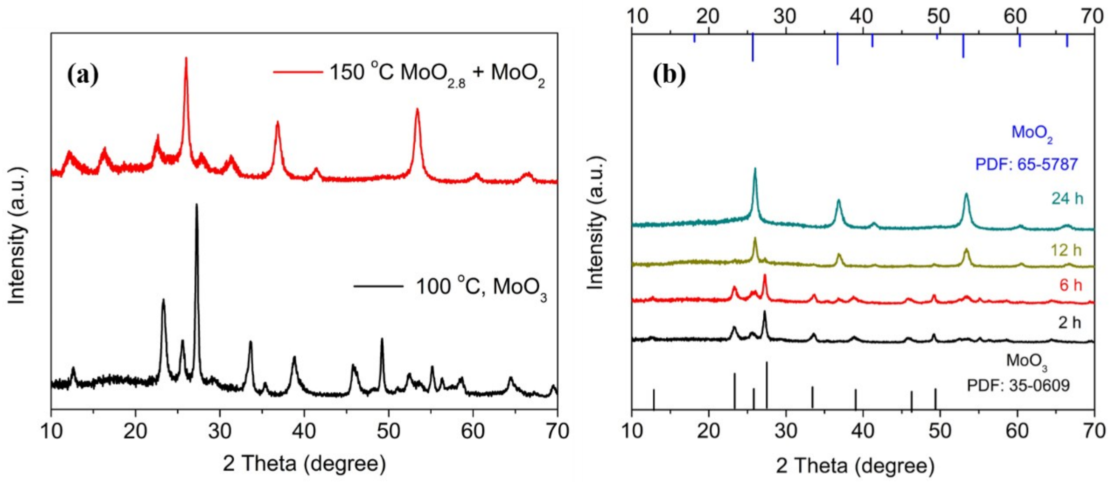

**Figure S2**. XRD patters of products

(a) different temperature; (b) different time

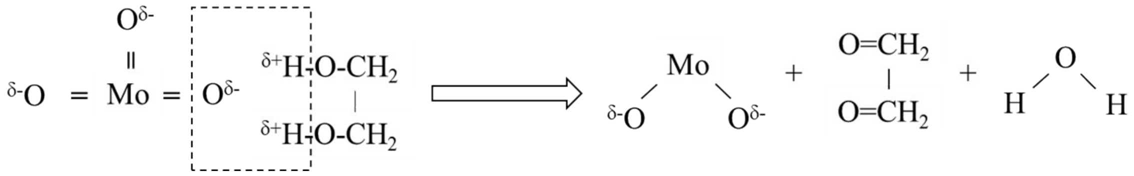

**Figure S3**. Possible formation mechanism of fresh $MoO_2$ through dehydrolysis.

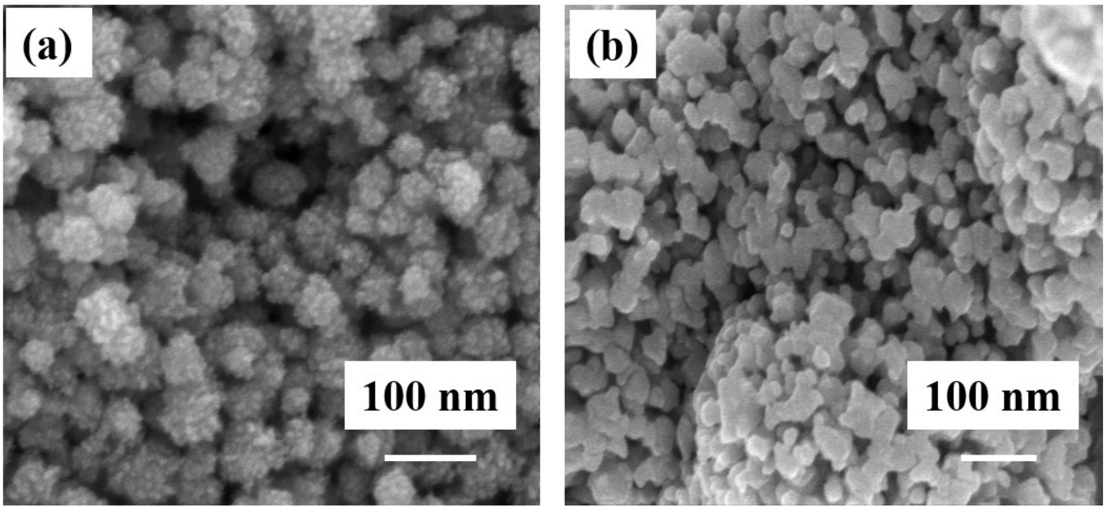

**Figure S4**. SEM images of (a) fresh and (b) annealed $MoO_2$

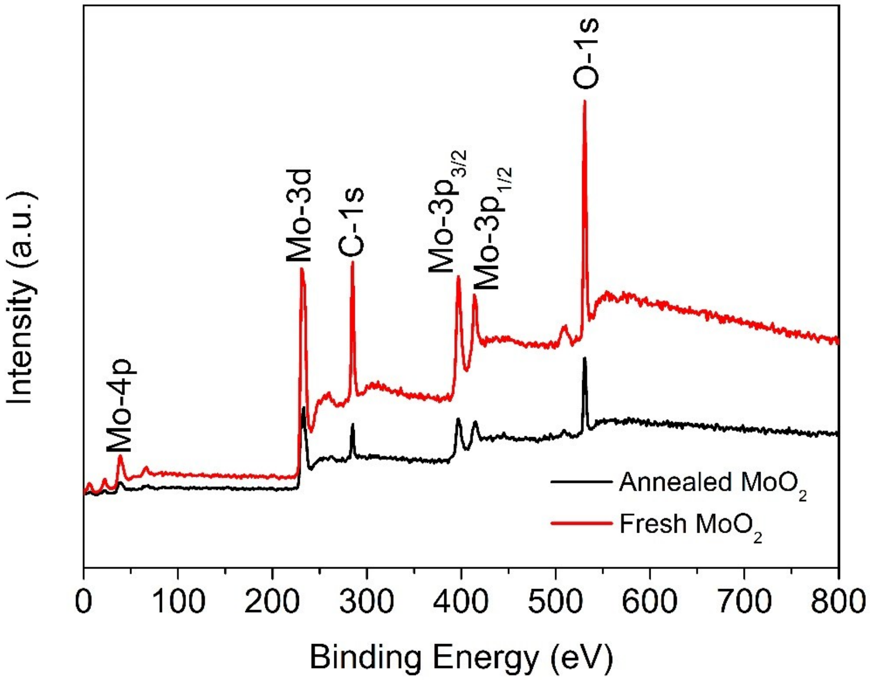

**Figure S5.** XPS survey of fresh and annealed $MoO_2$

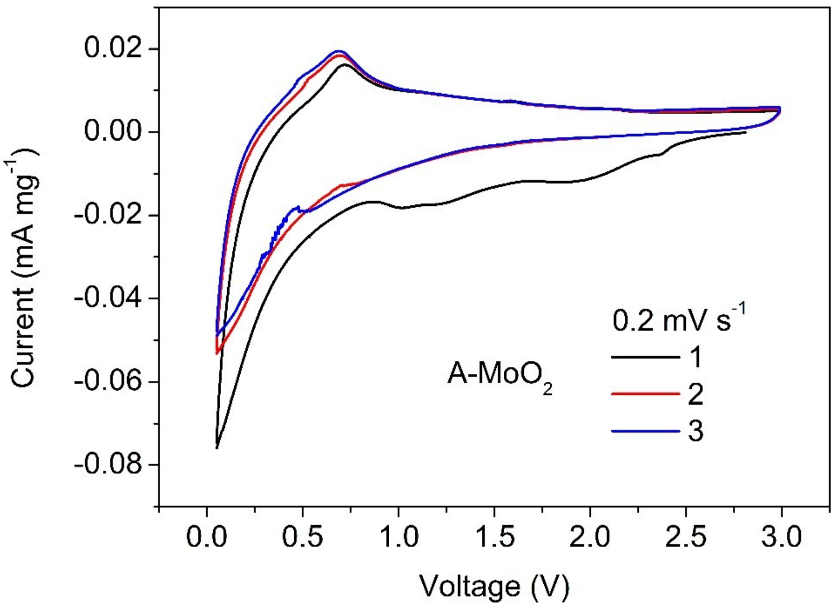

**Figure S6.** CV curves of annealed $MoO_2$

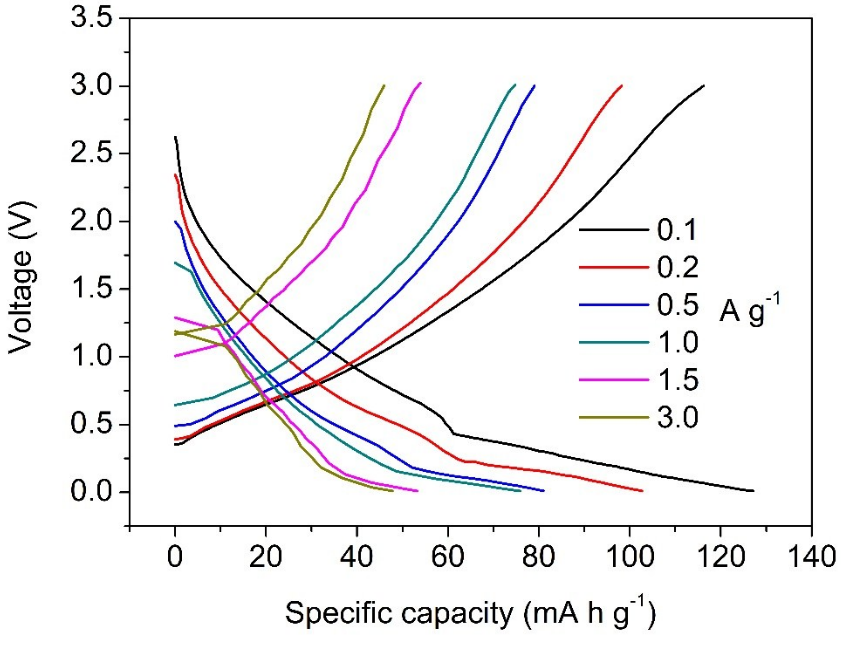

Figure S7. Discharge/charge curves of fresh $MoO_2$

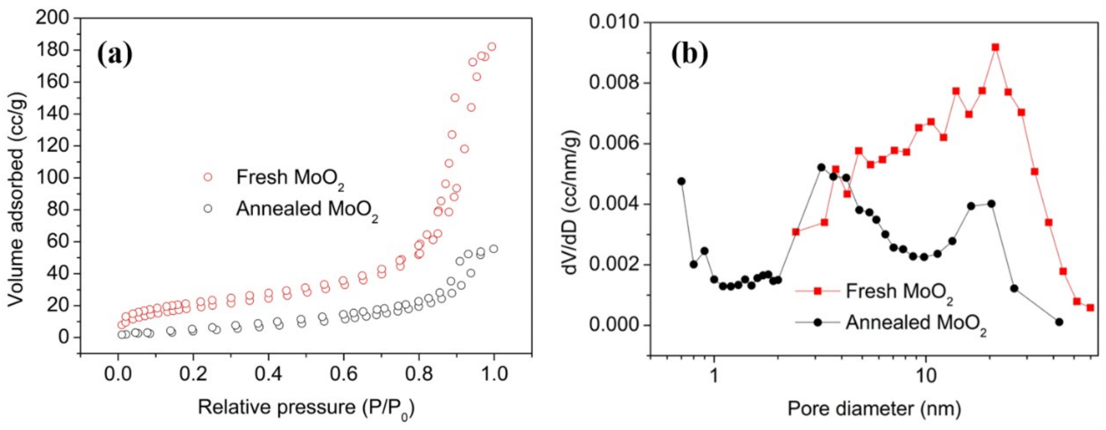

**Figure S8.** BET surface area and pore distribution of fresh and annealed $MoO_2$

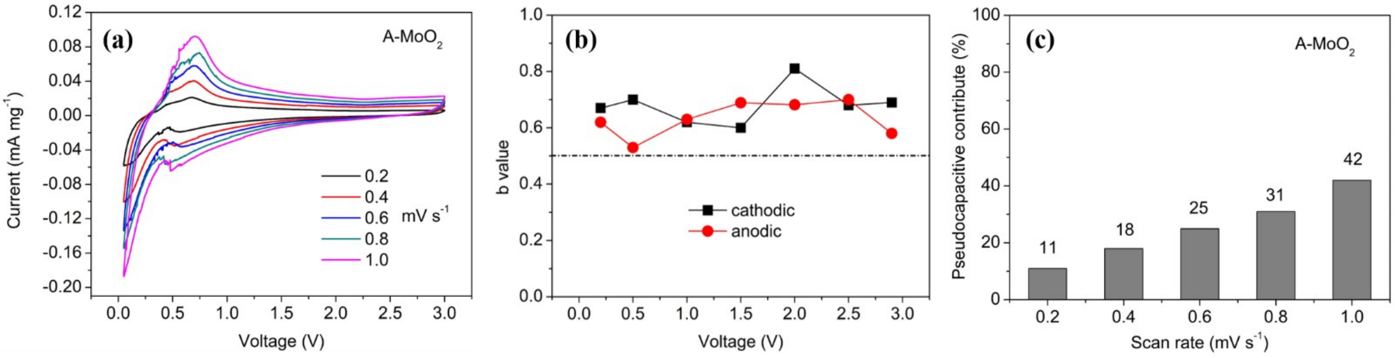

**Figure S9.** (a) CV curves of annealed $MoO_2$ (A-$MoO_2$) at 0.2-1.0 mV $s^{-1}$; (b) determination of the b-values during cathodic/anodic; (c) Capacitive controlled contributions at different scan rate

Annealed $MoO_2$ only processes a pseudocapacitive contribution of 42 % at 1 mV $s^{-1}$, while pseudocapacitive contribution in the fresh anode is 65 % at 1 mV $s^{-1}$. The differences might be attributable to the low BET surface area and high crystallinity of annealed $MoO_2$, a faradic process is dominated during discharge/charge.

Table S1. Comparison of the fresh $MoO_2$ nanocomposites with other typical $MoO_2$ based anode in literature.

| Materials | Method | Current density (A/g) | Capacity (mAh/g) | Pseudocapacitance (%) | Reference |
|---|---|---|---|---|---|
| $MoO_2$/GO | Preform decomposition | 0.1 | 483 | NA | [1] |
| $MoO_2$@C nanofbers | Electrospinning | 0.1 | 290 | NA | [2] |
| $MoO_2$@NC nanofibers | Electrospinning | 0.1 | 350 | NA | [3] |
| $MoO_2$/$TiO_2$-Carbon | Hydrothermal | 0.1 | 297 | 60 % @ 1 mV/s | [4] |
| Fresh $MoO_2$ | Solvothermal | 0.1 | 265 | 65 % @ 1 mV/s | This work |

Although present electrochemical results on capacity in this is not very competitive, a pseudocapacitive charge storage mechanism has been realized of 65 % at 1 mV $s^{-1}$, which leads the previous reports. The pseudocapacitance is a key parameter for enhancing power output of sodium ion batteries. Also, our solvothermal method is a relatively facile synthesis route with high yield at low cost, which could be a possible application in large-scale energy storage technologies.