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Size selection and thin-film assembly of MoS$_2$ elucidates thousandfold conductivity enhancement in few-layer nanosheet networks

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Printed electronics based on liquid-exfoliated nanosheet networks are limited by inter-nanosheet junctions and thick films which hinder field-effect gating. Here, few-layer molybdenum disulfide nanosheets are assembled by Langmuir deposition into thin films, and size selection is shown to lead to a thousandfold conductivity enhancement with potential applicability to all nanosheet networks.

Printed electronic devices such as thin-film transistors require solution-processable materials which are sufficiently thin to allow field-effect gating while retaining measurable device resistances. Liquid-exfoliated two-dimensional (2D) nanosheet networks have shown much promise for printed electronics but significant challenges remain for the development of practical devices based on networks of semiconducting nanosheet such as molybdenum disulfide (MoS$_2$). Firstly, network mobility and thereby conductivity are limited by inter-nanosheet junctions. Furthermore, random networks exhibit further-reduced conductivity below a critical thickness, meaning that thicker films are required to achieve measurable device resistances. Low mobilities and thick films have hampered efforts to realise field-effect gating of semiconducting nanosheet networks, with electrolyte gating required for practical devices. By contrast, electrochemical exfoliation of MoS$_2$ has been demonstrated to yield large few-layer nanosheets with improved junctions for high-performance field-effect transistors, albeit with compromising between performance, scalability and printability. In addition, this approach has enabled devices to be prepared from thin films assembled at liquid-liquid interfaces. It would therefore be desirable to realise such performance enhancements with scalable printable liquid-exfoliated nanosheets. To this end, this study explores size selection of liquid-exfoliated MoS$_2$ to assemble networks of few-layer nanosheets and utilises Langmuir deposition as a route to achieve thin dense-packed networks with potential for device applications.

Langmuir deposition is a film formation technique capable of assembling monolayers of particulates at the air-water interface. While this technique has been applied to a range of 2D nanosheets, its potential for pristine semiconducting thin films remains unexplored. This is likely because of the challenge of identifying appropriate solvents for exfoliation and deposition. As illustrated in Figure 1a, the need for low boiling point precludes prototypical exfoliating solvent N-methyl-2-pyrrolidone (NMP), while the need for surface energy and Hansen parameter matching for exfoliation precludes common Langmuir solvents such as chloroform. Based on these requirements and previous work on solvent spreading at the air-water interface, we have identified cyclopentanone (CPO) as an ideal solvent for exfoliation and Langmuir deposition of MoS$_2$. In practice, exfoliation in CPO by ultrasonication and size selection by centrifugation yields few-layer nanosheet dispersions with high concentration to facilitate Langmuir deposition.

As illustrated schematically in Figure 1b, these nanosheets can be assembled at the air-water interface to form floating films which can be compressed into dense-packed networks and deposited by horizontal Langmuir-Schaefer (L-S) deposition. Figure 1c shows a typical Langmuir film of MoS$_2$ with the green colouration highlighting the few-layer nature of the assembled nanosheets and the appreciable optical absorbance indicating that the films are formed of more than a single nanosheet’s thickness. This latter point is consistent with observation of islands of nanosheets forming during assembly, which is well-understood for hydrophobic materials. This film formation is also evident in the surface pressure-area isotherms shown in Figure 1d acquired during Langmuir assembly with sequential deposition and cycling of MoS$_2$, where surface pressure increases in response to the connectivity of the islands, shown in the inset micrographs. These films can be deposited onto sputtered gold electrodes on glass or, preferably, polyethylene terephthalate (PET) by horizontal L-S transfer to yield semi-transparent (T~40%) coatings over large areas, indicating an area-averaged thickness of <10 monolayers given the ~85% monolayer absorbance of MoS$_2$.

This semitransparency enables UV-visible extinction spectroscopy to be performed in transmission for direct comparison to their starting dispersions. To examine these changes as a function of MoS$_2$ nanosheet thickness, liquid cascade centrifugation was used to prepare size-selected samples with a range of average

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The extinction spectra for Langmuir films deposited from these dispersions are shown in Figure 1e, with the spectra for the dispersions in the supplementary information figure S3. Both the films and dispersion spectra show the expected blueshift of the A-exciton peak with decreasing layer number. Interestingly, the dispersions exhibit systematic peak shifts at longer wavelengths than those observed previously and, as a result, the films of the largest nanosheets exhibit a net blueshift relative to the starting dispersion as shown in Figure 1f. Since this would suggest unphysical reduction of layer number on deposition and nanosheets do not restack with the atomic registry required to modulate optical properties, these effects are attributed to solvatochromism of the excitonic peaks in the CPO dispersions which are eliminated to varying degrees in the deposited films. Indeed, ketone solvents are known to result in solvatochromic redshifts in the photoluminescence of single-flake MoS$_2$ of up to 16 meV. This corresponds to a factor of two increase in layer number using the established spectroscopic metrics and highlights the potential of solvatochromic effects to influence measurements of nanosheet properties (see Supplementary Information).

Having demonstrated that few-layer nanosheets can be assembled into dense-packed thin films, atomic force microscopy (AFM) was employed for direct measurement of morphology and film thickness. Figure 2a shows an AFM height image of a representative film edge with nanosheets forming a uniform film over tens of microns, despite local disorder typical of nanosheet networks. Figure 2b shows an AFM height image of a representative dense-packed region of the film where individual and overlapping nanosheets and the substrate can be resolved. Importantly, the film thickness is in the range 20-50 nm, as shown by the line sections in Figure 2c and 2d. This indicates that Langmuir deposition can indeed assemble dense-packed films of few-layer nanosheets with thicknesses which may be compatible with field-effect gating. Scanning electron microscopy (SEM), shown in Figure 2e, indicates the film uniformity over large length scales and suggests appreciable network conductivity.
Electrical properties of MoS$_2$ Langmuir films can be studied by measuring I-V characteristics such as that shown in Figure 2e. These I-V characteristics exhibit excellent Ohmic behaviour, with improved linearity even relative to previously-reported MoS$_2$ nanosheet networks with good Ohmic contacts.$^{24,25}$ This has been attributed to reduction in the Schottky barrier at the monolayers.

This suggests that some aspect of the particular processing employed improves charge transport in these films, which may enable subsequent applications in electronic devices.

It is therefore important to consider the processing and properties to those of previously-reported MoS$_2$ nanosheet networks. Figure 3a shows a plot of sheet resistance and thickness to allow comparison of both practical applicability and absolute conductivity, with the latter forming contours in the plot. Nanosheet networks from the literature were prepared by exfoliation in NMP and deposited variously by vacuum filtration$^{31}$, thick-film Langmuir-type assembly$^{26,27}$, or inkjet printing$^{28}$, yielding films with thicknesses between 100 nm and 2 µm and sheet resistances corresponding to conductivity clustered around 10$^{-6}$ S/m. By contrast, MoS$_2$ Langmuir films prepared by exfoliation in CPO have thicknesses as low as 20 nm and conductivity as high as 10$^{-3}$ S/m. While this discrepancy could be attributed to the different solvent and/or deposition process, additional few-layer dispersions were prepared using the same conditions in NMP and aqueous Triton X-100 and films prepared by vacuum filtration and spray deposition respectively. As shown in Figure 3a, these samples are consistent with the increased conductivity of the CPO-exfoliated MoS$_2$ Langmuir films, suggesting the enhancement to be the result of a general and transferable modification of MoS$_2$ nanosheets or networks or both.

As such, the outstanding difference between the nanosheet networks previously reported ($\sim$10$^{-6}$ S/m) and those reported here ($\sim$10$^{-3}$ S/m) is the size selection procedure. Previous studies either performed no size selection or preferentially removed smaller thinner nanosheets, variously to prevent negative photoconductivity$^{29,30}$ or charge traps due to band gap mismatch.$^{2}$ By contrast, this work has focused on small few-layer nanosheets to allow application of spectroscopic metrics and thin film formation. To investigate the effect of this size selection, a further centrifugation cascade was performed, exfoliating in surfactant solution to maximise yield and allow film formation from all fractions. Electrical conductivity as a function of nanosheet length is shown in Figure 3b, with network conductivity increasing from 10$^{-6}$ to 10$^{-3}$ S/m with decreasing nanosheet size, with the literature conductivities also described by this size dependence. This continuous scaling suggests the enhanced conductivity to be an emergent rather than anomalous effect which is predominantly dictated by nanosheet size and thickness.

These emergent effects can potentially be related to the structure and properties as nanosheet size and thickness is reduced. Small nanosheets inherently have an increased fraction of edge sites$^{31}$ which can comprise vacancies or functional groups. In MoS$_2$, in particular, sulfur vacancies are formed very readily$^{32,33}$ which can comprise vacancies or charge traps due to band gap mismatch$^{34}$ and contribute an increased density of dopant states and increase the carrier density of the network. Additionally, functionalisation at edge sites has the potential to modify properties through formation of oxides to which MoS$_2$ nanosheets are known to be susceptible, with improved hydrogen evolution catalysis with both increasing oxide content$^{35}$ and decreasing nanosheet size$^{36}$, potentially related through an underlying conductivity increase. While MoS$_2$ can be easily oxidised to conductive MoO$_x$, subsequent oxidation to insulating MoO$_3$ and the absence of strong oxide peaks in
the Raman suggest there is limited influence of edge functionalisation on the overall nanosheet properties. Furthermore, any doping of the nanosheets could only increase the network conductivity by a corresponding factor, suggesting increases in carrier density alone would be insufficient to account for the thousandfold conductivity increase. It is therefore likely that network mobility, understood to be dictated by transport-limiting junctions and network structure, is also significantly increased with decreasing nanosheet size. This is consistent with recent work which has observed increased conductivity for smaller nanosheets of other materials,8,9, suggesting this may be a general phenomenon likely related to modification of network structure and junction resistance for thinner, more flexible nanosheets.

Conclusions
Exfoliation and size selection of MoS₂ in CPO yields few-layer nanosheets which facilitate interfacial Langmuir film formation. These thin films exhibit conductivities of ~10⁻³ S/m, a thousandfold enhancement over MoS₂ nanosheet networks reported in the literature. By extending to other exfoliating solvents and deposition techniques, this enhancement is attributed to the size selection of few-layer small nanosheets with attributed reduction junction resistance and potentially enhanced network mobility. This highlights the potential of size selection and Langmuir deposition to improve transport properties and reduce film thickness for printed electronic devices.

Author Contributions
The study was devised by SPO and ABD. Experimental work was performed by SPO, MJL, HJW, AAG, FL, JPS and AAKK. SPO wrote the manuscript with assistance from MJL and ABD.

Conflicts of interest
There are no conflicts to declare.

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