

Metallic 1T phase MoS₂ nanosheets as supercapacitor electrode materials

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Materials and Methods

Chemicals and Reagents

MoS₂ bulk powder was purchased from Alfa Aesar. n-butyllithium (1.6 M in hexane), sulfuric acid (98%) was purchased from Sigma Aldrich. Sodium sulfate (99.0 %), potassium sulfate (99.0 %), lithium sulfate (99.0 %), and sulfuric acid (95-98 %), dried acetonitrile (AC), N,N,N,N-tetraethylammonium tetrafluoroborate (TEA BF₄) and 1-Ethyl-3-methylimidazolium tetrafluoroborate (EMIM BF₄) were obtained from Sigma Aldrich and used as received. Potassium chloride (99.0 %) and potassium bromide (IR grade) were purchased from Spectrum and Fluka respectively.

Experimental

Chemical exfoliation of MoS₂

Chemically exfoliated MoS₂ synthesized by lithium intercalation into bulk MoS₂ powder as reported previously ¹. Namely 3 mL butyl-Lithium (Sigma Aldrich, **Caution:** n-butyllithium is highly pyrophoric!) were added on 0.3 g of bulk MoS₂ powder under argon and heated up at reflux under argon for 48 h. The mixture was then filtered and washed with hexane (5 x 25 mL) to remove the excess of butyllithium.

The intercalated powder was then exfoliated in water at 1.5 mg/mL, sonicated for 1 h and centrifuged to remove lithium cations as well as the non-exfoliated materials.

Fabrication of chemically exfoliated 1T phase MoS₂ electrodes

The suspended chemically exfoliated single layer MoS₂ nanosheets were filtered over nitrocellulose membranes (25 nm-diameter pore size) and then transferred on 100 nm gold

coated substrate (quartz or 125 μm polyimide). The membrane was finally dissolved by using acetone. The thickness of the restacked 1T MoS₂ film was varied from 1 μm to 5 μm depending on the volume of the MoS₂ solution filtered.

Fabrication of chemically exfoliated 2H phase MoS₂ electrodes

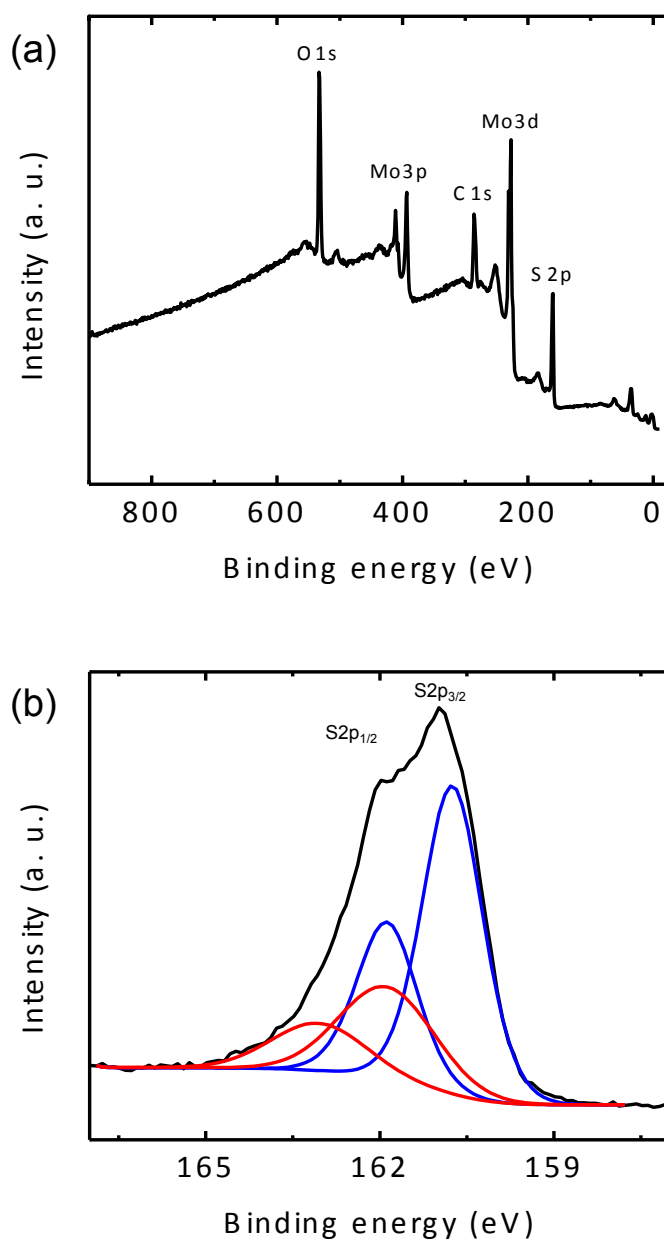
The 2H phase of MoS₂ can be restored by annealing the as-exfoliated 1T MoS₂ electrode at 300°C. 1T MoS₂ electrodes were placed in quartz tube and the atmosphere was evacuated for 15 min. The electrodes were then annealed at 300 °C for 15 min under Argon with a 80 sccm flow of argon.

Physical characterization

Scanning electron microscope (SEM) imaging was performed using a Zeiss Sigma Field Emission SEM with Oxford INCA PentaFETx3 EDS system (Model 8100). High Angle Annular Dark Field Scanning Transmission Electron Microscope (HAADF STEM) images were obtained using JOEL JEM-2100F TEM/STEM with double spherical aberration (Cs) correctors (CEOS GmbH, Heidelberg, Germany) at an acceleration voltage of 120 kV. The collecting angle was between 100 and 267 mrad. X-ray photoelectron spectroscopy (XPS) measurements were performed with a Thermo Scientific K-Alpha spectrometer. All spectra were taken using an Al K α microfocused monochromatized source (1486.7 eV) with a resolution of 0.6 eV and a spot size of 400 μm . Raman spectra were obtained using a Renishaw inVia system operating at 514 nm (2.41 eV). X-ray diffraction (XRD) experiments were carried out using a X-ray diffractometer from PANAnalytical (model PW3040/60) using a Cu K α radiation source ($\lambda = 1.5418\text{\AA}$).

X-ray photoelectron spectroscopy

Similarly to the XPS Mo3d region shown in Fig. 1h, the S2p region of MoS₂ can be decomposed with components from the 1T and 2H phases. The signals coming from the 1T phase are found down-shifted by ~ 0.9 eV (Supplementary Figure 1b).

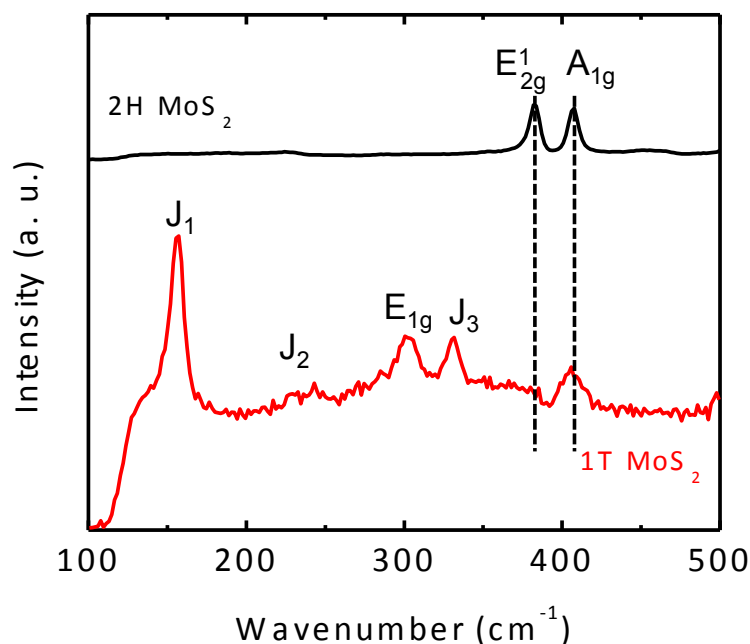


Supplementary Figure 1: (a) Survey spectrum for as-exfoliated 1T MoS₂. (b) High-

resolution x-ray photoelectron spectrum from the S2p region of as-exfoliated 1T MoS₂.

Raman spectroscopy

2H MoS₂ have two main Raman modes, the in-plane mode: E_{2G}^1 and the out-of-plane mode: A_{1G} . Several additional signatures appear in the case of single layer 1T MoS₂ labeled as J₁, J₂ and J₃ peaks at 156 cm⁻¹, 226 cm⁻¹ and 333 cm⁻¹ (Supplementary Figure 2)^{2,3}.

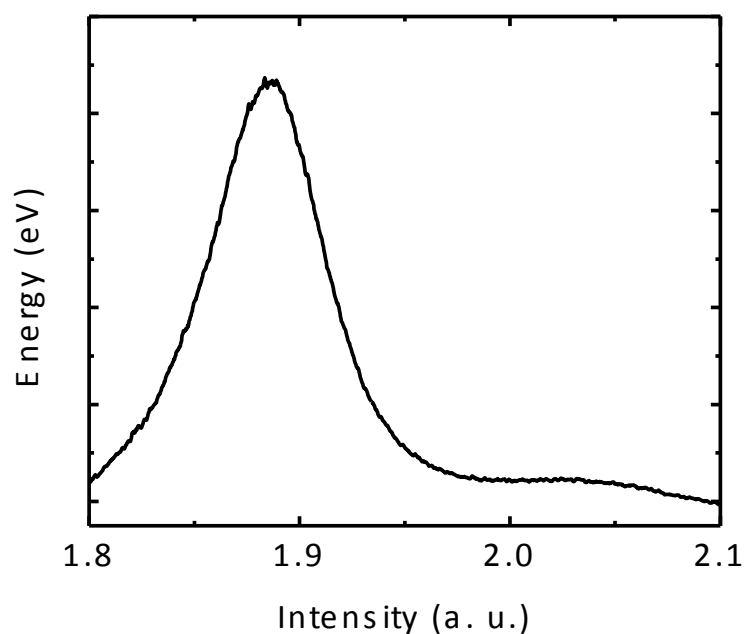


Supplementary Figure 2. Raman spectra of chemically exfoliated 1T MoS₂ compared to 2H MoS₂.

Photoluminescence of Chemically Exfoliated MoS₂

Single layer 2H MoS₂ is a direct band gap semiconductor emitting a photoluminescence response at ~ 1.9 eV. Ultra-thin film of chemically exfoliated MoS₂ nanosheets were deposited on SiO₂ via vacuum filtration¹. After annealing at 300°C under

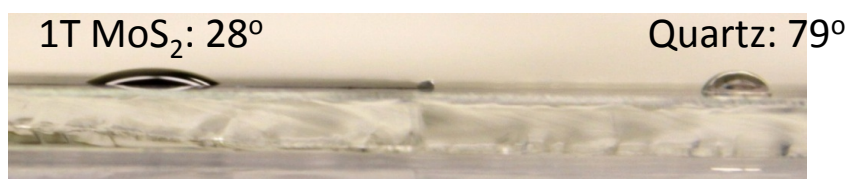
inert atmosphere, we detected photoluminescence response at ~ 1.9 eV confirming the single-layer nature of the MoS₂ nanosheets used in this study to fabricate the electrodes (Supplementary Figure 3).



Supplementary Figure 3. Photoluminescence spectra of single-layer chemically exfoliated MoS₂ for an excitation energy of 2.41 eV.

Contact angle measurements of 1T MoS₂

We measured the contact angle by drop casting a droplet of water (5 μ L) on the 1T MoS₂ film and measuring the angle between the droplet and MoS₂. We obtained a contact angle of 28°, much lower than quartz (79°) indicating the high hydrophilic nature of 1T MoS₂ (Supplementary Figure 4).



Supplementary Figure 4. Static contact angle images of 1T MoS₂ film compare to quartz.

Electrochemical measurements in aqueous electrolytes

Electrochemical measurements were conducted using a Solartron Multistat 1480 and Solartron 1255 FRA potentiostats. Electrochemical tests were performed with three-electrode cell configuration using 0.5 M H₂SO₄, Li₂SO₄, Na₂SO₄, K₂SO₄, KCl or KBr as electrolyte solutions. Saturated calomel electrode and platinum electrode were used as reference and counter electrode respectively. Alternatively a graphite rod was used as counter electrode in H₂SO₄. Cyclic voltammetry data were collected in between -0.15 V and 0.85 V vs. NHE with scan rates ranging from 5 mV/s up to 1000 mV/s. For a fair comparison of their electrochemical behavior, working electrodes were prepared with the same thickness of MoS₂ and their masses were normalized with the electrode surface. Operational potential ranges were chosen to avoid hydrogen evolution (HER) at low potentials and the oxidation of MoS₂ at high potentials.

Electrochemical measurements in organic electrolytes

The measurements in organic electrolytes were performed using a two-electrode configuration. Organic electrolytes were prepared using 1M TEA BF₄ or EMIM BF₄ dissolved in acetonitrile (AC) and potential windows of 3V and 3.5V were applied. The device fabrication and the measurements were conducted in an Argon-filled glove box.

Calculation of gravimetric and volumetric capacitances of electrode

Gravimetric and volumetric capacitances were calculated from cyclic voltammetry and galvanostatic charging discharging plots using the following formula:

$$C_g = \frac{\int IdV}{vmV} \quad (1)$$

$$C_g = \frac{I \times t}{m \times V} \quad (2)$$

$$C_v = C_g \times \rho \quad (3)$$

using C_g : gravimetric capacitance (F/g), C_v : Volumetric capacitance (F/cm³), I : current (A), v : scan rate (V/s), m : mass (g), V : potential range, t : discharging time and ρ (g/cm³): density of restacked MoS₂.

The density (g/cm³) of restacked MoS₂ was calculated using the weight of the electrode and the volume of the MoS₂ films.

The energy density and power density of the supercapacitors were calculated according to the following equations:

$$E(Wh/g) = \frac{0.5C_T \Delta V^2}{3600}$$

$$E_v(Wh/cm^3) = E \times \rho$$

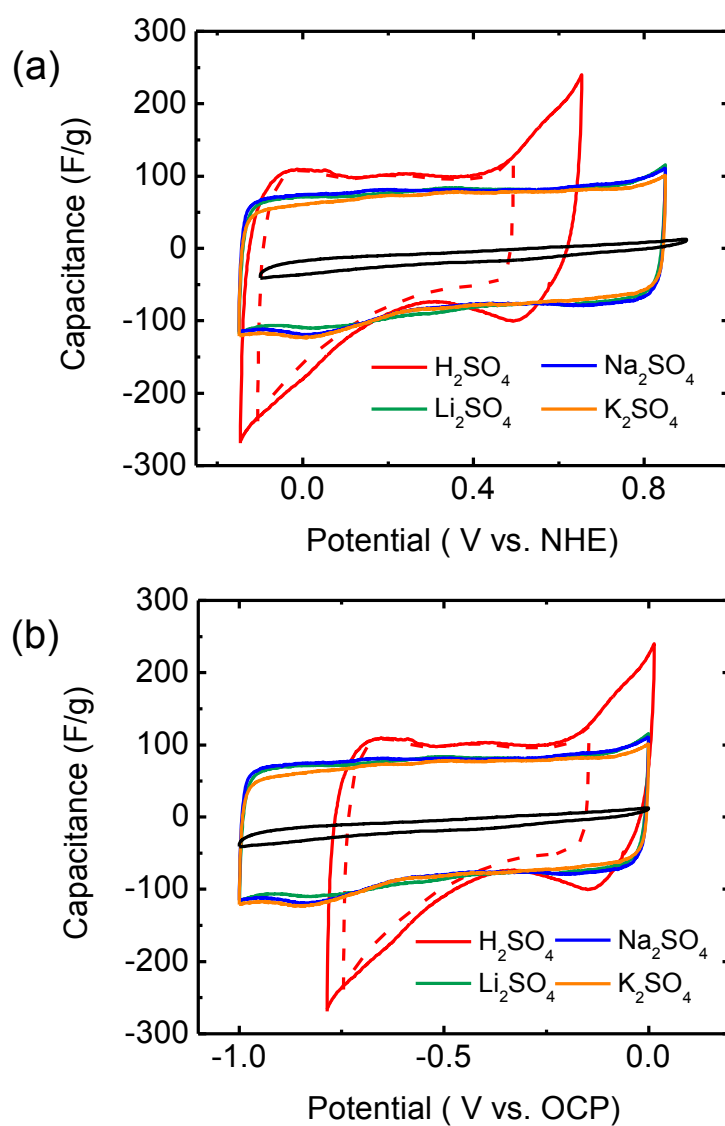
$$P(W/g) = \frac{E \times 3600}{t_{discharge}}$$

$$P_v(W/cm^3) = P \times \rho$$

where C_T is the total capacitance of the two-electrode cell, ΔV is the effective potential range during discharging process, $t_{discharge}$ is the discharging time (s), ρ is the density of the electrode, E is the energy density and P is the power density.

Cyclic voltammograms of 1T MoS₂ with potentials against OCP

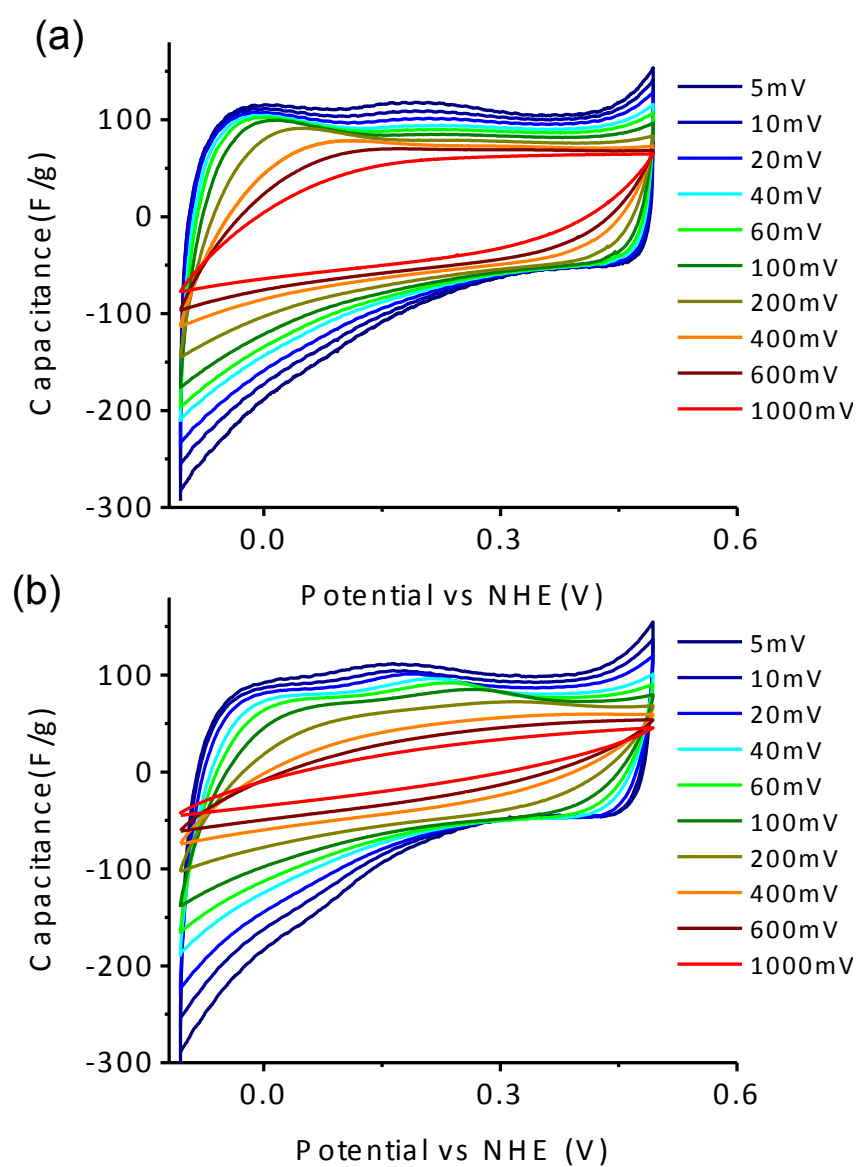
In order to compare the electrochemical behavior of 1T MoS₂ in different electrolytes, potential values with respect to NHE (Normal Hydrogen Electrode) or OCP (Open Circuit Potential) are provided (Supplementary Figure 5).



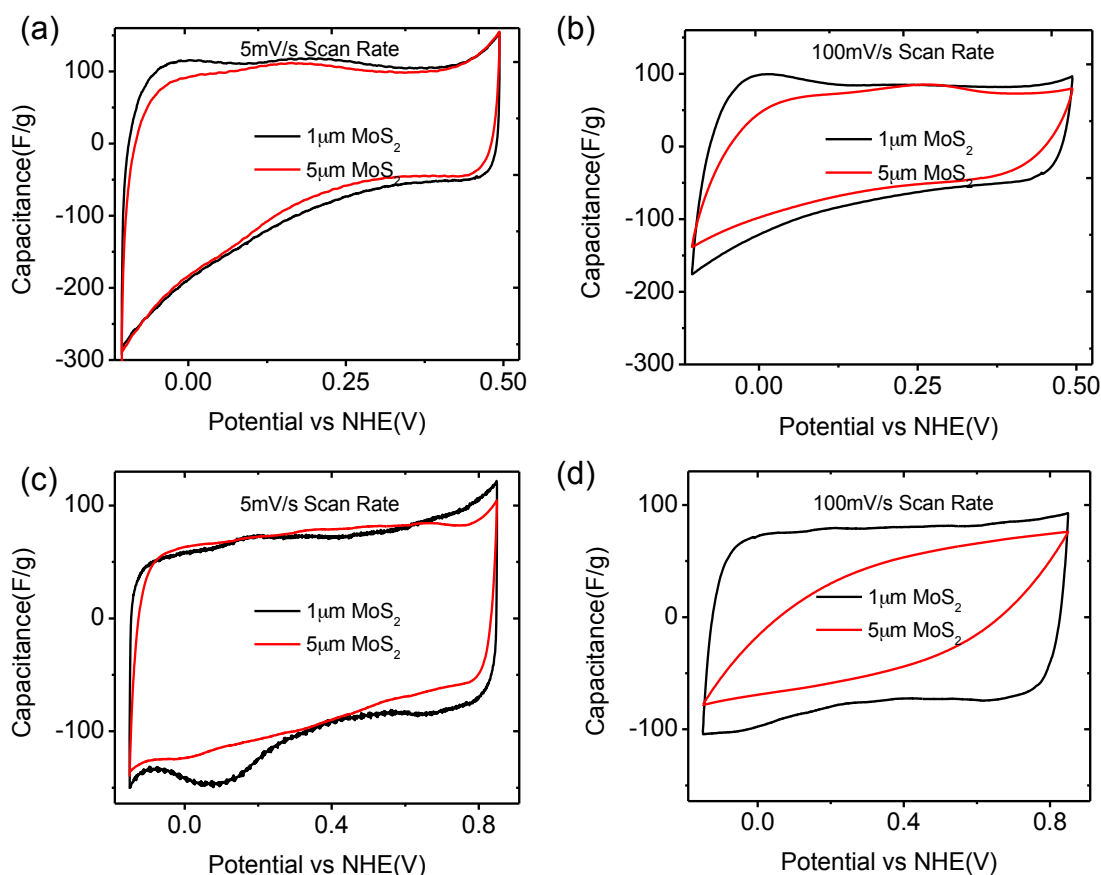
Supplementary Figure 5. Cyclic voltammograms of 1T MoS₂ electrodes with potentials against NHE (a) and OCP (b).

Thickness effect

1T MoS₂ offers high capacitance values even for thick-film electrodes with density over 2.5mg/cm² (equivalent to a thickness of 5μm) (Supplementary Figure 6). The pathway for ions in the layered structure increases with the thickness. Since Li⁺ ions are bigger, the thickness induces a reduction of the capacitance at high scan rates compare to the case of protons (Supplementary Figure 7).



Supplementary Figure 6. Cyclic voltammograms of 1 μm (a) and 5 μm (b) 1T MoS_2 in H_2SO_4 from 5 mV/s to 1000 mV/s.

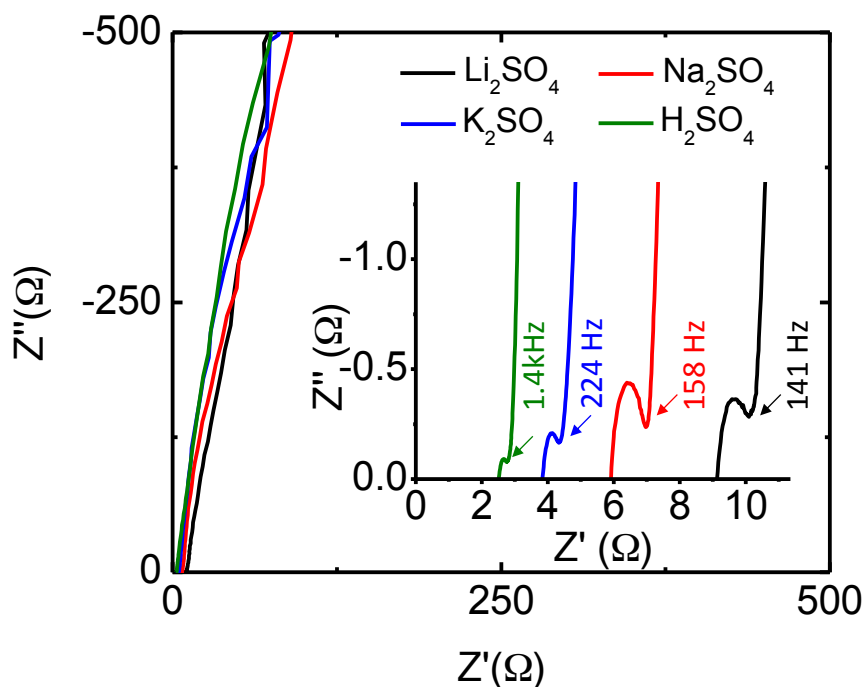


Supplementary Figure 7. Thickness effect on the capacitance of 1T MoS_2 at 5mV/s scan rate (left) and 100mV/s scan rate (right) in H_2SO_4 (a,b) and in Li_2SO_4 (c,d).

Electrochemical impedance spectroscopy (EIS)

Nyquist plots were obtained with 10 mV amplitude between 10 mHz and 100 kHz at a fixed potential of 0.35 V vs. NHE for each electrolyte. The curves show near-ideal behavior (Supplementary Figure 8). They also indicate that the impedance of the system depends on the type of electrolyte exhibiting semi circles at high frequencies and linear behavior at lower

frequencies⁴. The semicircles correspond to parallel combination of charge transfer resistance and double layer capacitance.



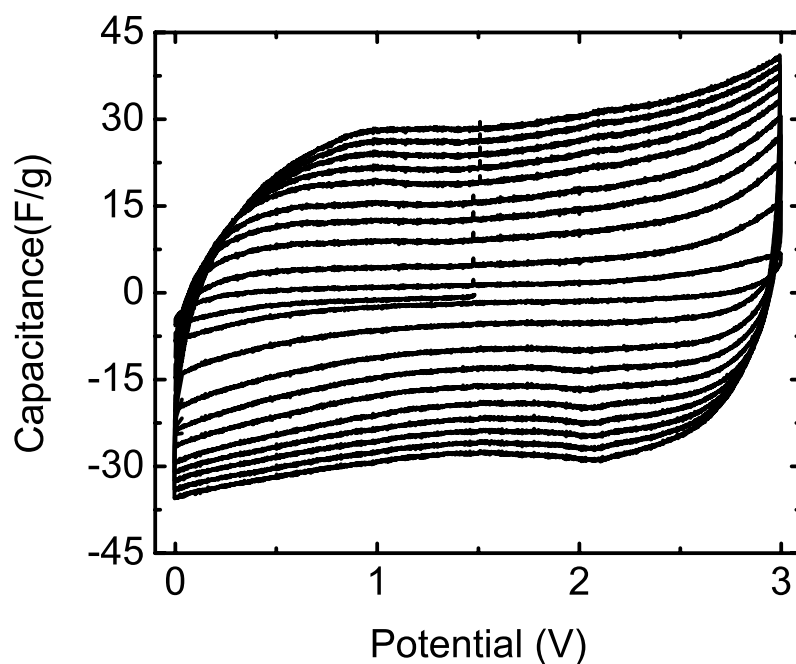
Supplementary Figure 8. Nyquist plot of 1T MoS₂ electrode in 0.5 M H₂SO₄, K₂SO₄, Na₂SO₄ and Li₂SO₄ electrolyte solution.

Electrochemical behavior of 1T phase MoS₂ in organic electrolytes

In order to expand the operating potential window, organic electrolytes were used. Supercapacitor devices contain two electrodes sandwiched with a porous separator. For a more accurate estimation of the 1T MoS₂ performance, the two-electrode configuration was used in this part.

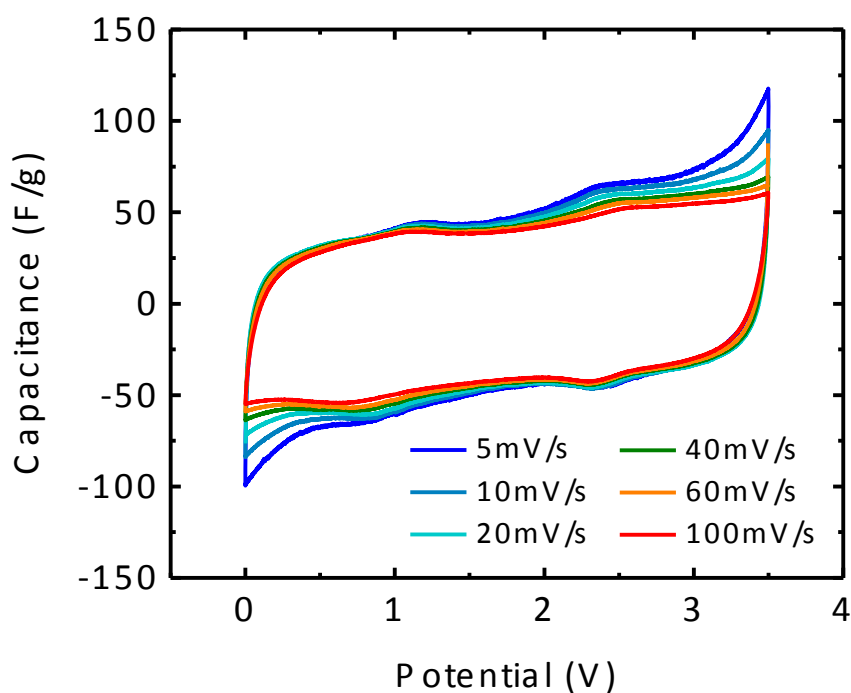
Initially the charge storage behavior of 1T MoS₂ is very limited in organic electrolytes, but it increases gradually (Supplementary Figure 9). During cyclic measurements, the electrolyte intercalates deeper into the electrode and the accessible surface area increases giving higher capacitance values. Unlike aqueous electrolyte, the intercalation processes slowly. Since 1T

MoS₂ is hydrophilic and the organic electrolytes are more hydrophobic, the intercalation process is diffusion limited. As shown in Supplementary Figure 9, initial capacitance is as low as 1F/g but after 50 cycles expansion saturates.



Supplementary Figure 9. CV curves of 1T MoS₂ electrodes in TEA BF₄/AC at 100 mV/s obtained from the first 50 cycles showing the broadening of the CV response during the initial cycles.

CV curves in EMIM BF₄ are presented in Supplementary Figure 10. Quasi-rectangular shapes are obtained in both organic electrolytes (Figure 4 and Supplementary Figure 10) even at scan rates of 100 mV/s.



Supplementary Figure 10. CV curves of 1T MoS₂ in 1M EMIM BF₄ in acetonitrile.

References

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2. Jiménez Sandoval, S., Yang, D., Frindt, R. & Irwin, J. Raman study and lattice dynamics of single molecular layers of MoS₂. *Phys. Rev. B* **44**, 3955–3962 (1991).
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4. Qu, Q. *et al.* Electrochemical Performance of MnO₂ Nanorods in Neutral Aqueous Electrolytes as a Cathode for Asymmetric Supercapacitors. *J. Phys. Chem. C* **113**, 14020–14027 (2009).