Supplementary information

Supercapacitive properties of amorphous MoS$_3$ and crystalline MoS$_2$ nanosheets in organic electrolyte

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S1. Experimental section

S1.1 Materials

Ammonium molybdate tetra hydrate \((\text{NH}_4)_2\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}\), ammonium sulfide \((\text{NH}_4)_2\text{S}\), and acetonitrile (AN), were purchased from Dae Jung Chemicals, South Korea. The electrolyte tetraethylammonium tetrafluoroborate (TEABF\(_4\)) was purchased from Alfa-Aesar chemicals, South Korea.

S1.2 Preparation of ammonium tetrathiomolybdate \((\text{NH}_4)_2\text{MoS}_4\) precursor

The ammonium tetrathiomolybdate powders were prepared by using ammonium molybdate tetra hydrate and ammonium sulfide as starting materials as reported elsewhere\(^1\). Briefly, 6.25 g of \((\text{NH}_4)_2\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}\) was added to 25 mL of distilled water following the addition of 7.5 mL ammonia and vigorously stirred using a magnetic stirrer. After that, 57 mL of \((\text{NH}_4)_2\text{S}\) solution was added into the above solution and the mechanical stirring process is continued for 30 min. Then, the entire solution was transferred into a water bath maintained at 80 \(^{\circ}\)C for 2 h. After completion of this process, it was cooled to room temperature and allowed crystallization process for 24 h. The resulting \((\text{NH}_4)_2\text{MoS}_4\) crystal was filtered, washed with distilled water, ethanol for several times and dried at room temperature for 12 h.

S1.3 Preparation of amorphous MoS\(_3\) and crystalline MoS\(_2\)

A facile one step thermal decomposition method was used to prepare amorphous MoS\(_3\) and crystalline MoS\(_2\) powders\(^1\)–\(^3\). Briefly, the \((\text{NH}_4)_2\text{MoS}_4\) crystal was treated in presence of N\(_2\) atmosphere at 200 and 600 \(^{\circ}\)C which results in the formation of MoS\(_3\), and MoS\(_2\), respectively.

S1.4 Instrumentation

A Rigaku X-ray diffractometer system with Cu K\(\alpha\) radiation (operated at 40 KeV and 40 mA) was employed to examine the phase purity and crystallinity of \((\text{NH}_4)_2\text{MoS}_4\), MoS\(_3\), and
MoS₂ powders. The Raman spectrum of (NH₄)₂MoS₄, MoS₃, and MoS₂ powders were obtained using a LabRam HR Evolution Raman spectrometer (Horiba Jobin-Yvon, France). The Raman system used an Ar⁺ ion laser operating at a power of 10 mW with an excitation wavelength of 514 nm; a 10 s data-point acquisition time was used to acquire the data. The surface morphology of the MoS₃ and MoS₂ powders were examined using a field emission-scanning electron microscopy (FE-SEM, JSM-6700F, JEOL Instruments) and high resolution transmission electron microscopy (HRTEM; Jem 2011, Jeol cop.) with CCD 4k x 4k camera (Ultra Scan 400SP, gatan cop.) The chemical state of elements present in the MoS₃, and MoS₂ powders was investigated using X-ray photoelectron spectroscopy (XPS) measurements using ESCA-2000, VG Microtech Ltd. A high-flux X-ray source at 1486.6 eV (aluminium anode) and 14 kV was used for X-ray generation, and a quartz crystal monochromator was used to focus and scan the X-ray beam on the sample surface. The N₂ adsorption-desorption isotherms of the (NH₄)₂MoS₄, MoS₃, and MoS₂ powders were measured at 77 K using a NOVA 2000 system (Quantachrome, USA) and the pore size distribution was calculated using Horvath-Kawazoe (HK) method.

**S1.5 Electrochemical characterization**

The working electrode was fabricated by grounding active material (MoS₃ or MoS₂), carbon black, and PVDF in the ratio (90:5:5) with appropriate amount of NMP (solvent) in an agate-mortar until a uniform slurry was obtained. Then, the slurry was spin coated on stainless substrates at a 200 rpm and dried at 80 °C for 12 h. The electroactive mass loading of the active material (MoS₃ or MoS₂) coated on to the stainless-current collector was measured as 0.5 mg, as calculated from the difference between the mass of the current collector before and after coating of the active material using Dual-range Semi-micro Balance (AUW-220D, SHIMADZU) with an approximation of five-decimal points. The SSC device was fabricated in coin-cell (CR2032)
configuration using active material (MoS\textsubscript{3} or MoS\textsubscript{2}) coated stainless steel current collectors as electrodes separated by Celgard membrane and 0.5 M TEABF\textsubscript{4}/AN as electrolyte. The fabricated SSC device was crimped using Electric Coin Cell Crimping and Disassembling Machine (MTI Korea). The handling of electrolyte and fabrication of coin cell were carried out inside a glove box with less than 1 ppm of moisture and oxygen. The electrochemical measurements such as cyclic voltammetry (CV) at different scan rates, electrochemical impedance spectroscopy (EIS) analysis (in the frequency range 0.01 Hz to 100 kHz, at amplitude of 10 mV) and galvanostatic charge–discharge (CD) measurements at different current ranges for the fabricated SSC device were performed using Autolab PGSTAT302N electrochemical workstation.

S1.6 Electrochemical analysis

**Determination of specific capacity from CV profiles:**

The specific capacity of the MoS\textsubscript{3} and/or MoS\textsubscript{2} SSC device is calculated from the CV analysis using the relation\textsuperscript{4}:

\[
C = \left[ \int \frac{I \, dV}{(s \times M)} \right] \quad \text{.......................... (1)}
\]

Here “C” is the specific gravimetric capacity (mAh g\textsuperscript{-1}), “I” is the current (A), “s” is the scan rate (mV s\textsuperscript{-1}), and “M” is the mass of the electrode (g).

**Determination of specific capacity from CD profiles:**

The specific capacity of the MoS\textsubscript{3} and/or MoS\textsubscript{2} SSC device was calculated from the CD profiles using the relation\textsuperscript{4}:

\[
C = \frac{I \times T_d}{(M \times 3.6)} \quad \text{.......... (2)}
\]

Here “C” is the specific gravimetric capacity (mAh g\textsuperscript{-1}), “I” is the discharge current, “\(T_d\)” is the time required for discharge, “M” is the mass loading of the electroactive material, and “\(\Delta V\)” is the potential window.
**Determination of Energy and power density:**

The energy and power density of the MoS$_3$ and/or MoS$_2$ SSC device are calculated in terms of using the relations given below$^{4,5}$:

\[
E = \frac{\int V(t) \, dt}{M \times 3.6} \quad \text{..................(3)}
\]

\[
P = \frac{E}{T_d} \quad \text{..................(4)}
\]

Here “$E$” and “$P$” are the energy and power density of the device, “$\Delta V$” is the potential window, and “$T_d$” is the discharge time.

**Determination of specific capacitance from EIS analysis:**

The specific capacitance of MoS$_3$ and/or MoS$_2$ SSC device with respect to applied frequency obtained from the EIS analysis using the relation$^6$:

\[
C = \frac{1}{2\pi f z''} \quad \text{..................(5)}
\]

Here “$C$” is the specific capacitance of the device, and “$f$” is the applied frequency, and “$z''$” is the imaginary part of impedance.

**Determination of maximal power density from EIS analysis:**

The maximal power density of MoS$_3$ and/or MoS$_2$ SSC device was obtained from the EIS analysis using the relation$^7$:

\[
P = \frac{V^2}{4ESR} \quad \text{..................(6)}
\]

Here “$V$” is the voltage window of the device, and “ESR” is the equivalent series resistance of the device.
Figure S1. FE-SEM micrographs of MoS$_3$ obtained at different magnifications.
Figure S2. FE-SEM micrographs of MoS<sub>2</sub> obtained at different magnifications.
Figure S3. X-ray photoelectron survey spectrum of MoS₃ and MoS₂ sheets.
Figure S4. (A) N$_2$ adsorption–desorption isotherm and (B) pore size distribution of the (NH$_4$)$_2$MoS$_4$, MoS$_3$ and MoS$_2$. 
Figure S5. Effect of voltage window on the specific capacity of MoS$_3$ and MoS$_2$ SSC device measured in between the regime of -3 to +3 V.
Figure S6. Effect of voltage window on the specific capacity of MoS$_3$ and MoS$_2$ SSC device measured in between the regime of 0 to +3 V.
Figure S7. Cyclic stability analysis of MoS$_3$ and MoS$_2$ SSC device over 2000 cycles obtained using a current range of 1 and 2.5 mA, respectively. It shows that MoS$_2$ SSC devices higher capacitance retention of about 90 % of its initial capacitance whereas MoS$_3$ SSC device holds only 79.66 % of its initial capacitance after 2000 cycles.
Table S1: Comparative performance metrics of MoS$_2$ and MoS$_3$ SSC with recently reported MoS$_2$ and other TMCs based SSCs

<table>
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<tr>
<th>S.No.</th>
<th>Electrode material</th>
<th>Energy density (Wh kg$^{-1}$)</th>
<th>Power density (W kg$^{-1}$)</th>
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<td>R1</td>
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<td>Ti$_2$CT$_x$ Mxene</td>
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References:


