Supporting Information

Electrodepositing Amorphous Molybdenum Oxides for Aqueous NH$_4^+$ Storage

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1. Experimental section

1.1 Materials

All the chemical reagents were purchased from Sinopharm Chemical Reagent Co., ltd. Graphite foil was purchased from SGL Carbon, Germany.

1.2 Electrochemical exfoliation of the graphite foil (EG)

EG (working area: 0.8×0.8 cm^2) was exfoliated in a three-electrode cell, using a saturated calomel electrode (SCE) as the reference electrode and a piece of graphite foil as the counter electrode, respectively. The graphite foil was first treated in a 0.5 M KOH solution using voltammetry (CV) at 0.5 to 1.75 V at the scan rate of 20 mV s^{-1} for 6 cycles. The graphite/graphene sheets were partially exfoliated from the graphite base, forming a three-dimensional morphology. To conduct secondary exfoliation and functional modification, the exfoliated graphite foil was further exfoliated in 0.5 M KNO$_3$ electrolyte using a constant potential of 1.85 V vs. SCE for 30 min. Third, the exfoliated graphite foil was treated in 0.5 M KNO$_3$ electrolyte to recover the conductivity via CV from -1.2 V to 0 V vs. SCE for 20 cycles at the scan rate of 50 mV s^{-1}.

1.3 Electrochemical deposition of MoO$_x$ in different concentrated electrolytes

The material deposition was conducted in a three-electrode system, using EG as the working electrode, SCE and a piece of graphite foil as the reference and counter electrodes. Different concentrated ammonium molybdate $[(NH_4)_6Mo_7O_{24} \cdot 4H_2O]$ solutions of 0.025, 0.2 and 0.3 m (mol kg^{-1}), corresponding to 0.025, 0.167, and 0.237 M (mol L^{-1}), were used as the deposition electrolytes. During the deposition, a constant current density of ~ -7.8 mA cm^{-2} was applied on the working electrode, to obtain the electrodes, denoted as MoO$_x$-0.025, MoO$_x$-0.2 and MoO$_x$-0.3, respectively. All the active mass loading of the electrodes was controlled at about 7.0~8.0 mg cm^{-2} via adjusting the deposition time (from 10 to 16 mins). The weight ratio of MoO$_x$: EG is about 30%.

1.4 Characterizations

The morphology and structure features of the samples were studied on transmission electron

microscope (TEM, JEM-ARM200F, JEOL, Japan) and scanning electron microscopy (SEM, HITACHI, SU8010, Japan). The crystal structures of the materials were studied by X-ray diffraction (XRD, PANalytical B.V., XPert Pro, Netherlands) using a Cu Kα radiation source (40.0 kV, 40.0 mA). Fourier transform infrared spectroscopy was performed on a Fourier transform infrared spectrometer (FTIR, Bruker, VERTEX70, Germany). The specific surface area and the pore size distribution of the electrodes were tested by a physisorption analyzer (ASAP 2460, micromeritics, America). The chemical composition of the materials was studied by X-ray photoelectron spectroscopy (XPS, Thermo Scientific, ESCALAB 250Xi, USA) with Al Kα radiation ($\lambda = 8.34$ Å) as the excitation source. The electrochemical measurements of the materials were studied by a multichannel working station (VMP3, Bio-Logic, France).
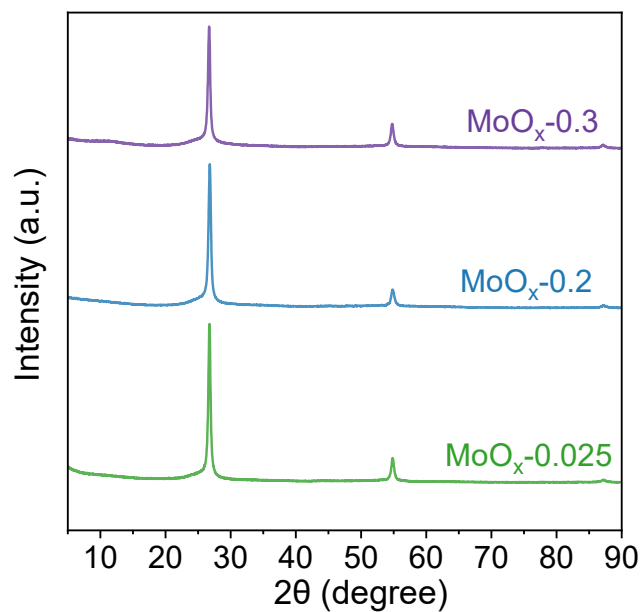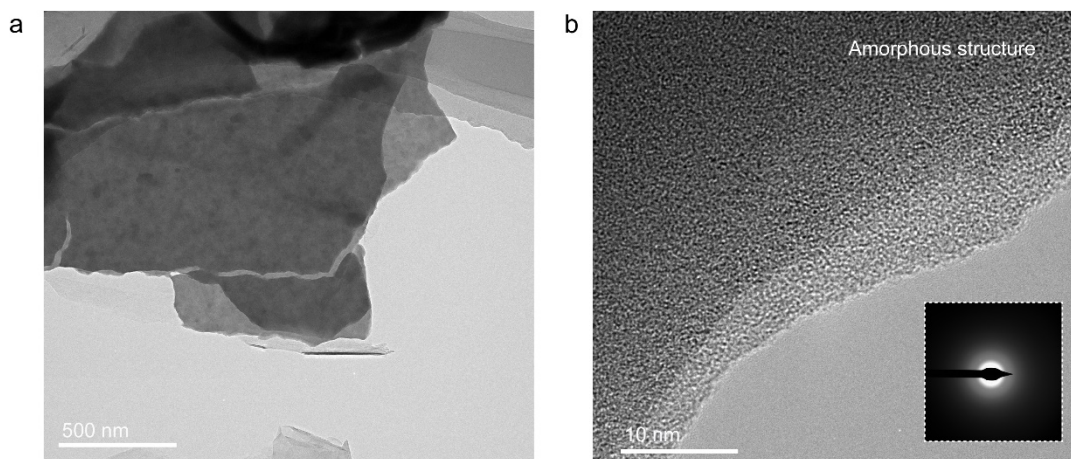
2. Supplementary Figures
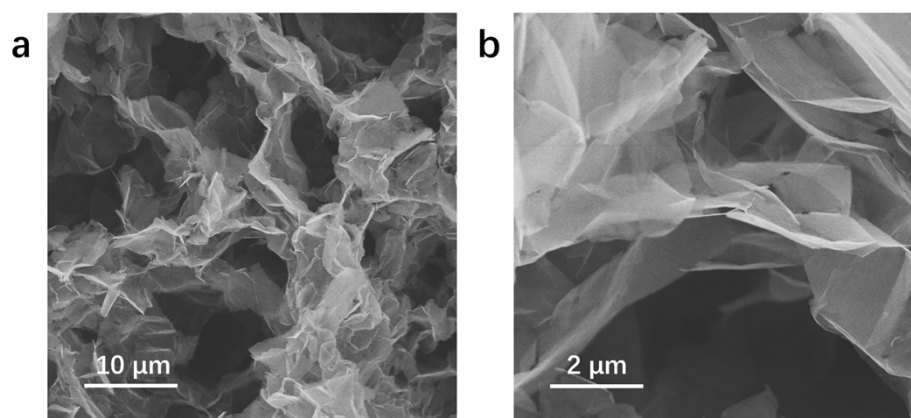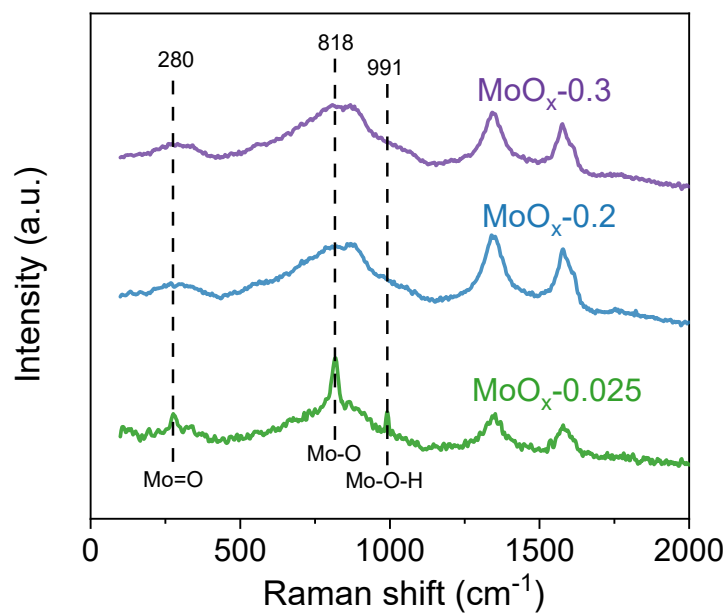

Fig. S1. SEM images of EG.
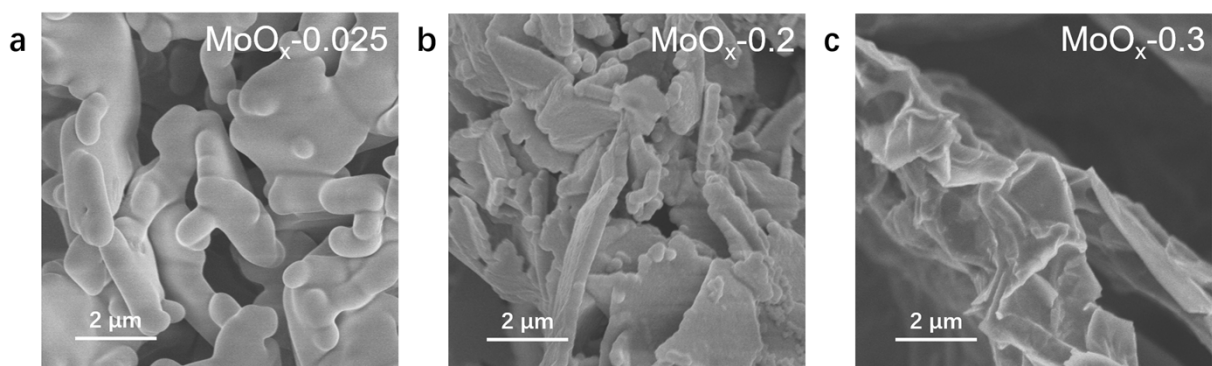
Fig. S2. SEM images of MoO_x-0.025、MoO_x-0.2 and MoO_x-0.3.

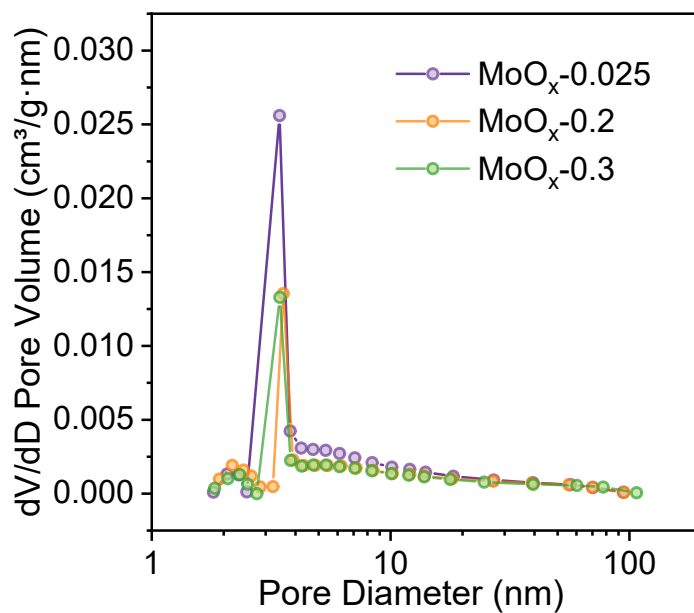**Fig. S3.** XRD patterns of MoO$_x$-0.025、MoO$_x$-0.2 and MoO$_x$-0.3.


Fig. S4 TEM images of MoO$_x$-0.2. Insert shows the SAED pattern. HRTEM and SAED pattern suggest that the deposited oxide is amorphous structure, in which a random arrangement of distorted Mo-O polyhedra with short range ordering is presented.
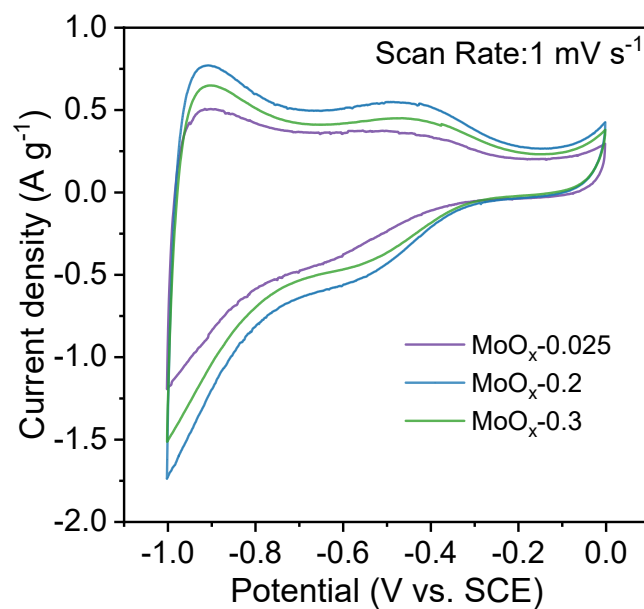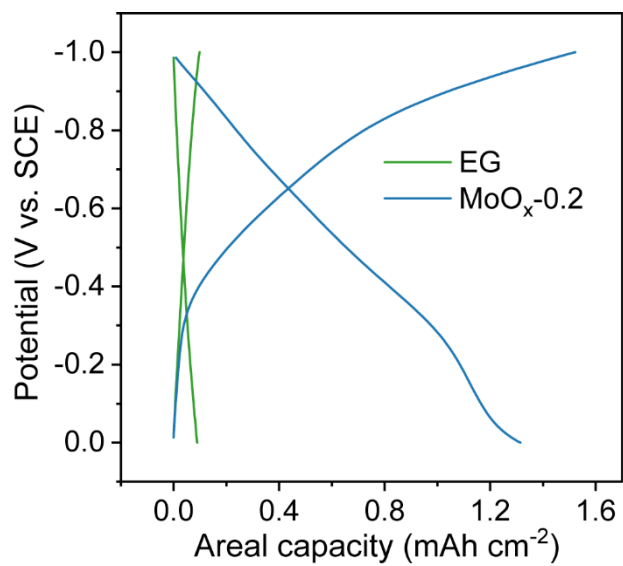
Fig. S5. Raman spectra of MoO$_x$-0.025、MoO$_x$-0.2 and MoO$_x$-0.3.

Fig. S6. The pore size distribution of MoO$_x$-0.025、MoO$_x$-0.2 and MoO$_x$-0.3 derived from the adsorption curves using BJH theory.
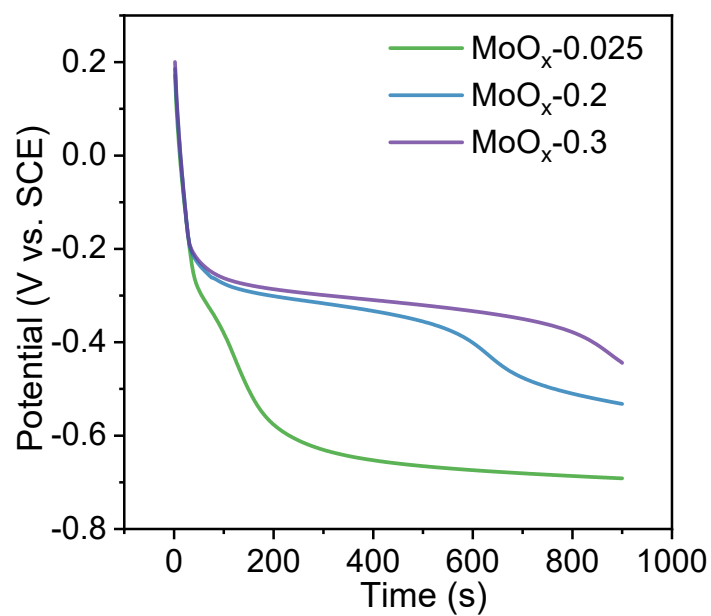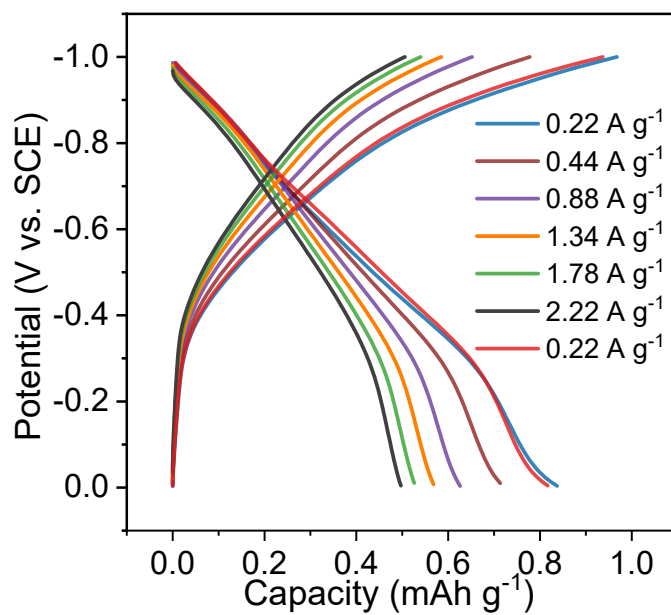
Fig. S7. The deposition curves of the samples in different concentrated plating electrolytes.

Fig. S8 The CV curves of MoO_x-0.025、MoO_x-0.2 and MoO_x-0.3.
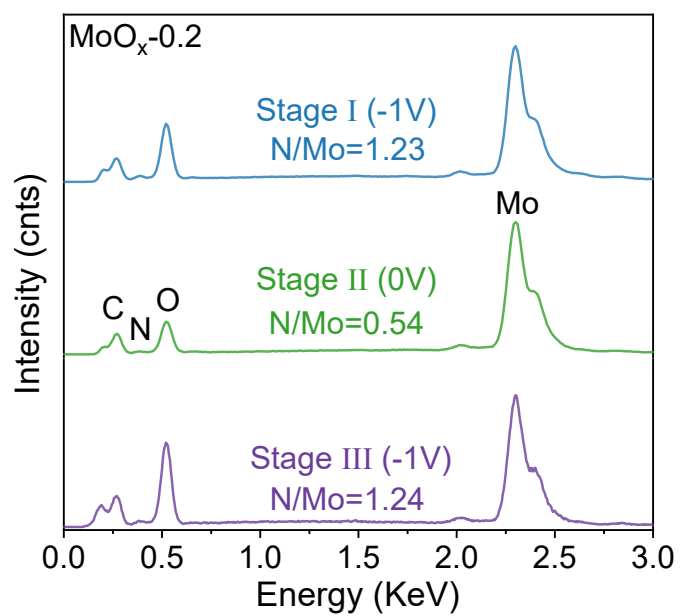
Fig. S9 Areal capacity of the EG substrate and MoO_x-0.2 at the current density of 1.56 mA cm^{-2}.

Fig. S10. The galvanostatic charge/discharge curves of MoO_x-0.2 from 0.22 to 2.22 A g^{-1}.

Fig. S11. The EDX spectra of the electrodes collected at different states of charge, (a) -1 V, (b) 0 V, (c) -1 V.