

# Intrinsic Capacitance and Charge Storage Behaviour of Molybdenum Disulphide Nanosheets

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## Introduction

Supercapacitors are energy storage devices with high power density, capable of fast and efficient charging.  $\text{MoS}_2$  is a compelling material for use in supercapacitor electrodes due to its high surface area and density. Despite this, little is known about how charge is stored and how much charge can be stored on  $\text{MoS}_2$  nanosheets. We deposit monolayers of  $\text{MoS}_2$  onto atomically flat graphite single crystals, and then analyze their electrochemical behaviour. From this data, we obtain the potential dependent behaviour, the intrinsic capacitance, restacking behaviour, and capacitance limits for different polytypes of  $\text{MoS}_2$ .



## Methodology

### Film Formation

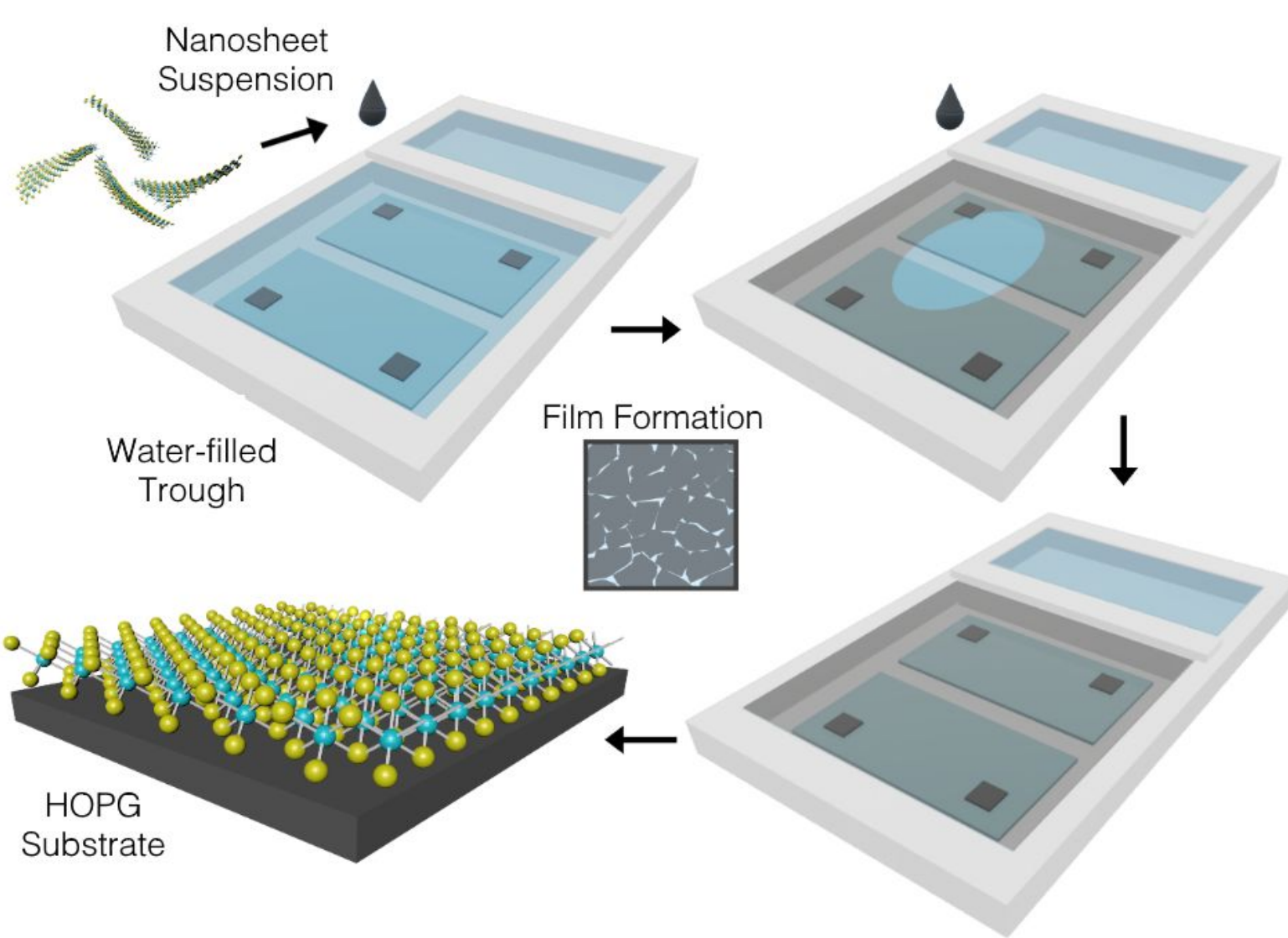


Figure 1. Illustration of modified Langmuir-Blodgett deposition method

### Characterization

- Electrostatic impedance spectrometry (EIS) in a custom-made, spring loaded three electrode electrochemical cell (Fig. 2)
- Measurements were taken in both aqueous (1M NaF) and organic (0.1 M TEABF<sub>4</sub> in acetonitrile) electrolyte.

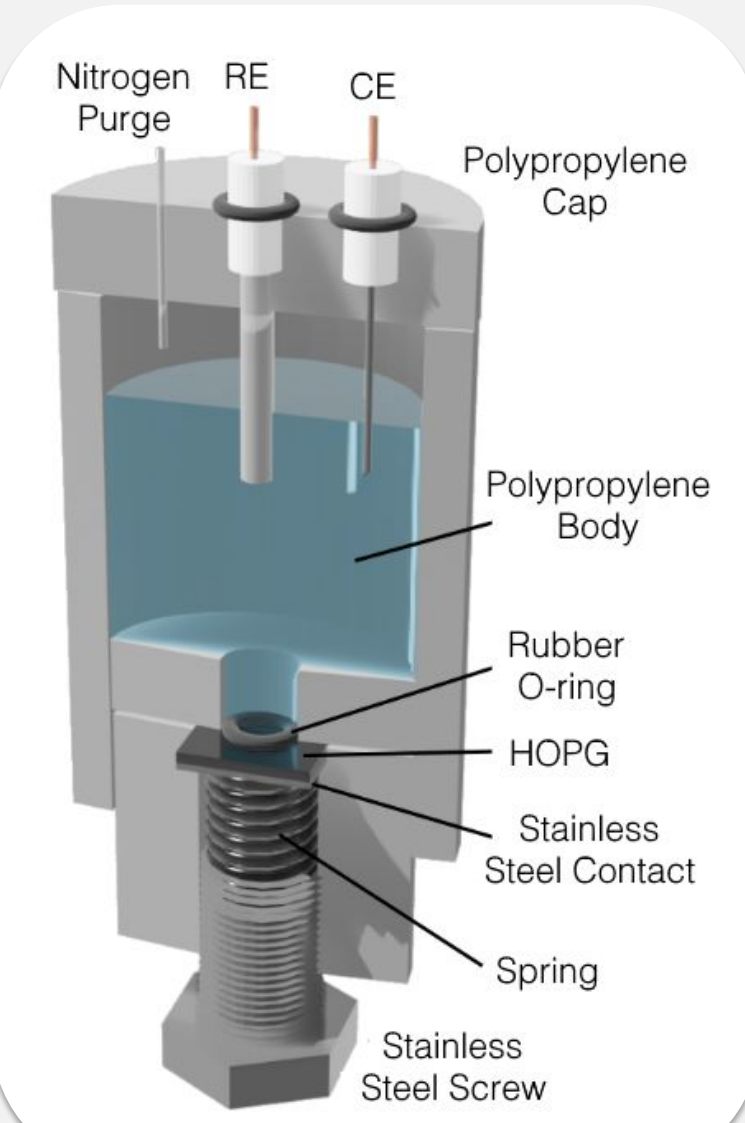


Figure 2. Diagram of electrochemical cell



## Results

### Film Characterization

For  $\text{MoS}_2$  and rGO, 97.8% and 92.2% surface coverage was obtained, respectively. (Fig. 3a, 3b) UV-Vis spectroscopy showed a layer dependent reduction in transmittance at 550 nm for multilayer films that agreed with literature values (Fig. 3c).

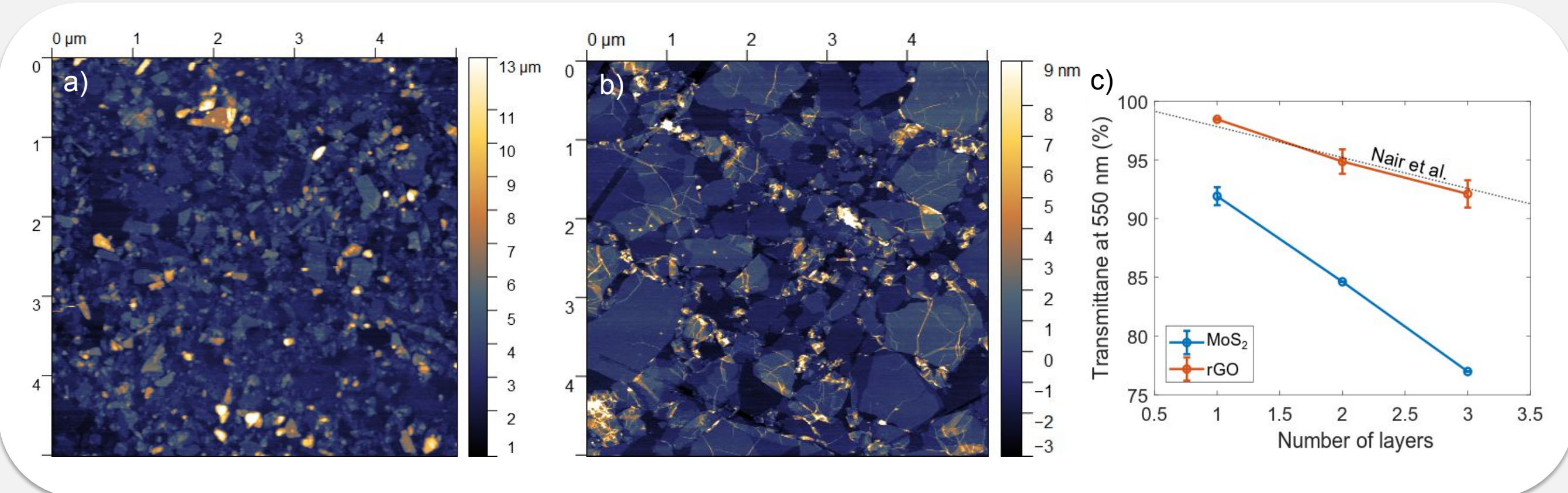


Figure 3. AFM images of a) rGO and b)  $\text{MoS}_2$  films on HOPG substrates and c) UV-Vis transmittance at 550 nm of  $\text{MoS}_2$  and rGO films as a function of coating layers

### Electrochemical Characterization

EIS showed a complex voltage dependent capacitance behaviour. At negative potentials, there is a six fold difference in capacitance between 1T  $\text{MoS}_2$  and 2H  $\text{MoS}_2$  in aqueous electrolyte (Fig. 4a). At positive potentials, there is comparatively little voltage dependence.

Fig. 4b demonstrates how the capacitance of films increases almost linearly with layer over nearly the entire potential range while Fig. 4c illustrates how the restacking of  $\text{MoS}_2$  still allows for ion intercalation between the nanosheets, resulting in layer-dependent capacitance behaviour.

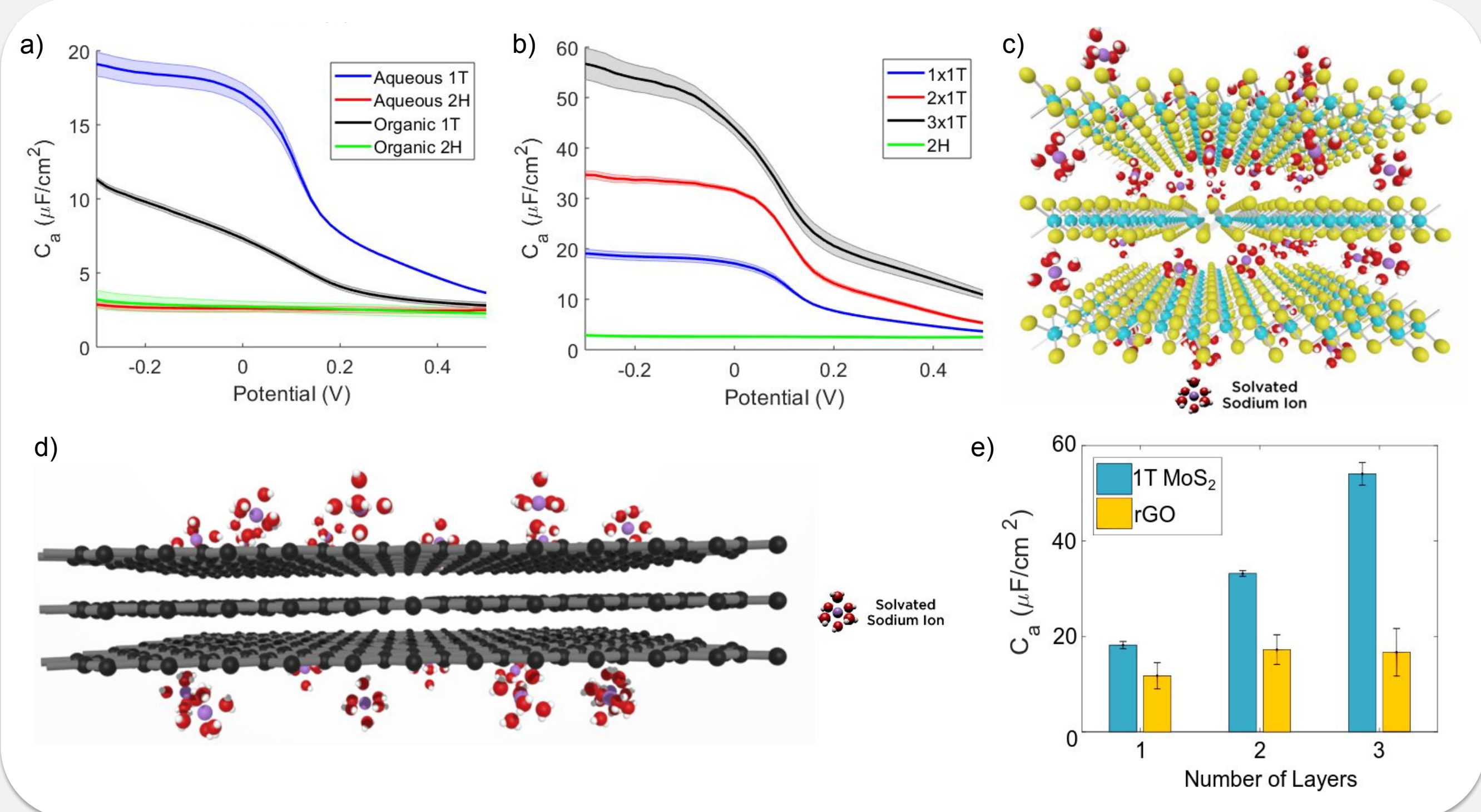


Figure 4. a) Areal capacitance of 1T and 2H  $\text{MoS}_2$  monolayer films in aqueous and organic electrodes as a function of potential, b) areal capacitance of multilayer  $\text{MoS}_2$  films as a function of potential, and c) schematic diagram of  $\text{MoS}_2$  restacking behaviour. d) Schematic diagram of rGO restacking behaviour and e) comparison of areal capacitance as a function of layer number for 1T  $\text{MoS}_2$  and rGO in aqueous electrolyte.

Conversely, Fig. 4d illustrates how the restacking of rGO nanosheets prevents ion intercalation. This is in contrast to the behaviour of multilayer  $\text{MoS}_2$  electrodes, which show continuous increase in capacitance with layer number, as seen in Figure 4e.

### Intrinsic Capacitance and Theoretical Capacitance Limits

From these measurements, we can obtain a value for the intrinsic capacitance ( $C_s$ ), an area-specific, material specific value which allows for the direct comparison of supercapacitor materials. The measured values for intrinsic capacitance were then compared to what was expected from theory (Table 1).

From the measured values for intrinsic capacitance, we can obtain theoretical gravimetric ( $C_g$ ) and volumetric capacitance ( $C_v$ ) limits for 1T and 2H  $\text{MoS}_2$  in aqueous and organic electrolyte (Table 2).

Table 1. Comparison between measured and calculated  $C_s$  for single, double, and triple layer 1T  $\text{MoS}_2$  and monolayer 2H  $\text{MoS}_2$  monolayers in aqueous and organic electrolyte in  $\mu\text{F}/\text{cm}^2$

	Aqueous		Organic	
	Measured	Calculated	Measured	Calculated
1x1T	14.90	13.41	6.55	8.14
2x1T	27.85	25.31	18.05	14.78
3x1T	45.95	37.22	28.25	21.42
2H	0.49	2.04	1.32	2.02

Table 2. Theoretical  $C_g$  (F/g) and  $C_v$  (F/cm<sup>3</sup>) for 1T and 2H  $\text{MoS}_2$  in aqueous and organic electrolyte

	Aqueous		Organic	
	$C_g$	$C_v$	$C_g$	$C_v$
1T	94.70	479.18	41.66	210.79
2H	3.08	15.61	8.36	42.32



## Conclusions

- We measured, for the first time, the intrinsic capacitance of 1T and 2H  $\text{MoS}_2$ . We observe capacitance values as high as  $13 \mu\text{F}/\text{cm}^2$  for 1T  $\text{MoS}_2$  while 2H  $\text{MoS}_2$  can only reach  $2 \mu\text{F}/\text{cm}^2$  in aqueous electrolyte. We show a complex voltage dependence that suggests higher capacitance at negative potentials.
- The capacitance of multilayer  $\text{MoS}_2$  films added together as if they were individual nanosheets, suggesting that  $\text{MoS}_2$  nanosheets restack in a way that doesn't reduce accessible surface area. This was in contrast to rGO nanosheets, which demonstrated layer-independent capacitance behaviour.
- Using measured values for intrinsic capacitance, we can extrapolate theoretical gravimetric and volumetric limits for supercapacitors comprised entirely of 1T  $\text{MoS}_2$ . The results suggest that these limits have already been reached, and introducing defects or other materials or incorporating  $\text{MoS}_2$  into the negative electrode of an asymmetric supercapacitor may be necessary to further improve  $\text{MoS}_2$  supercapacitors.



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### References

- (1) Kumar, K. S.; Choudhary, N.; Jung, Y.; Thomas, J. ACS Energy Lett. 2018, 3 (2), 482–495.
- (2) Theerthagiri, J.; Senthil, R. A.; Senthilkumar, B.; Reddy, P. U.; Madhavan, J.; Ashokkumar, M. J. Solid State Chem. 2017, 252 (May), 43–71.
- (3) Rao, C. N. R.; Gopalakrishnan, K.; Maitra, U. ACS Appl. Mater. Interfaces 2015, 7 (15), 7809–7832.
- (4) Conway, B. E. Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications; New York, 1999; Vol. 1.
- (5) Xu, L.; Tetreault, A. R.; Khaligh, H. H.; Goldthorpe, I. A.; Wettig, S. D.; Pope, M. A. Langmuir 2019.
- (6) Zhang, Y.; Xu, L.; Walker, W. R.; Tittle, C. M.; Backhouse, C. J.; Pope, M. A. J. Mater. Chem. C 2017, 5 (43), 11275–11287.
- (7) Acerce, M.; Voiry, D.; Chhowalla, M. Nat. Nanotechnol. 2015, 10 (4), 313–318.
- (8) Edo, G.; Yamaguchi, H.; Voiry, D.; Fujita, T.; Chen, M.; Chhowalla, M. Nano Lett. 2011.
- (9) Wypych, F.; Schöllhorn, R. J. Chem. Soc. Chem. Commun. 1992, No. 19, 1386–1388.
- (10) Edo, G.; Yamaguchi, H.; Voiry, D.; Fujita, T.; Chen, M.; Chhowalla, M. Nano Lett. 2011, 11 (12), 5111–5116.