Supporting Information

Layered-Structure $(NH_4)_2Mo_4O_{13}$@N-doped porous carbon composite as superior anode for lithium-ion batteries

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1. Experimental

1.1 Materials Preparation

All experimental reagents applied in this work were analytical grade and used as raw materials without further purification. The detailed synthetic procedure is as follows: Ammonium heptamolybdate tetrahydrate [$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$] and glucose were mechanically mixed in 1:1 molar ratio grinding for 30 minutes by hand. Then, the mixed powder was loaded to an alumina crucible with a matching cover and the crucible was wrapped with aluminium foil tightly. Further the wrapped crucible was heated to 650 ^{o}C at the heating rate of 5^{o}C/min and kept constant for 2 h in a muffle furnace in ambient atmosphere. After the system naturally cooling to room temperature, the obtained powder was centrifugal washed with distilled water and anhydrous ethanol for three times before freeze-drying for 24 hours. Finally, the freeze-dried sample was grinded in the mortar and collected as a dark gray powder (Fig S1a). The obtained dark gray powder is labeled as $(NH_4)_2Mo_4O_{13}$/NC. It needs to point that the $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ as both Mo and N source.

Under same condition except for not wrapping crucible with aluminium foil, a light yellow powder was obtained (Fig S1b). The obtained light yellow powder is labeled as MoO_3.

1.2 Materials Characterization

XRD patterns were recorded on a Rigaku D/max 2200PC V diffractometer operating with Cu Kα radiation (λ=1.5416 Å) in a 2θ range from 10° to 60° to characterize the crystal structure of the as-prepared products. Raman spectra were recorded with Renishaw in Via system with a line exciting wavelength of 785 nm. Fourier transform infrared (FT-IR) test was performed on a Bruker Vector-22 infrared spectrophotometer using KBr pellets in the range of 550-4000 cm^{-1}. TG was carried out at a heating ramp of 10 ºC/min^{-1} under air from room temperature to 700 °C to analyze the weight ratio of different components. The morphology and microstructure was investigated by field emission scanning electron microscopy (FE-SEM, S-4800) and transmission electron microscopy (TEM, FEI Tecnai G^2 F20 S-TWIN). Brunauer-Emmett-Teller (BET) surface area was measured by nitrogen adsorption and desorption method using an ASAP 2460 analyser (Mac, America) to obtain the surface area and pore size distribution. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Surface Science Instruments Spectrometer with monochromatic Al Kα source. The ex situ XRD, XPS, SEM and TEM tests of cycled electrodes were operated before washing by dimethyl carbonate (DMC) in argon-filled glove box before. The washed electrodes were sputtered with Ar about 60s before the depth ex-situ XPS analysis.

1.3 Electrochemical measurements

All the working electrodes were prepared by dispersing 80 wt% active materials $(NH_4)_2Mo_4O_{13}$/NC or MoO_3, 10 wt% conducting carbon black (super P) and 10 wt% binder (5 wt% CMC, 5 wt% PAA) in deionized water to form homogeneous slurry. The obtained slurry was pasted on a copper foil and dried at 80 ^{o}C for 12 h in a vacuum oven, and then punched into small disks with a diameter of 16 mm. CR 2032 type half-cells were assembled in an argon-filled glove box (Mbraun, Germany, O_2 and H_2O contents < 0.5 ppm) with pure lithium foils as the counter electrode and microporous polypropylene film as the separator. The electrolyte was made of 1 M $LiPF_6$ solution in a mixture of ethylene carbonate/ethyl methyl carbonate/dimethyl carbonate (EC/EMC/DMC) (1/1/1, vol.%).

The galvanostatic charge/discharge measurements were conducted on a CT2001A battery testing system (LANHE, Wuhan, China) under different current density with the potential range of 0.01 V-3.0 V (*vs* Li/Li^+). Cyclic voltammetry and electrochemical impedance spectroscopy (EIS) were conducted using an Electrochemical Workstation (CHI 660E, Chenhua, Shanghai, China). Before testing, all batteries were aged for 24 h. The electrochemical testing of all electrodes was performed at room temperature.

MoO_3 **$(NH_4)_2Mo_4O_{13}/NC$**

Figure S1 Product images

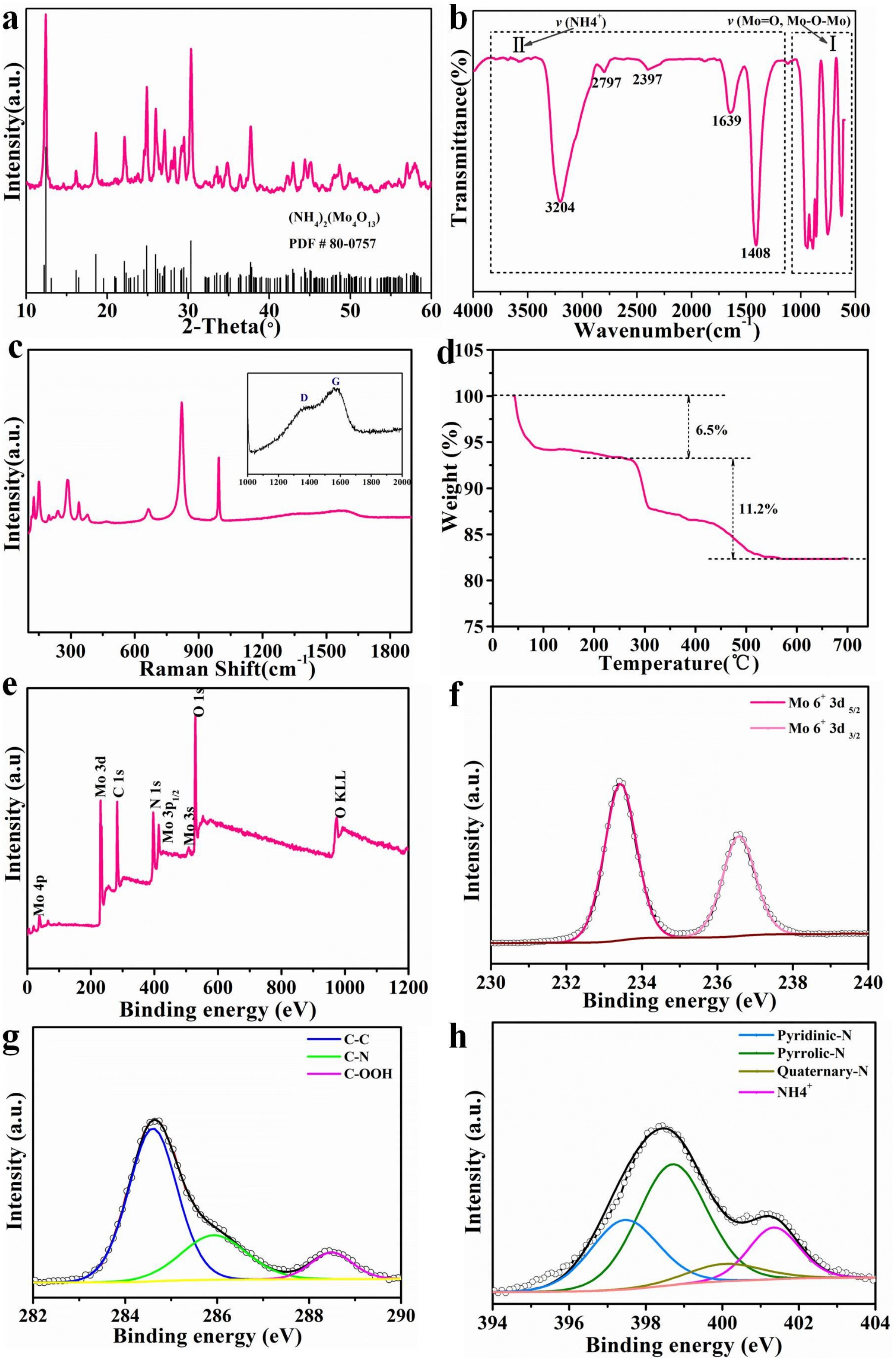


Figure S2 (a) XRD pattern, (b) IR spectrum, (c) Raman spectrum, (d) TG curve, (e) low-resolution XPS spectrum, high-resolution XPS spectrum of (f) Mo 3d, (g) C 1s and (h) N 1s of the $(NH_4)_2Mo_4O_{13}$/NC composite

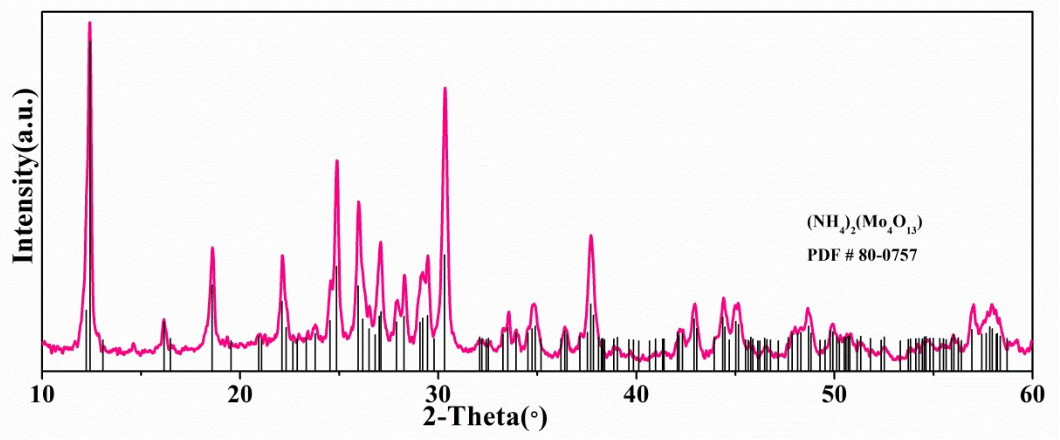
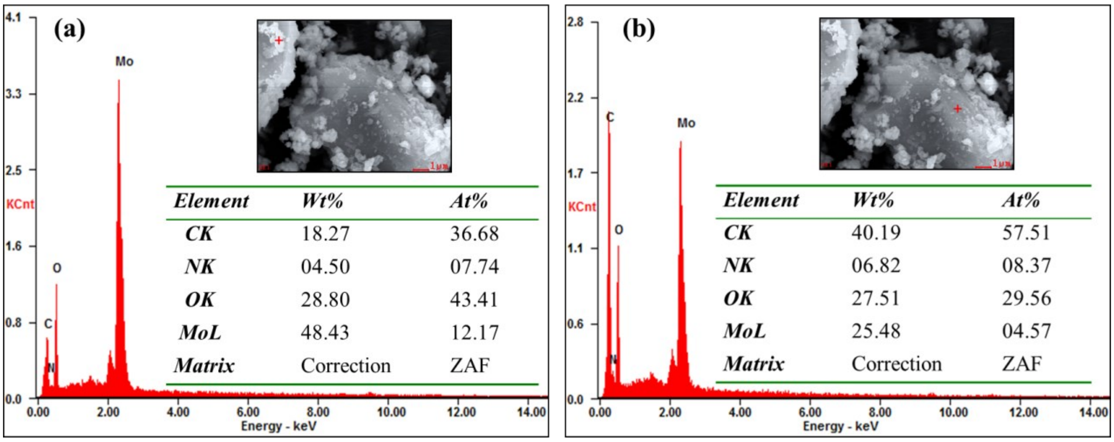


Figure S3 The enlarged view of the XRD of $(NH_4)_2Mo_4O_{13}$/NC



Element	*Wt%*	*At%*
CK	18.27	36.68
NK	04.50	07.74
OK	28.80	43.41
MoL	48.43	12.17
Matrix	Correction	ZAF

Element	*Wt%*	*At%*
CK	40.19	57.51
NK	06.82	08.37
OK	27.51	29.56
MoL	25.48	04.57
Matrix	Correction	ZAF

Figure S4 EDS data of $(NH_4)_2Mo_4O_{13}$/NC composite

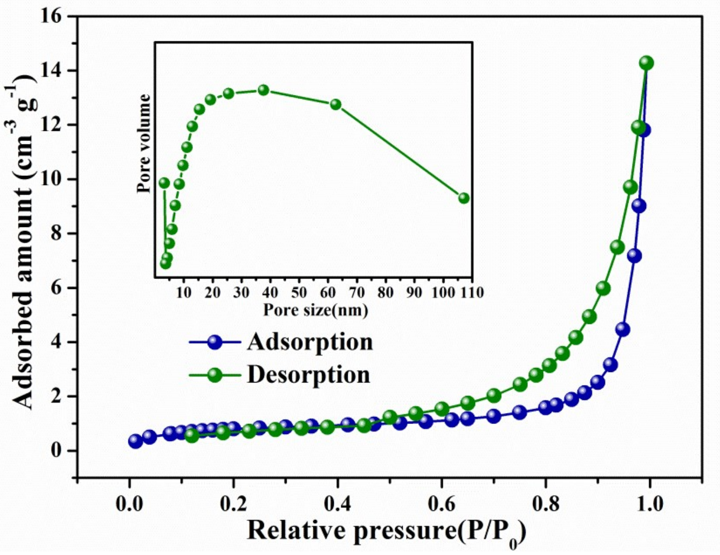


Figure S5 N_2-adsorption/desorption curve and pore distribution (inset) of $(NH_4)_2Mo_4O_{13}$/NC composite.

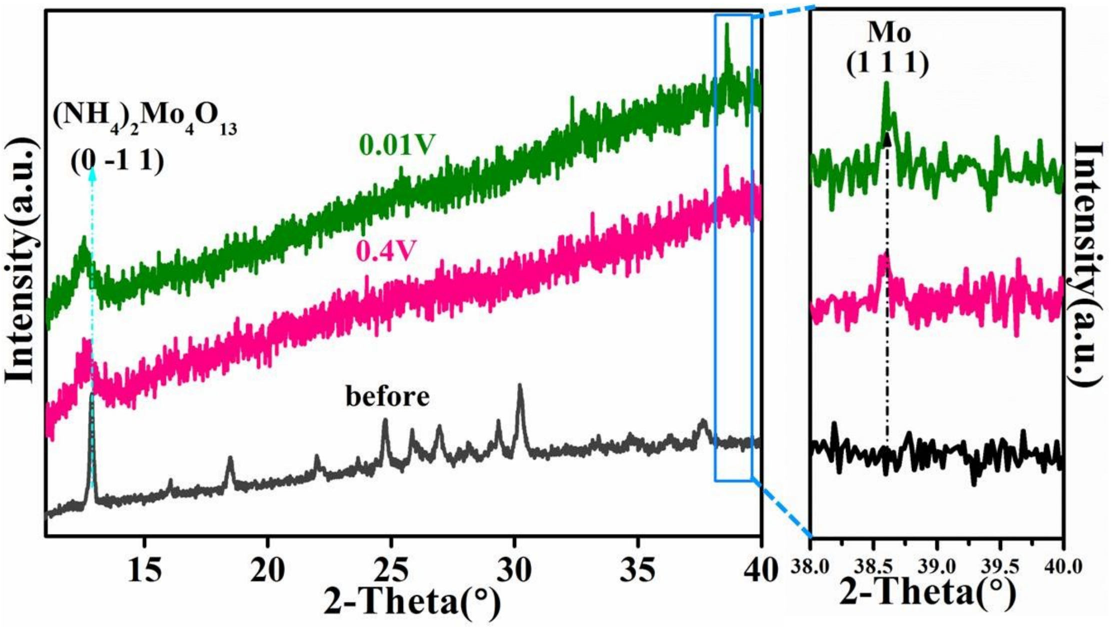
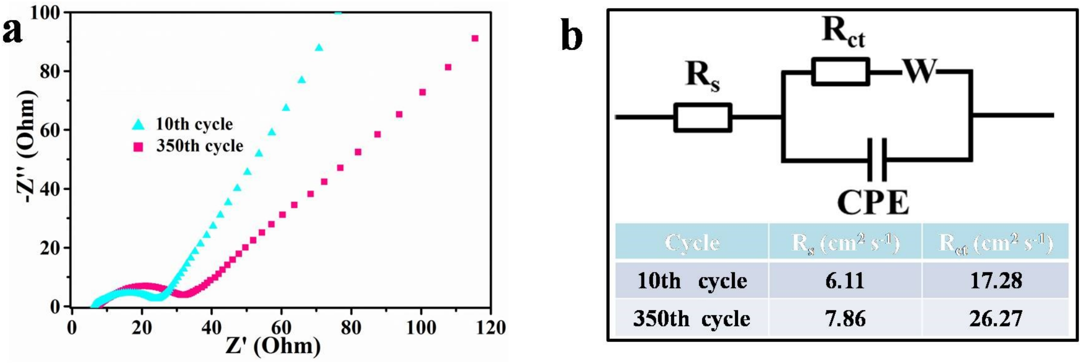


Figure S6 The ex situ XRD patterns of $(NH_4)_2Mo_4O_{13}$ electrode at different discharge potential



Cycle	R_s ($cm^2 s^{-1}$)	R_{ct} ($cm^2 s^{-1}$)
10th cycle	**6.11**	**17.28**
350th cycle	**7.86**	**26.27**

Figure S7 (a) electrochemical impedance spectroscopy (EIS) in the 10th and 350th cycle and (b) the corresponding equivalent circuit model for the impedance spectra (inset) and the fitted results of the electrolyte impedance (R_e) and the charge transfer impedance (R_{ct}) (inset) of $(NH_4)_2Mo_4O_{13}$/NC electrodes

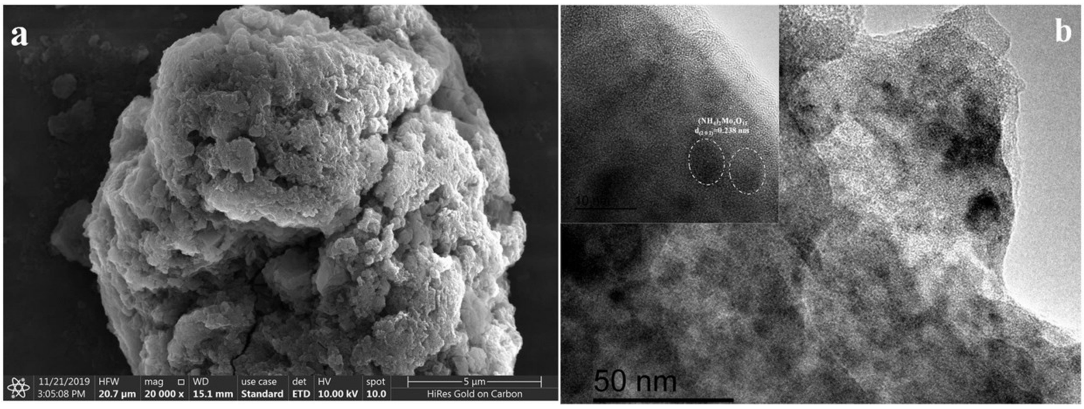


Figure S8 SEM and TEM images of cycled $(NH_4)_2Mo_4O_{13}$/NC electrodes after the 350th under full charged

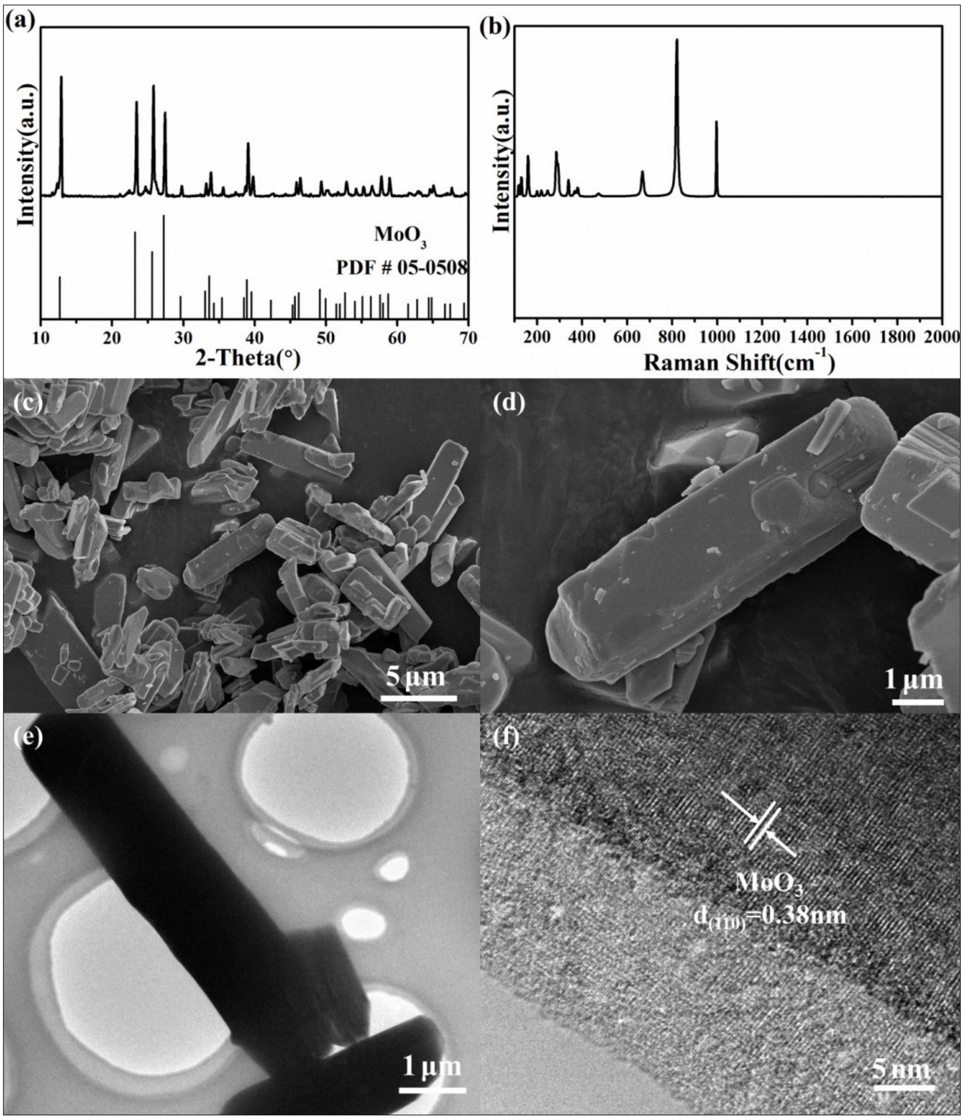


Figure S9 (a) XRD pattern, (b) Raman spectrum, (c-d) SEM images and (e-f) TEM images of MoO_3

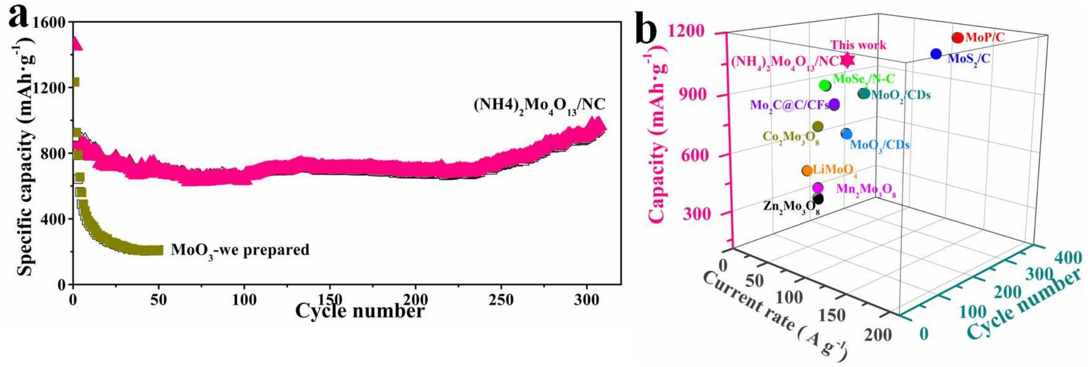


Figure S10 (a) cyclic performance comparison of $(NH_4)_2Mo_4O_{13}$/NC electrodes with MoO_3 prepared under same condition, (b) further comparison of Li storage performance with the reported Mo-based anode materials for LIBs.