# Supporting Information

# Highly Concentrated and Stabilizer-free Transition Metal Dichalcogenide Dispersions in Low Boiling Point Solvent for Flexible Electronics

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# S1. Liquid phase exfoliation

# S1.1 Synthesis of dispersions

The bulk MoS<sub>2</sub> precursor (Alfa Aesar, 99%, 325 mesh) is subjected to bath sonication in 2butanone (Finar, 99%) (used without any further purification) contained in a 250 ml volumetric flask in an Elmasonic TI-H 5 bath sonicator. This process of obtaining dispersions by sonication has been found to be influenced by many parameters, which also impact the reproducibility of the process. Thus, in order to obtain results with repeatability and higher degree of control on the process, the exfoliation was carried out under identical conditionsvessel dimensions, positioning in the bath, sonication frequency and power, etc. All the dispersions produced in this study are obtained by sonicating at 45 kHz (100 W). As dispersability drops with increased temperatures,[1] added to which is the low boiling point of 2-butanone, a simple circulation setup from an ice cold water reservoir helped circumvent these issues. For the other TMDC, the bulk powders of WS<sub>2</sub> (Sigma Aldrich, 99%), MoSe<sub>2</sub> (Sigma Aldrich, 99.9%) and WSe<sub>2</sub> (Alfa Aesar, 99.8%) were sonicated in 2-butanone for 24 hours, followed by resting for 12 hours to allow for sedimentation of unexfoliated precursor. S1.2 Determination of dispersed concentration and absorption coefficient

UV-Vis spectroscopy has proven instrumental in the quick characterization of the dispersions. The absorption spectrum is recorded with the dispersions in 1 cm quartz cuvettes using a Perkin-Elmer Lambda 750 UV-Vis spectrophotometer. As the concentration of the dispersions are high, samples have been diluted so as to obtain a spectrum discernible for analysis. The dilution factor has been considered while plotting. In order to determine the concentration of the dispersions, a known volume (5-8 ml) of the dispersion has been dispensed into a clean dry beaker and evaporated by placing on a hot plate at 80°C. This is followed by weighing the residue, which yields the concentration of dispersed MoS2. To determine the absorption coefficient of the MoS2 nanosheets, the concentration of the dispersions needs correlation with its absorption spectra. As shown by Coleman and co-workers, the extinction spectra obtained from UV-Visible spectroscopy comprises of absorption by the nanosheets, superposed on a power law scattering background.[2,3] This scattering component can lead to an erroneous determination of the absorption coefficient. This proves a challenge to the quick determination of concentration of dispersed material using Beer-Lamberts law,

#### A=eCl

Where A is the absorbance, C is the concentration and l is the cell path length. The extinction coefficient ( $\epsilon$ ) is the sum of the absorptive ( $\alpha$ ) and scattering ( $\sigma$ ) contributions from the nanosheets,

$$\varepsilon = \alpha + \sigma$$

To correlate gravimetry to spectroscopy, the extinction spectra of the dispersions has been taken after successive dilutions as shown in **Figure S1**(a). For determination of the absorption coefficient, the scattering component background in the extinction spectra has been neglected and only the absorption peak at about 660 nm is taken into consideration as shown in Figure S1(b).



Figure S1. Determination of the absorption coefficient of the MoS<sub>2</sub> nanosheets by gravimetry. The extinction spectra for MoS<sub>2</sub> after various dilutions have been shown in (a). The power law scattering contribution in the background can be neglected by considering only the absorption as in (b). The slope obtained in (c) yields the absorption coefficient of MoS<sub>2</sub>.

By these means, the value of  $\alpha$  has been determined to be 1044 ml mg<sup>-1</sup> m<sup>-1</sup> as shown in Figure S1(c), which is in close agreement to previously reported value.[2] This enabled the easy and quick determination of dispersed nanosheet concentration from UV-visible spectroscopy.

The variation of precursor concentration, sonication time and centrifugation speed gives rise to dispersions with a wide range of concentrations. Figure 1(d) in the main paper represents the extinction spectra of some of the dispersions obtained from varying these process parameters. **Table S1** shows the synthesis conditions for these and dispersions with other concentrations. To study the effect of precursor concentration on the final concentration, the dispersions have been prepared by sonication of different amounts of precursor (10 to 100 mg ml<sup>-1</sup>) in 200 mL of 2-butanone, for a period of 30 hours. This was followed by 12 hours of rest to allow for the settling of un-exfoliated precursor, following which the dispersions have

been centrifuged at 1000 rpm in a REMI PR-24 centrifuge for one hour. The supernatant from this as considered for further characterization.



Figure S2. The absorption spectra of dispersions obtained from prolonged hours of sonication for 40, 50 and 100 mg ml-1 have been depicted in (a), (b) and (c) respectively. This resulted in concentrations that are as shown in (d), (e) and (f) respectively, reaching upto 5.5 mgml<sup>-1</sup> in case of dispersions obtained with 100 mg ml<sup>-1</sup> of precursor

To study the effect of sonication time, a fixed amount of precursor was sonicated upto 90 hours, taking 10 mL aliquots of the dispersion at regular intervals. These were allowed to rest for 12 hours and then centrifuged at 500 rpm in a REMI Neya-12 for 1 hour. This was carried out at different precursor concentrations of 40, 50 and 100 mg ml<sup>-1</sup> as seen in the **Figure S2**.

The concentrations of the dispersions exhibited an increasing trend with time. For the dispersions obtained from  $100 \text{ mg ml}^{-1}$  of precursor material, the final concentration

was found to saturate at 5.5 mg ml<sup>-1</sup> after 36 hours. It was found that after a certain time period, the concentration of the dispersions decreased.

Dispersed	$C_i (mg ml^{-1})$	T <sub>s</sub> (hours)	Centrifuge
concentration (mg ml <sup>-1</sup> )			speed (rpm)
0.21	7.5	12	1500
0.25	10	12	1500
0.32	10	24	1500
0.33 (A)	7.5	30	1500
0.43	20	30	1000
0.47	20	54	1000
0.51	40	12	1000
0.63	20	42	1000
0.79 (B)	30	48	500
1.01	30	64	1000
1.23 (C)	30	54	500
2.09 (D)	50	24	500
2.15	40	24	1000
2.2	40	42	1000
2.68	30	78	500
2.8	40	30	500
3.04	50	36	500
3.1	40	42	500
3.41 (E)	40	54	500

Table S1: Control parameters for obtaining dispersions of various nanosheet concentrations

3.83	50	48	500
3.93	50	63	500
3.94	40	66	500
4.99	100	24	500
5.15	100	72	500
5.25	100	60	500
5.48 (F)	100	36	500

# S1.3 Stability

The stability of the dispersions is studied by measuring its absorbance with respect to time. The settling out of the nanosheets results in a drop in the optical absorbance. By measuring the time taken for the absorbance to reach half the initial value, the half-life of the dispersions has been determined.



Figure S3. The drop in absorbance with respect to time occurring due to the settling out of the nanosheets from the dispersion.

The procedure for the determination of stability is as follows. The absorbance has been measured on a Shimadzu UV-3101PC in a 1 cm cuvette. The initial absorbance of the dispersion has been maintained at a maximum value while making sure that the spectrophotometer detector does not go into saturation. This corresponded to a value of 1.76 mg ml<sup>-1</sup>. Due to limitations of the instrument, the absorbance spectrum has been calculated over a period of few days with breaks, at a wavelength of 660 nm. This is as shown in **Figure S3**, normalized with the initial absorbance value. This resulted in a drop to half the initial value after 111 hours. It is also observed that the settled nanosheets could be re-dispersed by mild sonication of about 20 minutes. Dispersions of nanosheets after size selection by liquid cascade centrifugation exhibited a higher degree of stability when compared to the as obtained polydispersed samples. Samples centrifuged at 5000 rpm and above showed no sedimentation for several months.

# S1.4. Other characterizations

In order to further understand the characteristics of the nanosheets, the dispersions have been coated onto Si or Si: SiO<sub>2</sub> (300 nm) substrates, by spray coating the dispersions at 15 psi onto the substrate placed on a hot plate at  $80^{\circ}$ C held 15 cm away. The samples have then been stored in vacuum. This method of sample preparation has been used for various microscopic and spectroscopic characterization techniques.



Figure S4. X-ray photoelectron spectroscopy of the exfoliated MoS2 nanosheets.

X-ray photoelectron spectroscopy is a useful tool to study the chemical structure of materials. The nanosheets spray coated onto Si substrate have been irradiated using K- $\alpha$  X-rays from an Al source. In **Figure S4**, the peaks around 229.4 eV and 232.5 eV correspond to

the Mo<sup>4+</sup> 3d<sub>5/2</sub> and 3d<sub>3/2</sub> respectively. The peaks positioned at 226.5 eV, 162.2 eV and 163.4eV correspond to S 2s, 2p<sub>3/2</sub> and 2p<sub>1/2</sub> respectively. The positioning of the peaks is indicative of the 2H phase of MoS<sub>2</sub>, and implies that the process has had no effect on the chemical structure of the precursor material. Microscopic methods have further been deployed in order to investigate the nature of the exfoliated nanosheets. The polydisperse samples have been diluted and spray coated onto a Si: SiO<sub>2</sub> (300 nm) substrate.



Figure S5. Optical micrograph of spray coated dispersions. The image in (a) is represented in grayscale in (b) to highlight the nanosheets across the large thickness variations existing in the sample.

The variation in the sizes of exfoliated nanosheets is evident from figure S5. The differing level of contrast among the nanosheets suggests the range of thickness between nanosheets contained in the dispersions. The image in Figure S5(a) has been processed in ImageJ software by splitting channels to obtain in black and white, as represented in Figure S5(b). Microscopic techniques of FESEM and AFM are carried out to understand the exfoliation efficiency. Shown in Figure S6(a) is the FESEM image of the bulk crystals of MoS2. The FESEM image in Figure S6(b) shows the range of lateral dimensions of the nanosheets post exfoliation in comparison to the bulk. The differing height variation is seen in the AFM image in Figure S6(c). In all, microscopy shows the polydispersity in lateral dimensions and thickness exfoliated of the liquid phase nanosheets. From an application perspective, it becomes desirable to have monodisperse nanosheets. Liquid phase synthesis is advantageous in the sense that it enables the usage of centrifugation for size separation. In order to obtain dispersions of nanosheets with sizes in a narrow range, liquid cascade centrifugation has been deployed.



Figure S6. The FESEM image shows the bulk MoS<sub>2</sub> crystals in (a). Compared to the large sizes, the exfoliated nanosheets in (b) are considerably smaller and thinner. The nanosheets are highly polydisperse in lateral dimensions. Along with the varying lateral dimensions, the thickness of the nanosheets also varies between flakes as shown in the AFM image in (c) (scale bar: 500 nm).

# S2. Liquid cascade centrifugation

# S2.1 Methods

Liquid cascade centrifugation (LCC) relies on subjecting dispersions to centrifugal force, resulting in the settling of the dispersed material when the buoyant forces from the dispersant are not large enough to balance the centrifugal force they experience. As the forces experienced by larger nanosheets are greater due to their higher mass, they pelletize during centrifugation at lower speeds, while the smaller nanosheets remain dispersed in the liquid phase. By successively increasing the centrifugation speeds, smaller nanosheets can be separated out from the dispersions. The nanosheets pelletized after centrifugation can then be separated from the supernatant and re-dispersed in fresh solvent. Exfoliating from the bulk powders could result in high amounts of extremely small fragmented nanosheets. To avoid this, a cleaning step has been carried out. The dispersions for LCC have been obtained by sonication of 30 mg ml<sup>-1</sup> of precursor in 200 ml of 2-butanone. The cleaning step involved the sonication of the precursors for 20% (6 hours) of the total time (30 hours) and resting for 6 hours. The dispersion containing the small nanosheets is then discarded and fresh solvent is added, followed by sonication for 30 hours. This is allowed to rest for 12 hours to allow for the sedimentation of bulk unexfoliated material. For the efficient removal of bulk material, the sample has been centrifuged at 500 rpm for one hour. This sediment is discarded. The supernatant dispersion so obtained is then subjected to centrifugation at 1000 rpm for one hour. This leads to the settling of large nanosheets leaving behind smaller sheets in dispersion. This sediment is collected by the complete removal of the supernatant, followed by its re-dispersion in 8 mL of fresh 2-butanone and mild sonication for 20 minutes. This sample is labelled as 1000 rpm. The supernatant from this step has then been subjected to a higher centrifugation speed of 2000 rpm to pelletize smaller nanosheets. This has been labelled as 2000 rpm. In this manner, the supernatants have been centrifuged at 3000, 5000, 7500 and 10000 rpm, collecting sediments in each step and re-dispersing them in fresh 2-butanone to obtain size separated samples and labelled accordingly. The supernatant of 10000 rpm is found to have low concentrations. This protocol is used for size-separating the nanosheets which are further characterised by various methods and have been discussed in the following section.

#### S2.2 Size determination

# S2.2.1 Nanosheet thickness

## UV-Visible spectroscopy

The UV-Visible spectra of MoS<sub>2</sub> exhibits 2 excitonic peaks, with the A-exciton peak around 660 nm and the B-exciton peak around 600 nm. It has been shown that the variation in the thickness of the nanosheets results in the shifting of its band gap from 1.2 eV to 1.9 eV, for bulk and monolayer respectively. The variation in thickness is pronounced by a blue shift in the A-exciton peak. The absorbance spectra of the dispersions obtained by this approach show a blue shift in the A-exciton peak, made prominent by normalizing at the minima at 345 nm, as shown in Figure 2(c) in main paper. Backes et al.,[4] related the spectroscopic results to AFM to provide a quick way of determining the thickness of the layers, given by the Equation 1 in main paper. This relation helped in the quick determination of the number of layers in the size separated samples and has been found to have good agreement with the results suggested by the AFM images, shown in the following section.

#### AFM



Figure S7. AFM image of nanosheets separated at (a )2000 rpm (scale bar: 500 nm) and (b) 5000 rpm (scale bar: 250 nm) showing the height of the MoS2 nanosheets.

The size selected dispersions were spray coated onto Si:SiO<sub>2</sub> (300 nm). The images were obtained in tapping mode with a Si tip (f=300 kHz). The decrease in nanosheet thickness was observed with increasing centrifuge speeds, as shown in the **Figure S7**. Along with the decrease in thickness, the lateral dimensions of the liquid exfoliated nanosheets are also found to decrease. The variation in the A-exciton peak along with the nanosheets thickness

as presented in Figure 2(d) of main paper holds good agreement with results suggested from AFM analysis.



## S2.2.2 Lateral dimensions

Figure S8. Size measurements of size separated nanosheets. DLS, FESEM micrographs and the corresponding statistical analysis for nanosheets separated by centrifugation at 2000(a,b,c), 7500(d,e,f) and 10000(g,h,i) rpm.

The determination of the lateral dimensions of the size separated nanosheets was carried out in a two step approach. Dynamic light scattering is carried out for various dispersions and these results have been correlated with microscopy. The dispersions have been spray coated onto Si substrate and the micrographs are analyzed using ImageJ software. The results from DLS and statistical analysis from FESEM for nanosheets isolated at 5000 rpm are shown in main Figure 3(a) and Figure 3(b). DLS works on the principle of light scattering from spherical particles. Although the geometry of the nanosheets is different from the ideal spherical shape assumed in DLS measurements, the data has been found to have good correspondence when conrmed with FESEM statistics as seen in main Figure 3(c).

Shown in **Figure S8** are the DLS, FESEM micrographs and the corresponding statistics of samples size separated at 1000 rpm, 7500 rpm and 10000 rpm. The measurements from DLS suggest that the nanosheets have an average of 432 nm, 121 nm and 114 nm respectively while FESEM statistics suggest 363 nm, 112 nm and 94 nm respectively.

# S2.3 Other characterizations



#### S2.3.1 Zeta potentials

Figure S9. Zeta potential measurements of the dispersions centrifuged at various speeds.

Zeta potentials of dispersed nanomaterials provide a good indicator to their stability. The electrostatic charge possessed by the nanosheets will prevent restacking. The charge possessed by the nanosheets was measured using a Malvern Zetasizer Nano ZS. The zeta potential represented in Figure 1(e)of the disperion obtained after is centrifuge at 1000 rpm. The zeta potentials for the dispersions obtained at higher speeds were found to have a charge of about -25 mV, as shown in Figure S9. Besides stability, this charge indicates the possible use of the dispersions for coating electrodes by electrophoretic deposition.

S2.3.2 TEM



Figure S10. A TEM image of MoS<sub>2</sub> nanosheets is shown in (a). A typical TEM micrograph of a single MoS<sub>2</sub> nanosheet in (b) shows exfoliation down to few layers. The processed image of an HRTEM is shown in (c), along with the labelling of the Mo (cyan dots) and S (yellow dots) atoms, with the intensity prole shown in (d) for the line represented in (c).

The samples for TEM are prepared by diluting the dispersion with pure solvent till it is optically clear. The Cu grids are placed on lint-free tissue paper so as to wick away the excess solvent. The dilute solutions are then dropped on to the grids and allowed to dry naturally before being stored in vacuum. Bright field, dark field and HRTEM imaging of the MoS<sub>2</sub> nanosheets shown in **Figure S10** were carried out on a FEI Titan (80-300 kV). The micrographs showed well-exfoliated nanosheets, with retention in crystallinity as suggested by the hexagonal ordering seen in high resolution TEM and SAED pattern shown in the main paper Figure 3(f).



Figure S11. TEM image of MoSe2, WSe2 and WS2 nanosheets respectively.

For the nanosheets of other TMDC, the obtained TEM micrographs have been represented in **Figure S11**. The micrographs have been obtained using a FEI Talos (200kV)

# S2.3.3 Photoluminescence spectroscopy



Figure S12. Photoluminescence spectra of the 7500 rpm sample, showing the effectiveness of LCC at obtaining a high monolayer fraction.

The phenomenon of photoluminescence arises from the radiative transition of a photoexcited electron from the bottom of the conduction band to the top of the valence band when the two are aligned. The transition has smaller probability of occurrence in a material of indirect band gap due to phonon mediation but becomes very prominent when the band gap is direct.

To study the photoluminescence of the MoS<sub>2</sub> nanosheets in dispersion, the dispersion centrifuged at 7500 rpm and 10000 rpm have been considered due to their rich monolayer content. The spectra shown in **Figure S12** has been obtained using a Horiba Jobin Yvon

spectro fluorometer (Fluorolog 3) with an excitation wavelength of 483 nm (slit width=5 nm), with the dispersion in a 1 cm cuvette.

## S2.3.4 Raman Spectroscopy

To ensure the size separation of nanosheets in terms of thickness, Raman spectroscopy has been used. A shift in the characteristic  $E^{1}_{2g}$  peak and the A<sub>1g</sub> peaks of MoS<sub>2</sub> which results in a reduced inter-peak spacing provides a fingerprint to the number of layers. [5]



Figure S13. Raman spectroscopy setup to characterize liquid samples in (a). The laser spot on focussing is as shown in (b). The Raman spectra of the dispersions compared to the solvent (c) with the deconvolution of material and solvents peaks (d).

The Raman spectra mentioned in main Figure 1(e) has been obtained by spray coating the dispersions onto a Si substrate. The process conditions involved in deposition could result in

the restacking of the nanosheets. Also, there exists the possibility of aggregation and the ininfluence of the substrate on the signal arising from the material.[6] In order to circumvent these concerns, we obtained the Raman spectra of the dispersions. The setup has been pictured in Figure S13(a). A 532 nm green laser provided the excitation. The laser spot was focussed to the surface of the dispersion as shown in Figure S13(b). As the focussed laser spot causes heating effects, it poses a challenge to obtain the spectrum from a low boiling solvent. With time, the evaporation of the solvent defocuses the laser spot. Thus, the laser spot is focussed inside the surface while beginning the scan and suitable acquisition times are used that enabled the recording of the entire spectrum. The spectrum comprises of the Raman peaks intrinsic to the solvent well those as as arising from the dispersed MoS<sub>2</sub> nanosheets depicted in Figure S13(c). The emergence of the  $E_{2g}^{1}$  and  $A_{1g}$  peaks (between 380 cm<sup>-1</sup> and 410 cm<sup>-1</sup>) occurs upon addition of the MoS<sub>2</sub> to the solvent. The solvent peak arising from the C<sub>2</sub>C<sub>3</sub>C<sub>4</sub> bending 409 cm<sup>-1</sup> closely overlaps with the A1g peak of MoS2.[7] The overlap of the peaks has been deconvoluted and represented in Figure S13(d). With fewer layer MoS2 dispersed in the solvent, a broadening of the A<sub>1g</sub> peak towards lower wavenumbers is observed. No appreciable change in peak position occurs with the  $E^{1}_{2g}$  peak.

#### S3. Device application

# S3.1 Photoresponse from nanosheets

The band gap of MoS<sub>2</sub> lies in the visible region, making it suitable for applications like photodetection. In order to study these properties, a photodetector device has been fabricated by spray coating the dispersions onto a 2.5  $\mu$ m interdigitated electrode device on Si:SiO<sub>2</sub> (280 nm) obtained from Fraunhofer IZM, seen in the inset of **Figure S14**(a). The nanosheets form a percolation pathway for the current between the electrodes, as shown in Figure S14(b). The I-V characteristics of the device have been probed between -3 V to +3 V. The device exhibited a semiconducting behaviour (Figure S14(a)). To probe the spectral response of the material, the device is irradiated with lasers of 404 nm, 532 nm and 808 nm of 4.5 mW power while biased at 1 V. The photoresponse is observed to be a maximum for the case of the green (532 nm) laser, when compared to the other two lasers. Interestingly, the device also showed photoresponse to zero bias, shown in Figure S14(c) and could detect the light from a cellphone flashlight. In order to determine the photoresponsivity of the device, the following procedure hasbeen used. The laser optical power output has been found to be 47 mW cm<sup>-2</sup>. The device area is measured from FESEM images. The effective optical power incident on the device has been found to be  $2.06 \ \mu$ W. The ratio of the current rise by the incidence of photons, to the input power yields the responsivity of the device. In the case of the 532 nm laser, the responsivity is found to be 0.52 mA W<sup>-1</sup>.



Figure S14. I-V response of the device (shown in the inset) in dark and under illumination from lasers of various wavelengths are shown in (a). Shown in (b) is a close up FESEM image of the device electrode gap where the nanosheets can be seen making a percolation pathway for current. The photoresponse of the device in (c) is under zero-bias conditions.

The responsivities of the device for various wavelengths is represented in (d). In a similar manner, the responsivities for the 404 nm and 808 nm lasers is found to be 0.25 mA W<sup>-1</sup> and 0.19 mA W<sup>-1</sup> and have been presented in Figure S14(d), all exhibiting a response time of under 50 ms (limited by instrumental resolution). The specific detectivity of the device has been calculated using the equation given below and was found to be 1.27 x  $10^9$  Jones.

$$\mathbf{D^*} = \frac{\mathbf{R}\mathbf{A}^{0.5}}{(2\mathbf{e}\mathbf{I}_{dark})^{0.5}}$$

Where R is the responsivity (under illumination of 532nm light), A is the active area of the device, e is the electronic charge and  $I_{dark}$  is the dark current. The low boiling point of the solvent enables its use in coating flexible polymeric substrates at low processing temperatures. This has been demonstrated by the fabrication of a flexible photodetector which has been realized in the following manner.

#### 3.2 Flexible device

A 100  $\mu$ m thick PET sheet is deposited with Au (seeded by a underlying Ti layer) by sputtering. The device has been obtained by hard masking with an electrode gap of 100  $\mu$ m. This was spray coated with theMoS<sub>2</sub> dispersions at 15 psi held at 15 cm distance, on a hot plate at 80<sup>o</sup>C. The photoresponse measurements are carried out in the similar way as shown before in the case of the rigid device using 532 nm laser. The effect of flexure is studied with respect to the number of flexing cycles (up to 1000 times) by bending around a rod with radius of 4.5 mm. The resistance of the device has been monitored along with the photoresponse. The normalized responses and resistances have been depicted in main Figure 4(f).

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