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Supporting Information

An Auto-oxidation of Exfoliated MoS_2 in N-Methyl-2-Pyrrolidone: from 2D Nanosheets to 3D Nanorods

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1. EXPERIMENTAL SECTION

1.1 Materials

MoS_2 powder (99%, ~6 μm, max. 40 μm), isopropanol (reagent grade) and N-methyl-2-pyrrolidone (NMP, ≥99% purity) were purchased from Sigma-Aldrich. Omnipore membrane filters (polyvinylidene fluoride, PVDF, hydrophilic surface, 0.1 μm pore size, 13 mm diameter) were purchased from Merck Millipore Limited. Activated carbon (YEC-8A, the particle size ca. 10 μm, surface area ≥ 2100 m^2 g^{-1}, moisture < 5%, ash 0.26%, iron content < 0.005%) was purchased from Fuzhou Yihuan Carbon, P. R. China.

1.2 Preparation of MoS_2 and $MoO_3 \cdot MoS_2$ dispersions

The MoS_2 dispersion was prepared using liquid-phase exfoliation (LPE) with ultrasound energy (sonication). Briefly, 1 g of bulk MoS_2 powder was sonicated in 100 ml of NMP at a frequency of 37 kHz and a power of 300 W for 12 h at 25°C. The exfoliated MoS_2 dispersion was then centrifuged twice at 6000 rpm (3139 g) for 20 minutes to remove residual bulk materials, as shown in Figure 1a. The supernatant was taken from the top 80% of the dispersion.[1, 2] The resulting MoS_2 dispersion was then added to ~10% fresh NMP solvent to minimize the nanosheet aggregation (concentration ~0.1 mg mL^{-1} in pure NMP).

The composite $MoO_3 \cdot MoS_2$ dispersion was prepared using sonication-assisted exfoliation from the exfoliated MoS_2 dispersion obtained in the previous step. The amounts of water varied from 5% to 25% by volume in the total NMP/water mixtures. The addition of water under ambient conditions played a crucial role in the auto-oxidation reaction of exfoliated MoS_2. This caused the formation of the orthorhombic α-MoO_3 nanorods as a function of water content (which will be discussed below), as shown in Figure 1b.

1.3 Preparation of electrodes

1.3.1 MoS_2 and $MoO_3 \cdot MoS_2$ electrodes

The prepared dispersions were mildly sonicated before the preparation of electrodes. The dispersions obtained were filtrated through a pre-weighed PVDF filter using pressure-assisted filtration with a constant flow rate of 5 mL h^{-1} to produce free-standing MoS_2 and $MoO_3 \cdot MoS_2$ electrodes. These electrodes were then rinsed with a plenty of deionised water to minimize any residual solvent remaining on the electrodes. The electrode was then dried at 50°C overnight and re-weighed to obtain the mass of material loading, which was 0.40 ± 0.05 mg (see Figure S1: Supporting information).

1.3.2 Quasi-reference and counter electrode

The quasi-reference and counter electrode (QRCE) was prepared using activated carbon as in previous studies.[3] The mixture between activated carbon and PVDF, at a 9:1 ratio, was dispersed in isopropanol and sonicated for 1 hour to produce a total concentration of 0.05 mg mL^{-1}. The QRCE electrode was prepared in a similar way to the MoS_2 electrode. The total mass of QRCE is roughly 2 mg (1.8 mg of activated carbon loading). The electrochemical performance and stability of the activated carbon QRCE were previously reported by Lee et al,[3] who demonstrated that that the QRCE provides high electrochemical stability in neutral aqueous electrolyte, showing a tiny potential shifted less than ~1 mV per day.

1.4 Characterization of dispersions and electrodes

Transmission electron microscopy (TEM) was carried out using an FEI Tecnai F30 microscope with an accelerating voltage of 200 kV. The samples were diluted in isopropanol and prepared on a lacey carbon copper grid. The TEM specimens were then dried at 60 °C in a vacuum oven

for 12 hours to remove all residual solvents and any contaminations. Scanning electron microscopy (SEM) was performed using an FEI/Philips XL30 E-SEM microscope with an accelerating voltage of 15 kV under high vacuum conditions using secondary electron detection. Powder X-ray Diffraction (PXRD) patterns of electrodes were studied using a PANalytical X'Pert Pro diffractometer operating at 40 kV and 30 mA. The patterns were recorded with 2θ of 5-70° using a Cu-Kα radiation source (λ = 1.5418 Å). X-ray photoelectron spectroscopy (XPS) was carried out using a Kratos Axis Ultra DLD spectrometer with Al-Kα as the X-ray source (1486.6 eV). All XPS spectra were calibrated using carbon (C 1s) at 284.8 eV, and peak fits were carried out using a nonlinear Shirley-type background (70% Gaussian and 30% Lorenzian line shapes). The Raman spectra were carried out using a Renishaw inVia Raman microscope at 532 nm (excitation of 2.33 eV) with an excitation power of 1 mW. The spectra were performed between 67 and 1840 cm^{-1}.

2.5 Electrochemical measurements

All electrochemical measurements were performed in the two-electrode configuration using a potentialstat (PGSTAT302N, Metrohm Autolab, Netherlands), running Nova software version 1.11. The coin cell (CR-2032) was assembled by separating two electrodes, which the prepared (MoS_2 and $MoO_3 \cdot MoS_2$) and the QRCE electrodes used as working and counter/reference electrodes respectively. The electrodes were stacked back-to-back inside a coin cell, where the PVDF filter performed the task of the polymer porous separator. The electrolyte used for all measurements was a 0.5 M Na_2SO_4 aqueous solution. The electrochemical properties of the electrodes were characterized by several electrochemical techniques in a coin cell, such as cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The CV was performed at the scan rate ranging from 5 to 100 mV s^{-1}

between -0.8 to 0.0 V and -0.6 to 0.0 V vs. carbon for the $MoO_3 \cdot MoS_2$ and pristine MoS_2, respectively, using 0.5 M Na_2SO_4. The EIS was performed at the open circuit potential (OCV) using an amplitude of 10 mV in the frequency range of 1 mHz to 100 kHz. The capacitance of the prepared electrodes can be calculated using the integral product of the CV in Equation (1):

$$C_s = \frac{Q}{mV} = \int \frac{id\,V/v}{m\Delta V} \tag{1}$$

where m is the total mass of the electrode (g), v is scan rate (mV s^{-1}), and ΔV is the window potential (V).

2. DISCUSSION SECTION

S1. Freestanding electrode fabrication

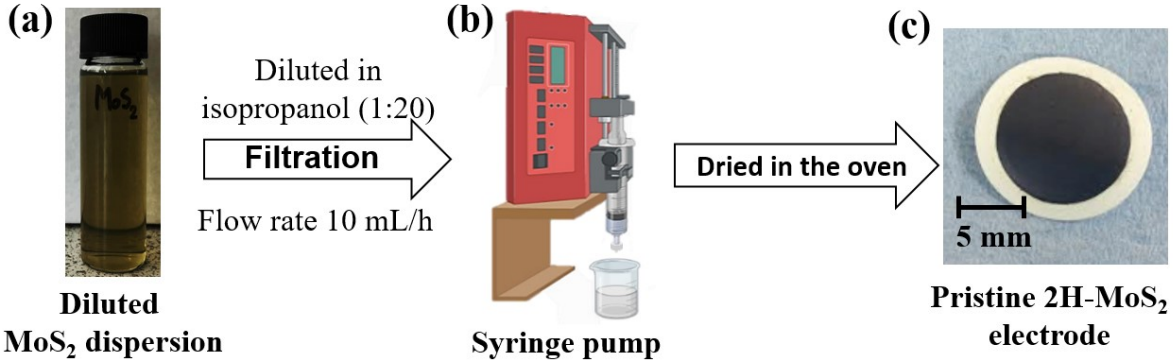

Figure S1: Freestanding electrode fabrication. (a) Photograph of MoS_2 dispersion in N-methyl-2-pyrrilidone. (b) The electrode preparation under pressure-assisted pump. The dispersion was diluted in isopropanol (1:20) before filtration. (c) Photograph of the pristine MoS_2 electrode on PVDF filter. This process was previously report.[1, 2]

S2. Surface morphology of bulk MoS_2 and the exfoliated MoS_2

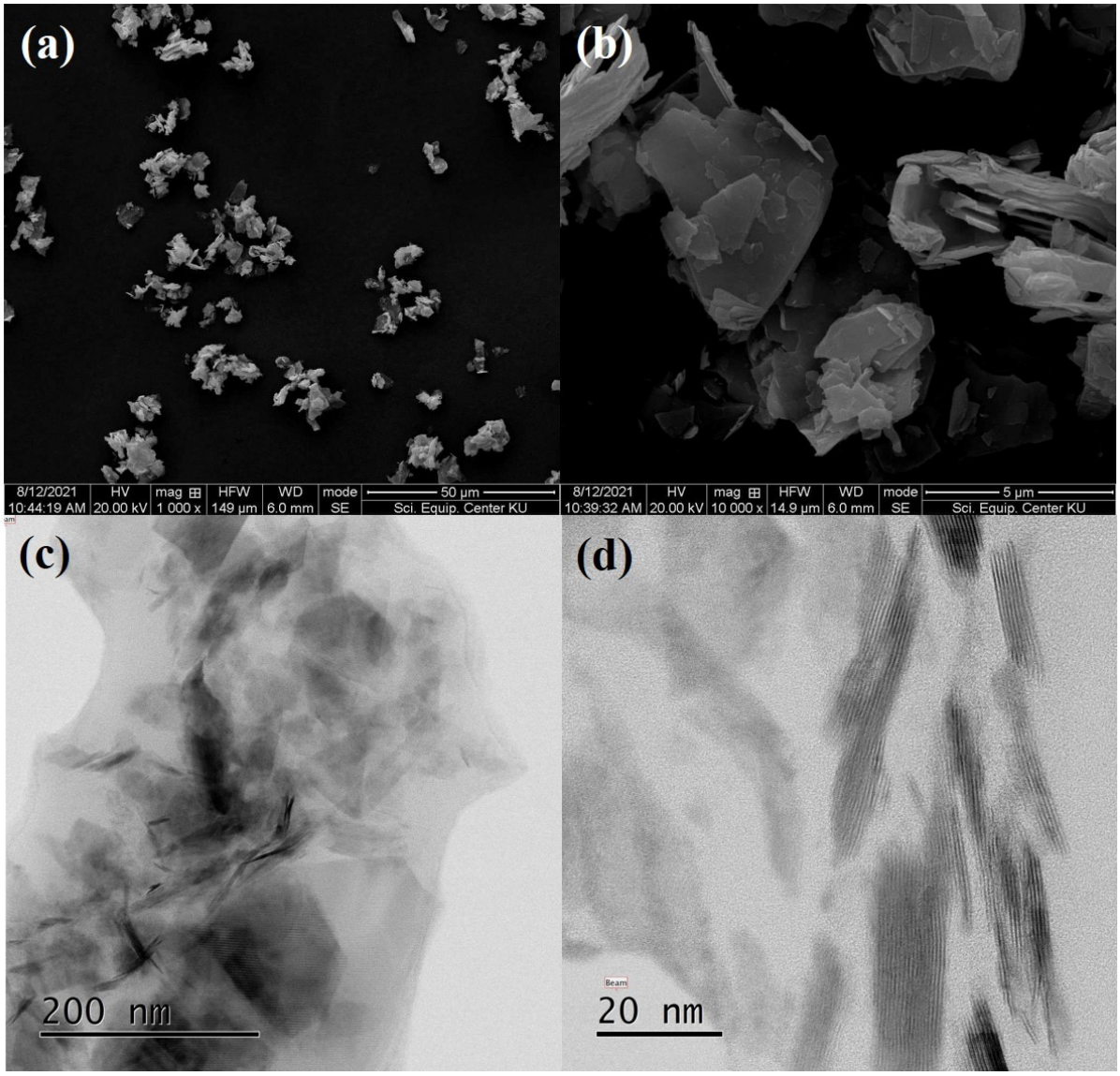

Figure S2: The SEM images of bulk 2H-MoS_2 powder (a) low magnification and (b) high magnification. After liquid phase exfoliation, the dimension of 2H-MoS_2 were then reduced as shown in the TEM images (c) low magnification, and (d) high magnification.

S3. Overview morphologies of the 2H-MoS_2 and the composite MoO_3•MoS_2 electrodes

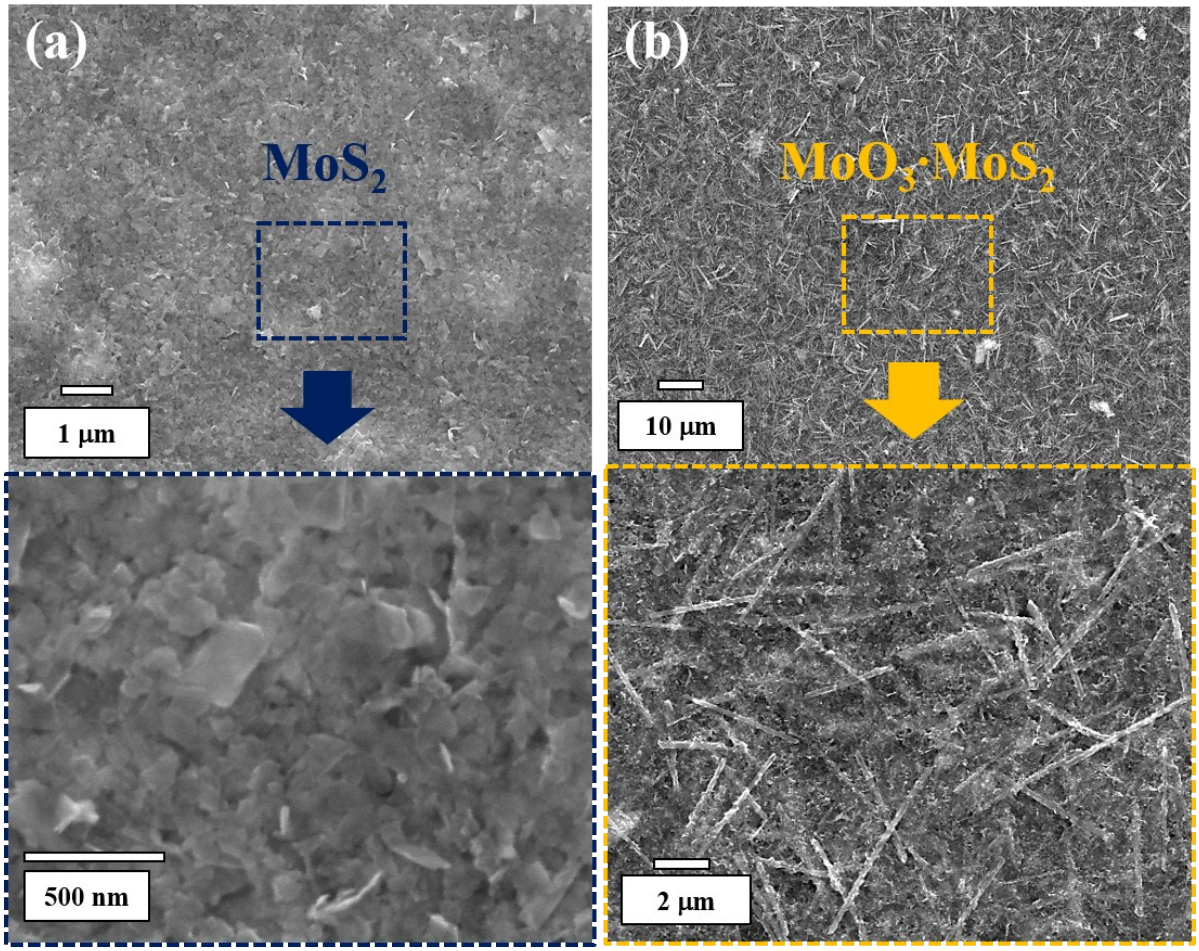

Figure S3: Overview of SEM images of (a) the 2H-MoS_2 and (b) composite MoO_3·MoS_2 electrodes with their corresponding enlarged SEM images.

S4. Rod distribution as determined by TEM analysis

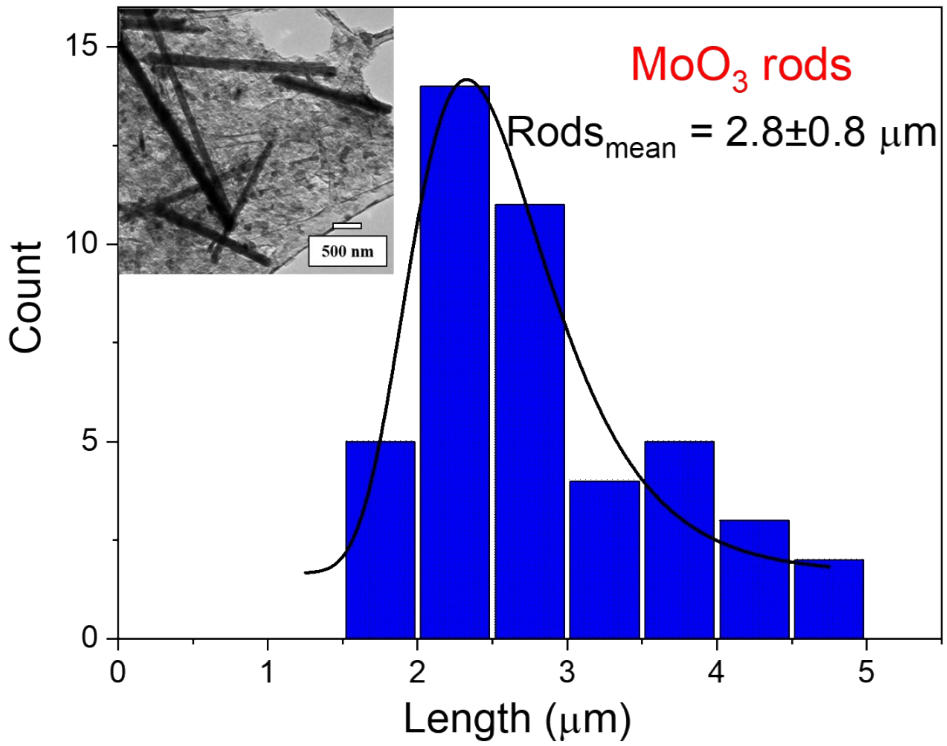

Figure S4: Size histograms of MoO_3·MoS_2 microrod lengths, as measured by statistical TEM. The rod was measured with the major length. The rod lengths were counted from *ca.* 44 rods. The mean rod length is 2.8 ± 0.8 μm. The histogram was mathematically fitted using the Extreme function as shown in black solid lines.

S5. XPS analysis of the composite MoO_3·MoS_2 electrodes

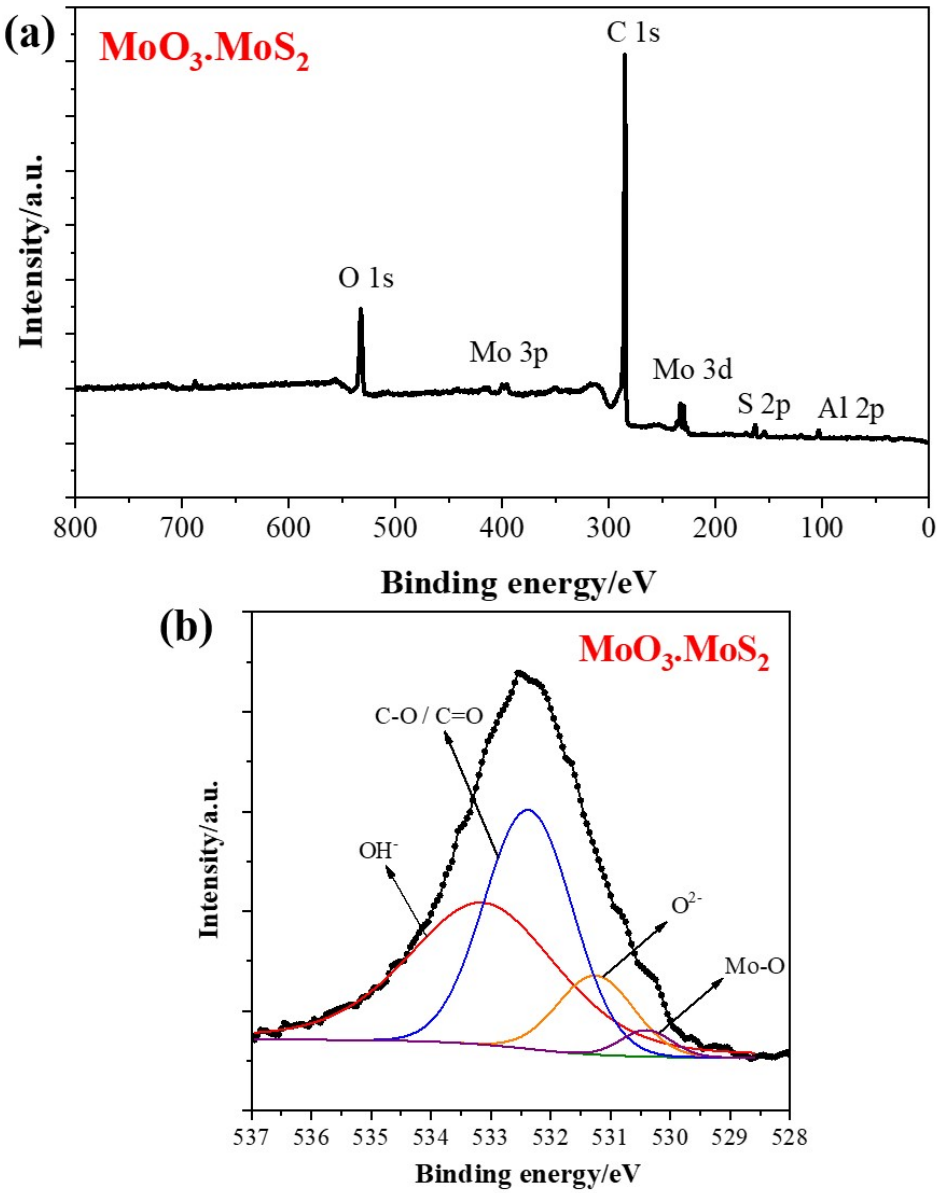

Figure S5: (a) The survey XPS spectrum of the composite MoO_3·MoS_2 electrodes showing the predominant oxygen intensity. (b) The O 1s spectra of the composite MoO_3·MoS_2.

S6. Characterisation of thin layer exfoliated MoS_2

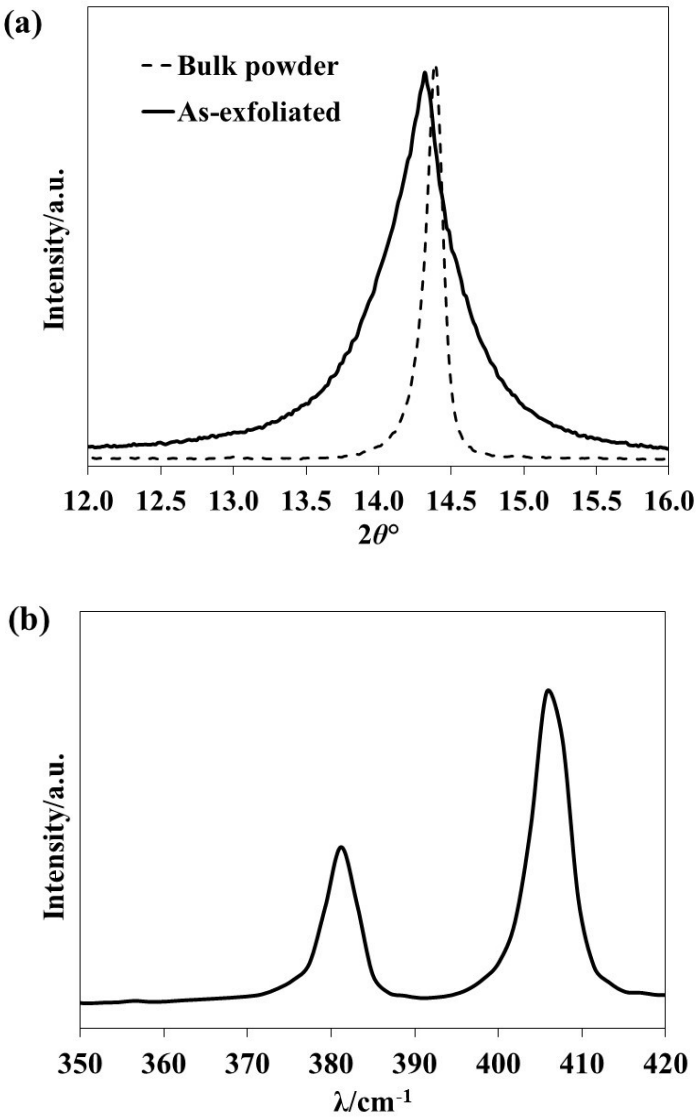

Figure S6: (a) The XRD pattern of the from the bulk crystal to the as-exfoliated MoS_2, and (b) Raman spectra of the as-exfoliated MoS_2.

S7. Electrochemical properties of the as-prepared composite electrode

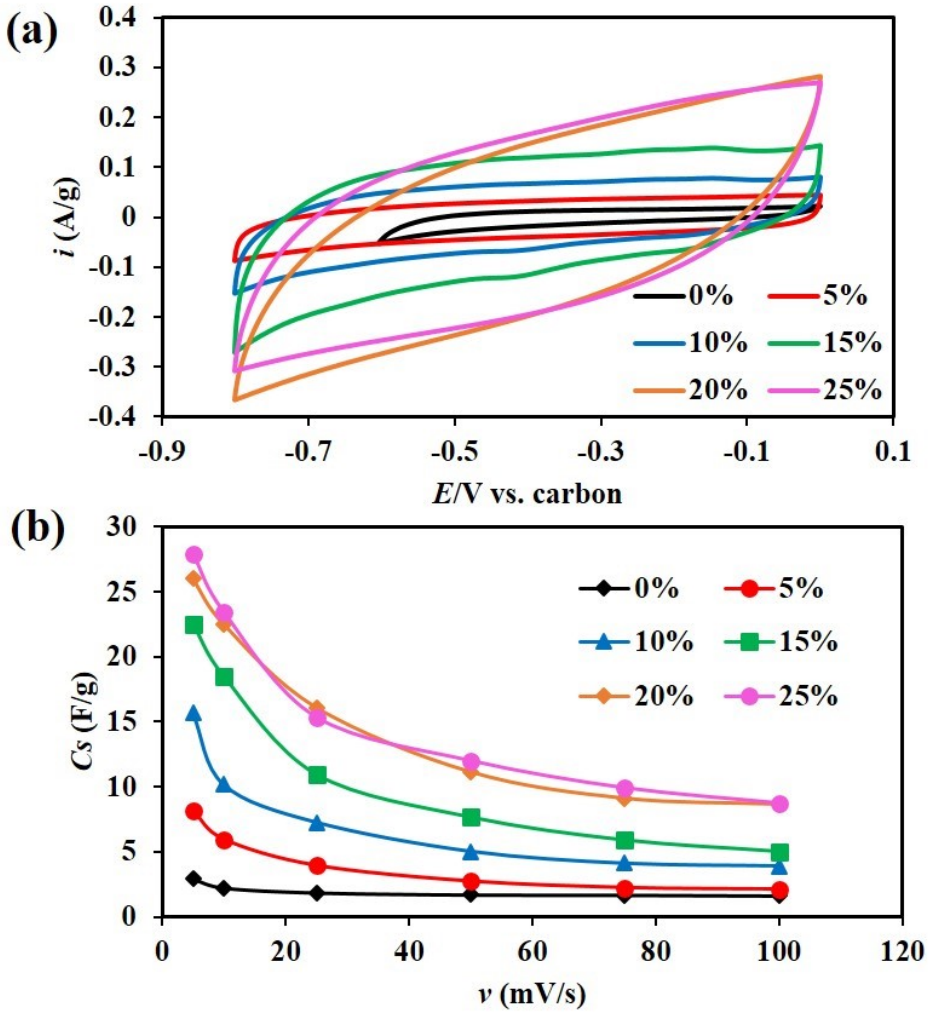

Figure S7: Electrochemical properties of the $MoO_3 \cdot MoS_2$ with the different percentage of water added to NMP (a) CV at 5 mV s^{-1}, and (b) Specific capacitance with respect to scan rate.

S8. Supporting information references

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2. W. Hirunpinyopas, E. Prestat, S. D. Worrall, S. J. Haigh, R. A. W. Dryfe and M. A. Bissett, *ACS Nano*, **2017**, **11**, 11082–11090.
3. J. Lee, N. Jäckel, D. Kim, M. Widmaier, S. Sathyamoorthi, P. Srimuk, C. Kim, S. Fleischmann, M. Zeiger and V. Presser, *Electrochimica Acta*, 2016, **222**, 1800-1805.