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Investigation of two-solvent grinding assisted liquid phase exfoliation of layered MoS₂

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Abstract: Grinding-assisted sonication exfoliation of stratified materials such as MoS₂ is a widely used method for the preparation of their single and few layer thick flakes. This work introduces a two-solvent step approach utilizing a separate solvent during the grinding phase, while implementing ethanol during exfoliation. It is found that the grinding solvent played a critical role, determining exfoliation yield, flake dimensions and morphology, highlighting the importance of such parameters in the process. Furthermore, it is found that the commonly used N-methyl-2-pyrrolidone (NMP) lead to persistent residues on the exfoliated flakes which may alter the properties of the flakes and interfere with the development of electronic devices and other applications. A solvent residue free exfoliation method is presented herein, which may be advantageous for future studies.

Introduction

In recent years, layered semiconducting nanomaterials have gained increased attention and have been intensely studied due their unique properties. Within the layered materials family, great interest has been given to transition metal dichalcogenides, where molybdenum disulfide (MoS₂) has gained the most attention. [1, 2]

The stratified 2H MoS₂ crystal structure is composed of layers of Mo atoms sandwiched between S atoms that are covalently bonded to form a trigonal prismatic arrangement.[3-5] In the bulk crystal, many of these layers are stacked in registry on top of each other *via* Van der Waals forces. [1, 2, 6] Bulk MoS₂ has a band gap of ~1.2 eV, however, upon reduction of the number of layers towards a single monolayer, the dominant band gap increases to ~1.8 eV. [1, 4, 6-8] Simultaneously, the indirect bandgap transitions to a direct bandgap leading to the rise of photoluminescence (PL), which is not observed in the bulk material. [5, 7, 9, 10] 2H MoS₂ exfoliated into just a few atomic layer thickness has found tremendous popularity in field effect transistors with impressively large ON/OFF ratios.[11] Further applications have been demonstrated in energy storage [12, 13], catalysis [6, 14], and sensing [15].

While mechanical exfoliation, as well as many physical and chemical vapour deposition techniques, have been developed for producing high quality two dimensional (2D) MoS₂ crystals, such methods are generally suited for electronic device fabrication.[16] Solution processed films are of more interest for applications such as catalysis, energy storage and, to some extent, sensing. In such cases, liquid exfoliation methods resulting in high yields and quality are greatly sought after to produce thick and porous films of two dimensional flakes.

So far, liquid phase exfoliation techniques have shown to be the highest yielding technique when starting from a

bulk material.[17-20] The main methods utilized are either ion intercalation or sonication assisted exfoliation. [17, 21] One of the most common ion intercalation approaches involves the intercalation of lithium ions (Li⁺) in the interlayer space of the bulk material, followed by an immersion of the resulting compound in water. The Li⁺ reacts with water to form LiOH and H₂, which expands the interlayered space causing the bulk material to exfoliate into 2D materials.[21-23] However, it was found that the harsh conditions led to defects and the introduction of phase impurity in the synthesized 2D MoS₂ flakes, which alter the electronic and physical properties of the product. [24] Additionally, the educts used in such processes, especially n-butyl lithium, are highly flammable and explosive, posing health hazards and complicating the upscale of such processes to industrial quantities. An alternative approach uses the electrochemical intercalation of Li⁺, avoiding the use of dangerous chemicals. Unfortunately, this method results in low yields, thus defeating the purpose.[25]

Another liquid phase exfoliation method utilizes high intensity ultrasound waves (sonication) to exfoliate the bulk material. Thin layers are exfoliated from the layered bulk material using sonication, while dispersed in polar solvents, with and without the aid of surfactants.[21] *Via* centrifugation, the resultant 2D material is then separated into different lateral dimensions and collected. These methods are favorable, as they do not involve any chemical reactions, are not air-sensitive and generally show acceptable yields.[21] Yao *et al.* have reported to obtaining relatively higher yields, up to 26.7 mg/mL, by incorporating grinding into their exfoliation procedure. [26]

For sonication methods the solvent selection plays an important part since physical properties such as boiling points [27], surface tension and energy, [21, 28] as well as solubility parameters [17] affect the resulting 2D material.

There are still many challenges and unknowns when utilizing the sonication exfoliation method and further work is necessary in order to understand the process and further improving the quality of the resulting 2D MoS₂ flakes.

Coleman *et al.* have compiled a list of many solvents and have evaluated their suitability for the sonication exfoliation of 2D materials. The most effective solvent was found to be N-methylpyrrolidone (NMP).[28] As a result, NMP is the solvent of choice used in the majority of published research. Even though good yields are obtained when using NMP, the solvent is difficult to be removed due to a relatively high boiling point. Residual NMP can often be found on the resulting 2D materials, even when post processing methods are used. [17] Methods such as refluxing at low temperatures proved to be ineffective and at high temperatures the material oxidises or transforms into its metallic states depending on the environment.[†] The complete removal of the process solvent is, however, instrumental to many applications, especially for the fabrication of novel sensors and catalysts which rely on the availability of large and pristine surface areas.

In this work, we aim to evaluate the effect of different organic solvents for the exfoliation of MoS₂ using the grinding-assisted liquid phase exfoliation method. The solvents used are acetone, acetonitrile (ACN), benzene, cyclohexane (C. Hex.), hexane (Hex.), isopropanol, methanol and toluene and for compression NMP. These solvents have lower boiling points, and surface tension energies, than that

Table 1: Boiling points and surface tension energies of the solvent used in this work[29]

Solvent	Surface tension (mJ/m ² at 20 °C)	Boiling point (°C)
NMP	40.79	202.0
Acetone	25.20	56.5
Acetonitrile	29.50	82.0
Benzene	28.90	80.1
Cyclohexane	24.95	80.7
Hexane	18.00	69.0
Isopropanol	23.00	82.6
Methanol	22.70	64.7
Toluene	28.40	111.0

of NMP (Table 1), which should ease the removal of the process solvent from the surface of the 2D MoS₂ flake. Herein the investigated organic solvents are used exclusively in the grinding stage of the exfoliation. After the grinding step, the samples are dispersed into ethanol for the sonication and centrifugation stages. Profound differences are found between the samples; which highlights the importance of the grinding step and the used solvent during this process in particular that are fully discussed. Raman spectroscopy and optical characterizations are utilized to assess the presence and the effect of residues on the surface of the grinding assisted liquid phase exfoliated 2D MoS₂.

Experimental Section

Exfoliation of MoS₂

2g of MoS₂ powder (Sigma Aldrich, ~6 µm) and 0.5 mL of the chosen solvent were manually ground using a mortar and pestle for 30 mins. While grinding, an extra 0.5 mL of

solvent was also added in 0.1 mL doses to replenish evaporated solvent. The powder was then left to dry overnight in a vacuum oven (~500 mmHg) at 60 °C to evaporate the solvent. The dried sample was then redispersed in 40 mL ethanol and probe sonicated (Ultrasonic with temperature controller, GEX 500) for 90 mins at 125 W (20 kHz) with stirring. Afterwards, the solution was centrifuged for 60 mins at 4000 rpm (Boeco, C-28A) and the supernatant was decanted. The supernatant was then centrifuged again for 30 mins at 4000 rpm and the supernatant, containing the nanoflakes, was collected. The two step centrifugation procedure ensured complete removal of bulk powder.

Characterisations

Raman spectra were obtained using a micro-Raman spectrometer (InVia Streamline microscope, Renishaw, UK) with a 485 nm laser source at 1 mW power. 2.5 mL of each suspension was drop-casted onto silicon substrate (wafer) and heated at 40 °C on a hotplate to evaporate the solvent.

A scanning probe microscope (SPM/AFM) (D3100, Digital Instruments) was used to measure the surface contours and the thickness of the exfoliated flakes. Conductive AFM images were obtained using a Bruker MultiMode with an installed Peak Force TUNA module (MM8-PFTUNA for MultiMode8 AFM system, Germany). X-ray diffraction (XRD) patterns were obtained using Rigaku miniflex II.

The nanoflake suspensions were diluted further for dynamic light scattering (DLS) readings. 1 mL of the suspension was pipetted into a DLS tube and was diluted by adding 1 mL of filtrated (220 nm membrane filter) ethanol. The tube was shaken and bench bath sonicated to mix its contents prior to measuring the particle size by DLS, using an ALV Fast DLS particle sizing spectrometer. PL measurements were obtained with a spectrofluorometer (Fluoromax 4C, Horiba Scientific) using a fluorescence cuvette. UV-Vis spectra were obtained on a UV-Vis spectrometer (Cary 60, Agilent Technologies), with a standard plastic cuvette. No dilution was required for the PL and UV-Vis measurements.

Figure 1: (a) AFM profiles (scale bar is 50 nm) and (b) DLS size distribution of MoS₂ when exfoliated in various solvents.

A droplet of each suspension was dropped onto a 300 mesh copper lacey carbon grid (ProSciTech, Australia). The dried samples were viewed with a Jeol 2010 transmission electron microscope (TEM) equipped with a SC600 CCD Camera (Gatan Orius).

Discussion

The suspensions of quasi 2D (Q2D) MoS₂ nanoflakes (they are called Q2D as their lateral length to thickness ratios do not exceed 100, which will be shown later) were prepared using the grinding-assisted liquid phase exfoliation method, adopted from Yao *et al.*[26] The solvents used during the grinding procedure include NMP, ACN, Hex., C. Hex., isopropanol, methanol, acetone, benzene and toluene. Following the synthesis procedure (see Methods), isopropanol, methanol, acetone, benzene and toluene ground MoS₂ did not result in measureable (the concentrations were too low to for the characterization purposes (see supporting information S1)) concentrations of Q2D MoS₂ in the final ethanolic suspension.

Grinding the bulk MoS₂ in NMP, ACN, Hex. and C. Hex. followed by probe sonication was found to lead to appreciable Q2D MoS₂ concentrations in the final solutions. This finding highlights the importance of the grinding step and the choice of solvent during this process. After grinding in the chosen solvents, the suspensions were dried at elevated temperatures and reduced pressure

for several hours in an attempt to remove any solvent residues. All samples were then redispersed, probe sonicated and centrifuged in ethanol.

The physical dimensions of the Q2D flakes were characterized by AFM imaging (Fig. 1a). AFM profiles showed that the surfaces were flat, an indication that 2D flakes were obtained. The exfoliated flakes produced with NMP and C. Hex. were typically 1.5 to 3.5 nm in height, which corresponds to 2-5 layers of MoS₂ (single layer thickness: ~0.7 nm [10, 30]), with lateral dimensions most frequently ranging about 20 to 200 nm. The flakes exfoliated with ACN varied in height, ranging from 1.5 to 7 nm (up to 10 layers), with the majority being between 3.5 to 5 nm thick (5 to 7 layers) while featuring 10 to 50 nm lateral dimensions. Exfoliation with Hex. produced the thickest flakes measuring heights of 5.5 to 11 nm (up to 16 layers) and lateral dimensions of 20 to 120 nm.

The lateral dimensions were also measured with DLS and the distribution of particle diameters were determined following Lotya *et al.*(Figure 1b).[31] The distribution of the particle size suggests that all samples have a high polydispersity. The median lateral dimensions for NMP, ACN, Hex. and C. Hex were 110, 30, 40 and 80 nm, respectively. The two dimensional character of the Q2D flakes can be approximated by

Figure 2: TEM images of the suspensions, illustrating lattice and layer gratings.

the aspect ratio of the lateral dimension to the thickness of the flake, with higher aspect ratios indicating an increased 2D character. The aspect ratios were in the ranges of 73.3-31.4 (NMP), 8.6-6.0 (ACN), 7.3-3.6 (Hex.) and 53.3-22.9 (C. Hex.), highlighting that the choice of grinding solvent has a significant influence on the final product. NMP produced the largest aspect ratio for the flakes, which could be attributed to the relatively higher surface tension energy, when compared with the other solvents (see table 1). Studies have suggested that a close match of the surface energy between the solvent and the layered material (40 mJ/m^2 [28, 32]) leads to the exfoliation of larger flakes with increased aspect ratios. [20, 33] The increased boiling point of the solvent may also have played a role leading to reduced evaporation losses in the case of NMP and increasing the participation of the solvent during the grinding process. The fact, however, that the other investigated solvents, featuring a variety of boiling points and surface tensions, led to negligible 2D MoS_2 concentrations in the ethanolic supernatant suggests that the exfoliation mechanism during the wet grinding process is more complex than anticipated and further studies are necessary to fully elucidate the underlying mechanisms.

Each sample was observed to be well exfoliated in general when investigated under the TEM (Figure 2). Many mono and few layered flakes were identified upon inspection of the edges. Lattice gratings with lattice spacing of 0.27 nm (d_{1-100} of MoS_2 [ICSD no. 84180]) were easily observed in all samples. The TEM images are in good agreement with the AFM measurements, confirming thicknesses of the flakes and the interlayer spacing of $\sim 0.7 \text{ nm}$, which could be observed at the flakes' edges.

The TEM images in Figure 2 show that exfoliation with NMP produced more angular shaped flakes. The MoS_2 layers exfoliated with ACN, Hex. and C. Hex. featured rounder edges and are more random in shape. The Hex. sample was observed to show increased aggregation with

clusters of flakes being visible in the TEM images. Flakes exfoliated with C. Hex. tend to have their edges rolled up (see supplementary), indicating that the choice of solvent during the grinding step has influence on the morphology of the exfoliated flakes. Electron diffraction and XRD patterns can be seen in the supplementary.

Optical characterization utilizing UV-vis spectroscopy, Raman spectroscopy and PL measurements were employed to further characterize the suspensions. The exfoliated suspensions were transparent and appear yellow/green in color, where the darkest, and most concentrated, was the ACN sample and the lightest, and least concentrated, was the NMP sample, which appears to be almost colorless (figure 3 inset). Using the method proposed by O'Neill *et al.* [33], the concentrations were calculated to be 4.2 , 9.7 , 7.8 and $6.5 \text{ } \mu\text{g/ml}$ for NMP, ACN, Hex. and C. Hex., respectively. The concentrations are about two orders of magnitude lower than those reported others, [6, 26, 28] which typically employ NMP during the sonication step and as a suspension solvent.

The UV-Vis spectra for Q2D MoS_2 suspensions are shown in figure 3. The characteristic absorption bands appear at 660 , 610 , 450 and 395 nm and are referred to as the A, B, C and D peaks, respectively. [34-36] The A and B peak arise from direct excitonic transitions at the K point of the Brillouin zone. [35, 36] The C and D peaks can be assigned to the direct excitonic transition of M point. [5, 35] These characteristic peaks can be observed most clearly in the absorption spectrum obtained for the sample exfoliated with ACN. The D peak is not as conspicuous for the suspensions in Hex. and C. Hex. In the case of NMP these peaks are lacking in the UV-Vis spectra. This can be partly attributed to the lower concentration obtained in comparison to the other

suspensions.

Figure 3: UV-vis spectra of Q2D MoS₂ samples exfoliated with grinding in various solvents. Inset: photo of the suspensions ground with (i) NMP, (ii) ACN, (iii) Hex. and (iv) C. Hex.

Raman spectroscopy is routinely utilized to characterized thin layered materials. Figure 4(a) shows the full Raman spectra of the suspensions in the 200 to 2000 cm⁻¹ range. The sharp peak at 520 cm⁻¹ appears due to the silicon substrate.

Two very broad and intense Raman peaks (1360 and 1580 cm⁻¹) and broad background scattering throughout the organic fingerprint region (500 to 2000 cm⁻¹[37]) were observed for the NMP ground MoS₂ samples. The two peaks can be allocated to NMP,[38] which indicates that the solvent was not fully removed from the surface, despite heating at 60 °C and reduced pressure for several hours and redispersing in ethanol. The 300 to 500 cm⁻¹ region in which the main MoS₂ signature Raman peak shifts are located is overshadowed by the broad background Raman scattering, leading to comparatively weak Raman signals. The presence of NMP on the surface

of the dried flakes is detrimental for the many potential applications of Q2D MoS₂, especially for sensing and catalysis, for which the MoS₂ surface needs to directly interact with the analyte or educts. Furthermore, the intense signal of NMP could not be removed from the surface is strong evidence that NMP coordinates to the MoS₂ surface and cannot simply be seen as just a solvent. In this case, NMP is likely also to alter the electronic properties of MoS₂. NMP is a highly polarized material that affects the location of charges within the Q2D material. C. Hex. ground particles also exhibit a broad background scattering throughout the higher wavenumbers, however the intensity is smaller when compared to the NMP sample and no characteristic peaks were observed. Suspensions ground with Hex. and ACN show no broad background or solvent peaks, indicating a nearly solvent free pristine surface.

The E_{2g}¹ and A_{1g} peaks of MoS₂ can be observed in all samples (figure 4 (b)). It is well known that Raman spectroscopy can be used to distinguish between bulk and exfoliated 2D material [3, 4, 9] and can thus be used to assess the quality of the exfoliation. It has been reported that shifts in the E_{2g}¹ (383 cm⁻¹) and A_{1g} (408 cm⁻¹) peaks occur when reducing the number of layers of the 2D material.[3, 4, 35] A red shift of the E_{2g}¹ peak and a blue shift of the A_{1g} peak are typically observed for thin layers. This is commonly accompanied by a change in intensity of these peaks, which has also been observed for the here investigated samples. This shift in the wavenumber is associated with thinner flakes obtained for NMP and C. Hex and thicker ones for Hex. and ACN., which are in agreement with the AFM investigations.

Increased PL of 2D MoS₂ suspensions arises due to the transition from indirect bulk MoS₂ to direct band gap few or single layer MoS₂. [7, 8, 21, 39] Emission arises from the from the K point in Brillouin zone [5, 7, 34] as well as the quantum confinement effect when their lateral dimensions are comparable to those of

Figure 4: (a) Normalised Raman spectra (485 nm) and (b) enlargement of the MoS₂ peaks E_{2g}¹ and A_{1g}.

Figure 5: Photoluminescence spectra of the Q2D nanoflake suspensions excited at 300, 350, 400, 450 and 500 nm.

excitons. [10, 14, 15, 21] The PL spectra of each sample excited at various wavelengths (300, 350, 400, 450 and 500 nm) can be seen in Fig. 5. PL was found for all samples, indicating the presence of direct band gap few layer semiconducting MoS₂.

The observed emission peak exhibited red-shifts with increasing excitation wavelengths in all cases. This red-shift of the PL signal has been described in the literature and can be rationalized by quantum confinement effects due to the distribution of lateral sizes of the flakes.[15, 35, 39] Strengl *et al.*, have shown that the PL of MoS₂ quantum dots shifts with the excitation wavelength

allowing to distinguish between quantum dots with different sizes.[39] Applying this concept to our samples, we can expect that low energy photons will excite the larger flakes present in the suspension, leading to a red shift in the PL spectrum, while high energy photons will also excite smaller flakes resulting in the observed blue shift of the PL. Analysing the PL spectra at various excitation wavelengths allows us to infer information on the particle size distribution, which is complementary to the DLS, AFM and TEM analysis. However, since PL occurs exclusively in the thin, direct band gap flakes, it allows us to distinguish between the not desired thicker, indirect bandgap bulk flakes and the sought after thin, direct band gap semiconducting flakes. DLS is unable to distinguish between these two distributions.

Q2D MoS₂ flakes ground in NMP show intense PL for excitation wavelengths between 300 and 500 nm, while C. Hex. ground flakes do not feature PL for excitation wavelength above 450 nm. ACN and Hex. ground samples do not feature PL about 400 nm excitation. This leads to the conclusion that the largest direct band gap Q2D MoS₂ flakes are present in the NMP ground sample, whereas smaller flakes are present in the C. Hex., ACN and Hex. showing the smallest size of direct band gap flakes.

Figure 6: Conductive AFM demonstrating (a) conductive areas (b) and non-conductive areas. The scale bar is 100 nm.

Conductive AFM was performed on the ACN ground nanoflakes to investigate the quality of the samples in terms surface conductivity. Previous work [2, 18] suggests that nanoflakes with defects (loss of sulphur atoms) on the surface edges possess more conductivity along the flake edges when compared to the flake's center. Two different regions are shown in Fig. 6 as an example. It was observed that some nanoflakes were more conductive than others indicating that some flakes possess more defects than others. Furthermore, the higher conductivity regions of the sample were not confined to the edges, indicating that the defects are not limited to the flake edges.

Conclusion

The grinding assisted exfoliation of MoS₂ was investigated using a two-solvent approach. Ten organic solvent were investigated during the grinding phase, which was followed by the removal of the solvent and sonication in ethanol. It was found that the grinding step and the choice of grinding solvent prior to the ultrasound liquid phase exfoliation is playing a crucial role which has been overlooked to date. Just four grinding solvents led to the

successful exfoliation of Q2D MoS₂ nanoflakes in moderate yields. AFM, DLS and PL measurements revealed that the lateral size and thickness of the exfoliated flakes highly dependent on the chosen solvent during the grinding step. NMP was found to produce the highest quality flakes in regards to lateral size and flake thickness. Raman spectroscopy, however, provided strong evidence that NMP remained on the surface of the exfoliated flakes despite the efforts to remove the solvent after the grinding step, suggesting that NMP may be coordinated to the MoS₂ surface, prohibiting its removal. This may have detrimental effects on certain applications of Q2D MoS₂ that require pristine, clean surfaces such as gas sensing, energy storage and catalysis. ACN was identified as a promising alternative to NMP due to satisfactory exfoliation yields and the complete removal from the MoS₂ surface after grinding. The size of the exfoliated flakes was however smaller when compared to NMP ground MoS₂. Conductive AFM showed that lattice defects are present in the ground flakes, giving rise to conductivity. The defect density however varied between flakes.

This work highlights the importance of the grinding step during the grinding assisted ultrasound exfoliation of 2D materials which is poorly understood to date. Further research may lead to increased exfoliation yields and larger lateral dimensions of the flakes. The results also highlight that the commonly used exfoliation solvent NMP remains on the surface and may in fact coordinate to the surface. Future work should carefully evaluate, if NMP residues on the Q2D MoS₂ surface can interfere with the intended function.

ASSOCIATED CONTENT

More TEM images, Electron Diffraction and XRD patterns can be found in the supporting information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

All authors have given approval to the final version of the manuscript.

Notes

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ABBREVIATIONS

ACN, acetonitrile; C. Hex., cyclohexane; Hex. hexane; NMP, N-methyl-2-pyrrolidone; Q2D, quasi two dimensional; MoS₂, molybdenum disulfide; AFM, atomic force microscopy; DLS, dynamic light scattering; TEM, transmission electron microscopy; PL, photoluminescence;

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