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Liquid Exfoliation of Layered Materials in Water for Inkjet Printing

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Abstract. MoS_2 *is a layered material which is abundant and non-toxic and has been increasingly studied during the last few years as a semiconducting alternative to graphene. While most studies have been performed on single* MoS_2 *nanosheets, for example to demonstrate high-performance electronic transistors, more work is needed to explore the use of* MoS_2 *in printed electronics. The importance of using* MoS_2 *as a printed electronic material could be understood by considering the several orders higher electron mobility in* MoS_2*, even in several nanometer thick layers, compared to the organic and other materials used today. In the few studies performed so far on printing* MoS_2*, the developed dispersions used mainly organic solvents that might be detrimental for the environment. Here, we show an environmentally friendly liquid-based exfoliation method in water where the solution was stabilized by sodium dodecyl sulfate (SDS) surfactant. The dispersions consisted of very thin* MoS_2 *nanosheets with average lateral size of about 150 nm, surface tension of* 28 mN m^{-1}*, and a shelf life of a year. Although both the concentration and viscosity was less than optimal, we were able to inkjet print the* MoS_2 *solution on paper and on PET films, using multiple printing passes. By tuning the concentration/viscosity, this approach might lead to an environmentally friendly* MoS_2 *ink suitable for printed electronics.* *© 2016 Society for Imaging Science and Technology.*

INTRODUCTION

The discovery of graphene[1] and the developments thereafter led to the research of other layered materials which, like graphene, have remarkable properties at atomic scale that are explored when exfoliated into single layers or thin films. Molybdenum disulfide, MoS_2, and other transitional metal dichalcogenides, are layered materials where the metal layers are sandwiched between two atomic layers of chalcogen atoms.[2] While strong covalent forces hold these individual atomic interlayers together,[2] stacking of these layers are held together by weak van der Waals forces that are easily overcome by mechanical forces during exfoliation. The main body of MoS_2 studies of these layered semiconductors have been performed on monolayer thick single nanosheets with lateral sizes in micrometer range[3,4] with high electron mobility (200–700 Vs/cm^2), demonstrating, for example, high-performance transistors.[5,6]

However, these materials are inert and allow processing in solvents that point out the opportunity to explore these materials in printed electronics and other large-area applications such as solar cells. In printed electronics, the aim is seldom a single-layer film; instead it is a thin film with properties closer to bulk. Compared to other common printed electronic semiconductors, the mobility of thicker films or bulk MoS_2 mobility are still high, about 50 Vs/cm^2, while the ones based on organic, metal oxides or amorphous silicon have mobilities of the order of 1 Vs/cm^2. If MoS_2 and other layered semiconductors could be printed, it would be a promising solution for high-performance printed electronics.

To be able to print MoS_2, suitable inks are needed that have these essential features: (1) non-toxic solvent, since printing is usually done in environments without extensive ventilation; (2) proper viscosity for the particular printing process addressed; (3) surface tension for the particular printing process addressed; (4) optimal concentration, since it is difficult to evaporate solvents at low concentration inks and an overly high concentration may led to clogging nozzles; (5) particle size; (6) long shelf life of the inks (stability); (7) provide good electrical conductivity of the printed pattern; and (8) good interaction ink/substrate in order to achieve good printability and resolution.[7,8]

Some methods described by Coleman and co-authors[9,10] pointed out that organic solvents are the most ideal ones to disperse and stabilize nanomaterials but to circumvent the toxicity of some of those solvents other stabilization methods have been reported employing small amounts of surfactant[11–13] or functionality agents.[14]

The first step to make an ink based on layered materials is exfoliation. Through exfoliation, the MoS_2 layers present in the bulk powder or crystal will be broken down into smaller particles[12] as illustrated in Figure 1. The more successful this exfoliation process the fewer layers will be observed.

There are several methods developed to exfoliate layered materials. Liquid-based exfoliation (LBE)[12] is one of the most promising due to its scalability and simplicity. There is no need for a controlled environment for achieving the layered materials in a easy-to-transfer medium, in this case the solvent. The solvents are either organic or water-based. Other methods[12] such as electrochemical exfoliation have some drawbacks, such as low yield, long processing time, need to control the environment due to the flammability of the intercalate source, loss of stability if the intercalate ions are

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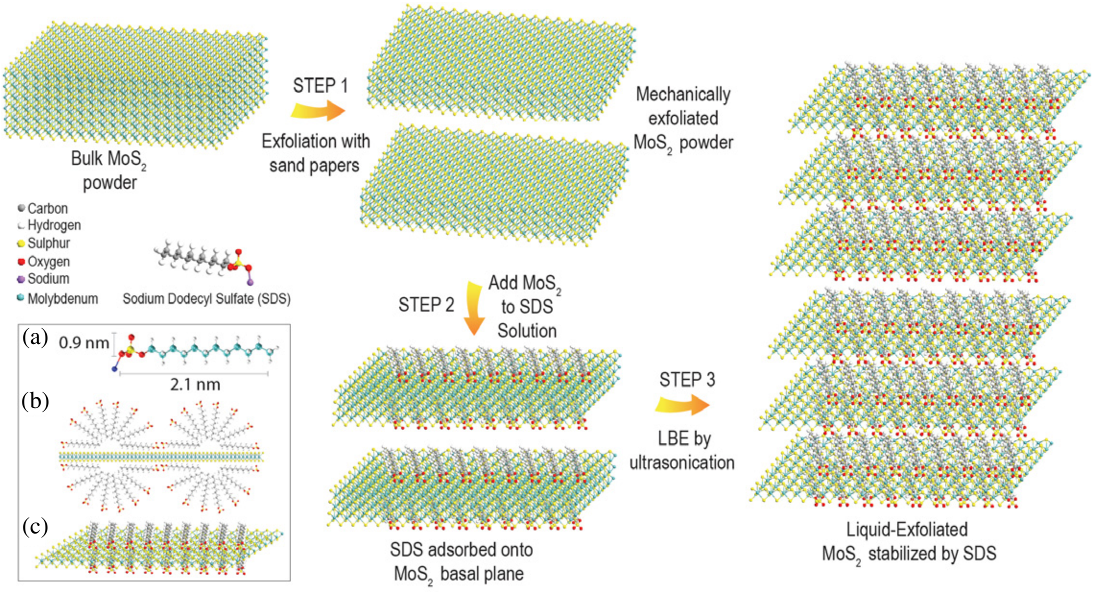


Figure 1. Exfoliation steps for the production of MoS$_2$ dispersions with mechanisms of surfactant adhesion onto the basal plane of MoS$_2$ in the inset at the bottom left (a) SDS molecule (b) semi-micelle adsorption mechanism (c) simplified adhesion illustration.

removed, or distortion in the crystal structure changing the physical characteristic of the material from semiconductor to metal.[15]

To mechanically separate the layers in LBE, two major methods are employed: ultrasonic exfoliation and different kinds of shear-force exfoliation.[12] After achieving a successful dispersion, one needs to study means to apply it. Wang et al.[16] reported a large scale application of graphene using rod-coating, a method that is very promising if full coverage of the surface is desired. However, when the target of the application is specific areas, printing may be more suitable, inkjet being the preferable method for this, taking into consideration the physical properties of the inks such as low viscosity and low concentration. Only a few studies have been performed on printing MoS$_2$.[17,18] Finn et al.,[17] inkjet printed NMP (N-methylpyrrolidone) exfoliated MoS$_2$ resulting in a low concentration solution, but by printing each line 30 times, this problem was circumvented. We employed the same method in our printing tests.

Special precautions must be met when printing with the toxic solvents such as NMP and DMF. Li et al.[18] dealt with this problem by using a distillation method for DMF-exfoliated MoS$_2$. In this process, the toxic DMF (dimethylformamide) solvent was exchanged to non-toxic solvent terpineol. This exchange process also increased the viscosity of the final dispersion from 0.9 cP to about 40 cP. Too much viscosity may also be detrimental to the inkjet process as a higher onset bias is necessary to jet the drops creating long filaments and small drops.[7] Therefore, they tailored the viscosity to 10 cP using ethanol. Also the concentration increased significantly. They also added ethyl cellulose to improve printing quality as well as shelf life of the ink.

Here, to investigate an environmentally friendly alternative, we exfoliated MoS$_2$ in water[19] and added surfactant to improve the stability and adjust the surface tension of the dispersion to facilitate the ink jetting process. Although both the concentration and viscosity was less than optimal, we were able to inkjet print the MoS$_2$ dispersion on paper and on PET films, using multiple printing passes. By tuning the concentration viscosity, this approach might lead to an environmentally friendly MoS$_2$ ink suitable for printed electronics.

MATERIALS AND METHODS

The MoS$_2$ (Molybdenum IV sulfide) powder (99% < 2 μm) and the surfactant SDS (sodium dodecyl sulfate) were purchased from Aldrich and used as supplied. To mechanically exfoliate the MoS$_2$ powder we used an orbital sander at the nominal speed of 11000 rpm (Meec Tools). The powder was placed between sand papers with mesh size 1000 or higher and exfoliated for 2 minutes.[19]

We sonicate the dispersions prepared with the mechanical exfoliated powder using the method described by O'Neill.[10] Fig. 1 illustrates the steps used during the preparation of the dispersions. The inset indicates the SDS molecule in Fig. 1(a), the mechanism of semi-micelle surfactant adhesion observed by Manne and co-authors[20] in Fig. 1(b), and a simplification of the surfactant adhesion for purpose of illustration employed by us is illustrated in Fig. 1(c).

The liquid exfoliation was performed using a Sonics Vibracell CV334, 750 W probe unit set to operate at 30% amplitude. The dispersion was placed in a 100 mL jacket glass vessel (Ace Glass Incorporated), connected to a pump (Polyscience 801 heat circulator) to allow cold water at 5°C to flow through the jacket to avoid overheating of the dispersion and damage to the sonication probe. We also set the probe processing time to 60 min with intervals of operation for 8 s with 2 s pause.

We measured the viscosity with the rotational viscometer Rheomat RM180 using the spindle set 11, shear rate of 1108 s^{-1}, torque of 0.4 mN m, and temperature 19°C.

AFM (atomic force microscopy) images were made using a Dimension 3100 AFM (Digital Instruments) operated in tapping mode. The samples were centrifuged (Jouan A14) at 1500 rpm for 45 min, and decanted to remove non-exfoliated particles. The liquid of the remaining dispersion was removed and the nanosheets were re-dispersed in 99.5% ethanol. We then deposited drops of this dispersion onto a silicon wafer for the imaging analysis.

SEM (scanning electron microscopy) images were made using a FEI Nova NanoSEM 450, the acceleration voltage was 2 kV and the working distance 5 mm. The dispersions were deposited onto cellulose membranes by vacuum filtration and dried. Prior to imaging the samples were gold-sputtered for 20 s to obtain an electrically conductive surface.

The optical properties of the dispersions were evaluated using the UV–vis absorption measurement device UV-1800 Shimadzu spectrophotometer. Measurements were performed 30 days after sample preparation.

Surface tension measurements were done using the Wilhelmy Plate method in a Kruss K20 tensiometer.

X-ray diffraction analysis (XRD) was performed using a Bruker D2 Phaser diffractometer with CuK_α radiation in $\theta - 2\theta$ geometry. The dispersions were vacuum filtrated onto PVDF (polyvinylidene fluoride) membranes with pores of diameter 0.22 µm. The surfactant was washed away from the surface using 2 L of distilled water.

For the AFM, SEM, UV–vis, and XRD measurements, we prepared the MoS_2 dispersions at the initial concentration of 5 g/L in 1 g/L SDS solution or in water (dispersion without surfactant).

To evaluate the dispersion stability, we employed electrophoretic mobility measurements to estimate the zeta potential using the Malvern Zetasizer Nano ZSP instrument. We used the same instrument and measurement cell to evaluate the particle size distribution (PSD) of the dispersions. We varied the surfactant concentration around the critical micelle concentration (CMC)[21] of SDS which is 2 g/L and kept the MoS_2 concentration constant at 1 g/L. The minimum concentration of SDS used was 0.2 g/L and, the maximum surfactant concentration was the CMC or 2 g/L of SDS. We collected samples of the dispersions over time within a period of one month. These dispersions were sonicated for 15 minutes in a low power sonication bath before the measurements. We also evaluated the stability of one dispersion with SDS concentration 1 g/L and MoS_2 concentration 5 g/L 6 months after sample preparation.

A MoS_2 dispersion in 1 g/L was successfully jetted using a Dimatix 2831 piezoelectric materials printer (Fujifilm, USA), with a Dimatix 11610 cartridge with 21 µm printing nozzles, nozzle spacing of 254 µm and drop size of 10 pL. The substrates used were a photo paper (HP Photo Paper Advanced) and a 100 µm thick PET film. The substrates were kept in position by a vacuum plate with a controlled temperature of 30°C.

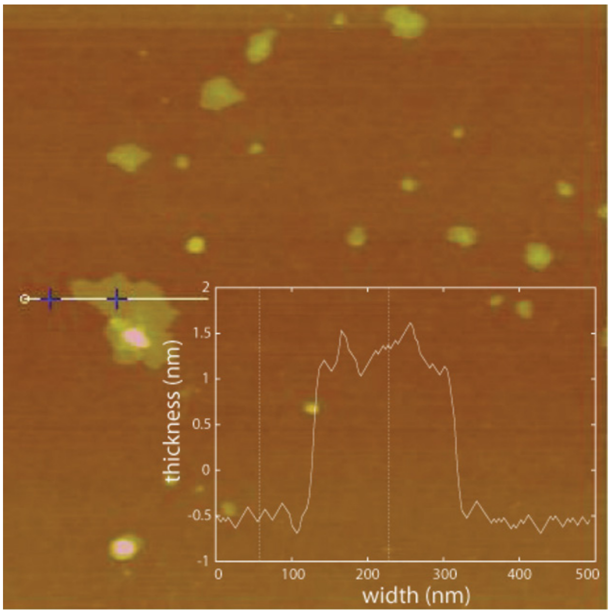


Figure 2. AFM image of nanosheets with thickness profile in the inset.

RESULTS AND DISCUSSION

AFM

We observed a few monolayers by microscopy images taken of the dispersion presented on Figure 2. Thin nanosheets with thickness of approximately 1.5 nm indicating up to two layers of MoS_2[22] and approximately 200 nm in lateral size were measured.

Particle Size Distribution

Using AFM microscopy, we could evaluate the size and thickness of the nanosheets present in our dispersions. Since this method is too time-consuming for the analysis of many nanosheets, we complemented this measurement with PSD analysis, which is less accurate but can measure a larger population of nanosheets within seconds.

PSD is based on light scattering and is a very accurate method for spherical particles but only an estimation for non-spherical particles.[23]

PSD of the nanosheets change significantly as the stacks of MoS_2 layers are broken down into smaller ones. The initial size of the particles in the bulk powder is around 10 times bigger than after exfoliation.[19] Sonication, besides separating the layers of the materials leads to some sonication scission, meaning that the particles break down especially for prolonged sonication times.[24] We measured PSD of about 126 ± 58 nm for a sample prepared in (1 g/L) SDS solution. This sample was prepared 6 months before the measurement. We observed that the PSD drop from around 227 nm to 163 nm and remain constant for a month as illustrated in Figure 3. The surfactant concentration seem to play a role in the stabilization of the bigger particles as can be seen

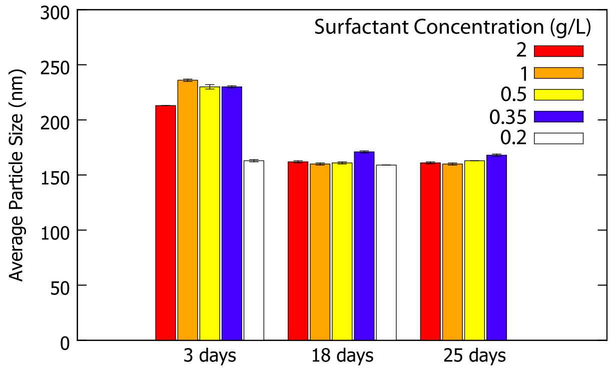
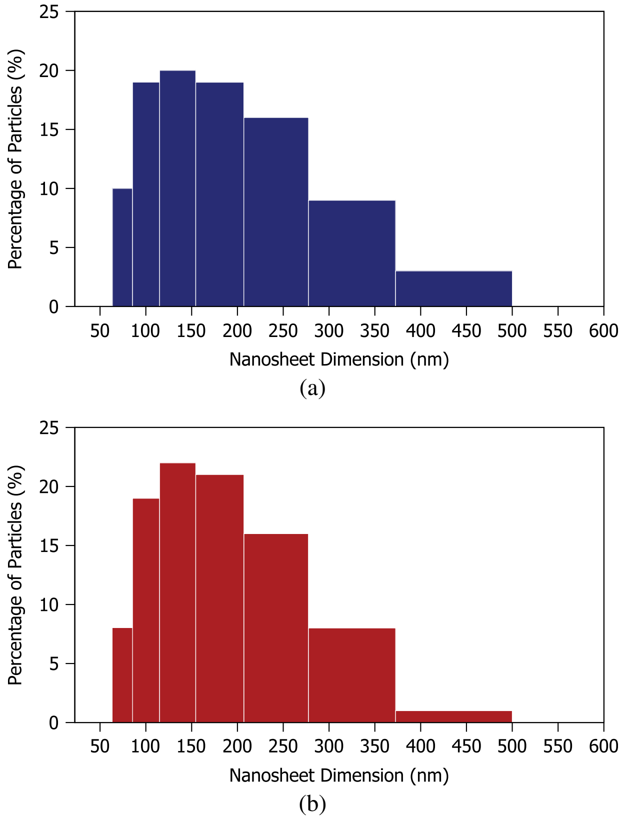


Figure 3. Average particle size distribution of nanosheets measured by dynamic light scattering. Samples taken 3 days, 18 days, and 25 days after sample preparation. The legend indicates the surfactant concentration in the solution in which MoS$_2$ was dispersed at an initial concentration of 1 g/L.



(a)

(b)

Figure 4. Particle size distribution of nanosheets in a dispersion at different surfactant concentrations (a) at 2 g/L and (b) 0.2 g/L with the same MoS$_2$ initial concentration. Measurement was made 25 days after sample preparation.

from Figure 4 as a larger population of bigger particles was observed at the surfactant concentration 2 g/L than at 0.2 g/L. For the lowest SDS concentration (0.2 g/L), the size of the particles remained around the same value, which indicates that the amount of surfactant does not greatly impact the size distribution as observed by the PSD measurement. The dimensions of the surfactant molecules are much smaller than the dimensions of the nanosheets (100 times smaller, as can be seen from Fig. 1(a)) and it did not greatly affect the size of the particles.

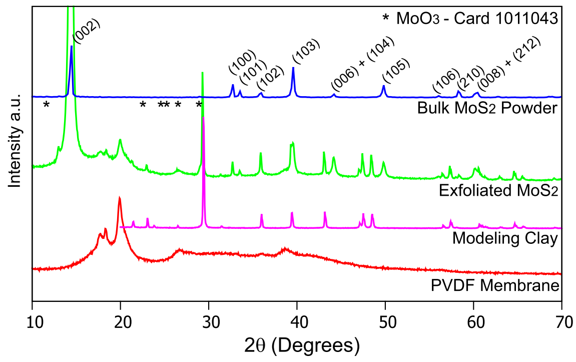


Figure 5. XRD of the MoS$_2$ dispersions vacuum filtrated onto PVDF membranes. The miller indexes are indicated on the peaks of the bulk powder according to the database card 9009144.[27] The pattern for the membrane filter which the sample was deposited by vacuum filtration is also shown and the pattern for clay which was used to fix the sample onto the measurement cell. (*) Indicates the location of a few characteristic molybdenum trioxide (MoO$_3$) peaks according to the database card 1011043.

X-Ray Diffraction Analysis and Scanning Electron Microscopy

We did XRD analysis to get information not only about the crystal structure of the exfoliated nanosheets but also to identify phases which could have resulted from chemical reactions such as oxidation that may take place during the exfoliation process[25] (see Figure 5).

The pattern for the MoS$_2$ bulk powder indicated a lower intensity 002 peak compared to the exfoliated sample. It is expected that the more exfoliated the sample, the lower the intensity of the (00l) peaks.[15,26] The (00l) peaks refer to planes parallel to the basal plane of the crystal MoS$_2$, which is diminished during exfoliation and therefore should show lower intensity in peaks in the XRD pattern.

The orientation of the crystals during measurement also play a role on the measured intensity of the (00l) peaks. Therefore, we did SEM analysis (Figure 6). The nanosheets are ordered in the *c*-axis pointing upwards in the sample as illustrated on the SEM image, and therefore more pronounced (00l) peaks should be observed, which is consistent with our findings; the particles are not ordered in the bulk powder and, therefore, a lower intensity 002 peak was measured.

The exfoliation procedure described here resulted in thin films of MoS$_2$ as visualized in the AFM (Fig. 2) and SEM (Fig. 6) images. The XRD pattern measured for the exfoliated samples suggested that we probably have predominately more than 5 layers of MoS$_2$ in our dispersions. Fewer than 5 layers would result in the absence of the 002 peak.[26]

Since we did not observe any shifts in the two theta values from the exfoliated sample compared to the bulk one, we can say that no changes on the crystalline structure occurred during exfoliation, unlike what normally occurs for liquid exfoliation with lithium intercalation for example.[25]

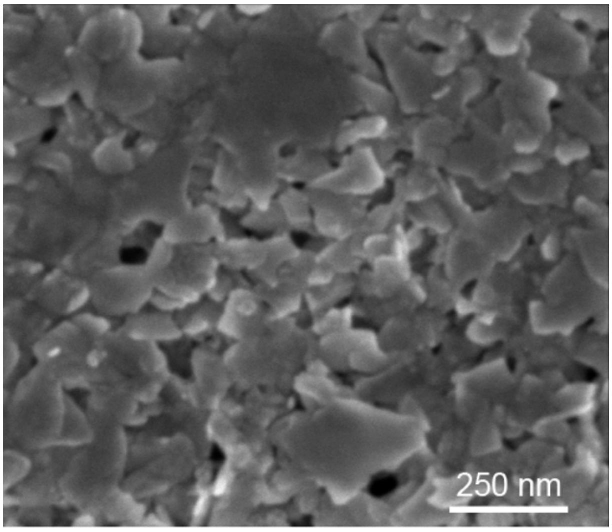


Figure 6. SEM image of dispersion deposited onto nitrocellulose membranes by vacuum filtration.

We did not observe peaks for molybdenum trioxide, as can be seen in Fig. 5, although X-ray photoelectron spectroscopy (XPS) would have been a more accurate measurement for this particular evaluation.[25]

Optical Properties

Due to the presence of surfactant, two phases were observed after sample preparation. This happened when the sample was left to decanted on a bench or if it was centrifuged. The top phase is the phase with lower concentration of MoS_2 as illustrated in Figure 7. On the right of Fig. 7 we have two vials, one with the dispersions before exfoliation showing a very clear liquid with the MoS_2 powder in the bottom and the other the exfoliated dispersion left to settle for a month. We measured the absorption at both phases. It was evident that the concentration of MoS_2 was much higher in the bottom phase.

According to Frey et al.,[28] the absorption peaks A and B are positioned respectively at 660 nm (1.88 eV) and 602 nm (2.06 eV) for pristine MoS_2. After the exfoliation process, the position of these peaks is shifted, as we can see from Fig. 7. We observed a red shift for these excitons of approximately 14 nm located at 674 nm (1.84 eV) and 614 nm (2.02 eV) for the top phase of the dispersion, this red shift is related to the number of layers and not to the particle size and indicates that more than 6 layers are present on the particles.[28] The addition of surfactant may also have contributed to this red shift due to the displacement of anions by the surfactant which adsorbed to the particles surfaces.[29] For the bottom phase, the shift was much smaller, the peaks were much broader and the values very similar to bulk values 668 nm and 608 nm indicating that the particles were bigger.[28]

Electrophoretic Mobility

To evaluate the stability of the inks over time we used electrophoretic mobility measurements,[13] which can be used to estimate the zeta potential (ζ) of the nanosheets. For the dispersions using SDS, we measured a higher zeta potential than the ones in pure water[19,30]; this higher negativity of the zeta potential values was probably due to the anionic characteristic of the surfactant.[31] The surfactant concentration did not affect much the values for zeta potential especially when the particles were left to settle for a few days as can be noticed in Figure 8. Notice also that all measured values were $|\zeta| > 25$ mV[32] which indicated good dispersion stability. For the sample left to settle for 6 months, the zeta potential was -39 ± 3 mV, which was somewhat lower than the ones measured within a month of sample preparation. The mechanism of stabilization using surfactants can be explained by the DLVO and Hamaker theory.[31] A deviation of about 20% of the actual zeta potential for rod-like particles could be observed as the method employed here, which is based on a combination of electrophoresis and laser Doppler velocimetry techniques, was designed to measure particles with a spherical shape[13] which is not the case for nanosheets.

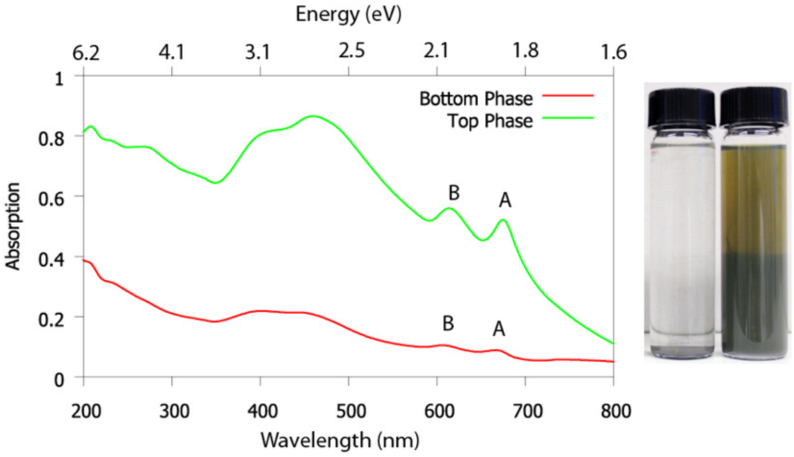


Figure 7. UV–vis absorption measurement for a MoS_2 dispersion in a 1 g/L SDS solution.

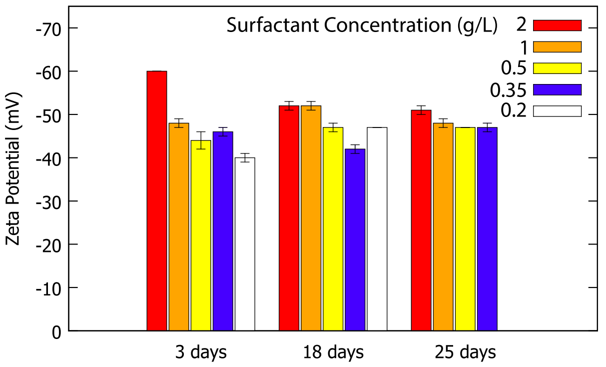


Figure 8. Average zeta potential of samples measured 3 days, 18 days, and 25 days after preparation. The legend indicates the surfactant concentration in the solution in which MoS_2 was dispersed at an initial concentration of 1 g/L.

Inkjet Printing

The test pattern used consisted of an 8 mm long and 450 µm wide line between contact pads. We used a MoS_2 dispersion sample that was stable for almost a year to print the electrodes. Figure 9(c) and (d) show printed MoS_2 test lines consisting of 30 subsequent printed layers on top of each other on PET. The effect of the number of printed layers can be seen when comparing images Fig. 9(c) and (d), as better coverage of the surface was achieved using 30 printed passes. The printed line contains voids, which is most likely due to the matching of the surface energy of the PET and the MoS_2 dispersion. This effect is more visible on the microscopy Fig. 9(a) and (b) (higher magnification). The edges of the printed lines are shown in Fig. 9(a). The printed lines with only 6 printed passes in paper were almost transparent; therefore, we presented only the one with 50 passes (Fig. 9(e)).

To be able to print the dispersions and avoid clogging of the printing head nozzles, a ratio of 50:1 printing head nozzle to particle size is suggested.[33] The size of the nozzles of the Dimatix printer we used were 21 µm, which would give a ratio of approximately 42:1 if one consider the maximum range of the particles measured according to the PSD, 500 nm (see Fig. 4). Adjusting the particle size range is crucial to avoiding clogging of the nozzles. This adjustment can be done either by prolonging the sonication time of the samples which would break the nanosheets into smaller ones and/or through centrifugation.[10]

Other properties of the dispersions were: the surface tension in 1 g/L SDS solution, which was 28 mN m^{-1} (ideally range is 25–35 mN m^{-1})[8] and the measured viscosity 5 cP (ideally range is 8–15 cP for piezoelectric printing heads).[8] The nozzles were separated by 254 µm.

Using the drop evaluation tool available for the Dimatix printers, we did not observe any clogged nozzles during printing. A still image (Figure 10) showed a number of nozzles and a few drops that were jetted. The jetting produced uniform drops in general, but they were often broken up, producing satellite drops. One approach to reduce the satellites formation is to increase the viscosity. For this, one can increase the concentration, add chemicals such as polymers or do a solvent exchange to transfer the dispersed nanosheets to a solvent with a higher viscosity.[18] The jetting conditions should also be studied more carefully as the applied voltage affect a number of the properties of the droplets such as droplet break-up from the nozzle, morphology of the drops, drop velocity, and size.[7,34]

The presence of stabilizing agents such as surfactant can be detrimental to form an interconnect phase between the nanosheets as it would form non-conducting layers between the nanosheets which would affect the conductivity.[8] The surfactant particles can be removed by sintering but it was not the scope of this study to analyze the conductivity of the inks.

The printing test shows that it is possible to use the MoS_2 dispersion as an inkjet ink. Optimization for specific printer and substrate combinations should be performed, which would improve printing quality dramatically.

CONCLUSION

We have demonstrated an environmentally friendly approach to produce MoS_2 inks for inkjet printing. The ink was produced by stabilizer-based exfoliation using the anionic surfactant SDS and by a combined mechanical and ultrasonic process. The viscosity and concentration may be further optimized to reduce the number of printing passes needed and improve printing quality.

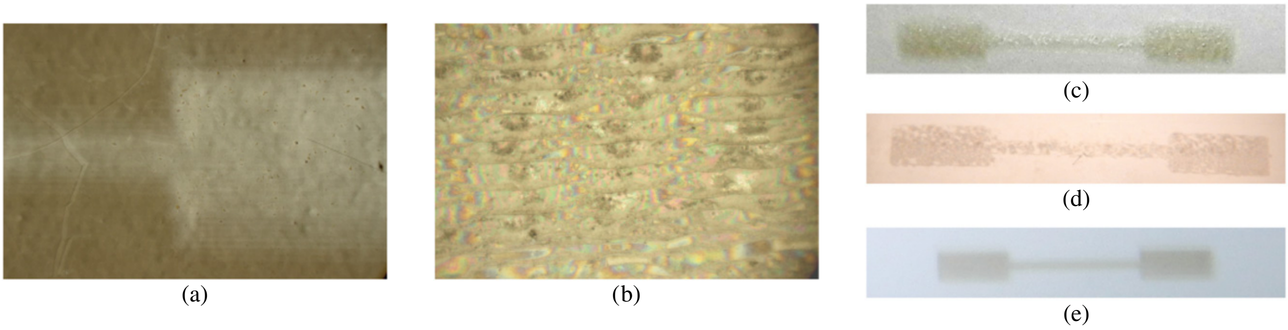

(a)
(b)
(c)
(d)
(e)

Figure 9. Print results of a MoS_2 test line printed on PET and paper. (a) Microscopy image with 50× magnification on the printed test line with 30 printed passes on PET. (b) Same as in (a) but with 100x magnification. (c) Printed on PET with 30 printed passes (d) Printed on PET with 6 printing passes (e) Printed on paper with 50 printed passes.

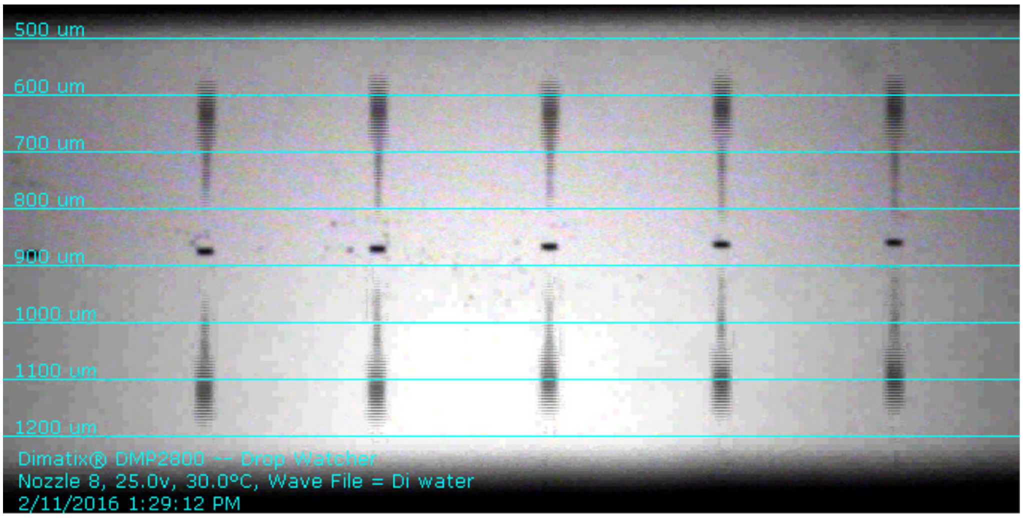


Figure 10. Drop evaluation tool image captured during the inkjet printing of the MoS_2 test lines using the Dimatix printer. The nozzle spacing is 254 μm. The waveform used was for distilled water with 25 Volts bias.

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REFERENCES

[1] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, Science **306**, 666 (2004).

[2] M. Chhowalla, H. S. Shin, G. Eda, L.-J. Li, K. P. Loh, and H. Zhang, Nature Chem. **5**, 263 (2013).

[3] Q. H. Wang, K. Kalantar-Zadeh, A. Kis, J. N. Coleman, and M. S. Strano, Nature Nanotechnology **7**, 699 (2012).

[4] D. Jariwala, V. K. Sangwan, L. J. Lauhon, T. J. Marks, and M. C. Hersam, ACS Nano **8**, 1102 (2014).

[5] B. Radisavljevic, A. Radenovic, J. Brivio, V. Giacometti, and A. Kis, Nature Nanotechnol. **6**, 147 (2011).

[6] S. Das, H.-Y. Chen, A. V. Penumatcha, and J. Appenzeller, Nano Lett. **13**, 100 (2012).

[7] M. Singh, H. M. Haverinen, P. Dhagat, and G. E. Jabbour, Adv. Mater. **22**, 673 (2010).

[8] A. Kamyshny, J. Steinke, and S. Magdassi, Open Appl. Phys. J. **4** (2011).

[9] J. N. Coleman, M. Lotya, A. ONeill, S. D. Bergin, P. J. King, U. Khan, K. Young, A. Gaucher, S. De, R. J. Smith, I. V. Shvets, S. K. Arora, G. Stanton, H.-Y. Kim, K. Lee, G. T. Kim, G. S. Duesberg, T. Hallam, J. J. Boland, J. J. Wang, J. F. Donegan, J. C. Grunlan, G. Moriarty, A. Shmeliov, R. J. Nicholls, J. M. Perkins, E. M. Grieveson, K. Theuwissen, D. W. McComb, P. D. Nellist, and V. Nicolosi, Science **331**, 568 (2011).

[10] A. O'Neill, U. Khan, P. N. Nirmalraj, J. Boland, and J. N. Coleman, J. Phys. Chem. C **115**, 5422 (2011).

[11] R. J. Smith, P. J. King, M. Lotya, C. Wirtz, U. Khan, S. De, A. O'Neill, G. S. Duesberg, J. C. Grunlan, G. Moriarty, J. Chen, J. Wang, A. I. Minett, V. Nicolosi, and J. N. Coleman, Adv. Mater. **23**, 3944 (2011).

[12] L. Niu, J. N. Coleman, H. Zhang, H. Shin, M. Chhowalla, and Z. Zheng, Small **12**, 272 (2016).

[13] Z. Sun, V. Nicolosi, D. Rickard, S. D. Bergin, D. Aherne, and J. N. Coleman, J. Phys. Chem. C **112**, 10692 (2008).

[14] C. Backes, N. C. Berner, X. Chen, P. Lafargue, P. LaPlace, M. Freeley, and A. R. McDonald, "Functionalization of Liquid-Exfoliated Two-Dimensional 2HMoS2," Angew. Chem., Int. Ed. **54**, 2638–2642 (2015) doi:10.1002/anie.201409412.

[15] P. Joensen, R. Frindt, and S. R. Morrison, Mater. Res. Bull. **21**, 457 (1986).

[16] J. Wang, M. Liang, Y. Fang, T. Qiu, J. Zhang, and L. Zhi, Adv. Mater. **24**, 2874 (2012).

[17] D. J. Finn, M. Lotya, G. Cunningham, R. J. Smith, D. McCloskey, J. F. Donegan, and J. N. Coleman, J. Mater. Chem. C **2**, 925 (2014).

[18] J. Li, M. M. Naiini, S. Vaziri, M. C. Lemme, and M. Östling, Adv. Funct. Mater. **24**, 6524 (2014).

[19] V. Forsberg, R. Zhang, J. Bäckström, C. Dahlström, B. Andres, M. Norgren, M. Andersson, and H. O. Magnus Hummelgård, Plos One **11**, e0154522 (2016).

[20] S. Manne and H. E. Gaub, Science **270**, 1480 (1995).

[21] A. Dominguez, A. Fernandez, N. Gonzalez, E. Iglesias, and L. Montenegro, J. Chem. Educ. **74**, 1227 (1997).

[22] K. S. Novoselov, D. Jiang, F. Schedin, T. J. Booth, V. V. Khotkevich, S. V. Morozov, and A. K. Geim, Proc. Natl. Acad. Sci. USA **102**, 10451 (2005).

[23] M. Ibanez, A. Wijdeveld, and C. Chassagne, Clays and Clay Minerals **62**, 374 (2014).

[24] A. O'Neill, U. Khan, and J. N. Coleman, Chem. Mater. **24**, 2414 (2012).

[25] G. Eda, H. Yamaguchi, D. Voiry, T. Fujita, M. Chen, and M. Chhowalla, Nano Lett. **11**, 5111 (2011), http://pubs.acs.org/doi/pdf/10.1021/nl201874w.

[26] H. Ramakrishna Matte, A. Gomathi, A. K. Manna, D. J. Late, R. Datta, S. K. Pati, and C. Rao, Angew. Chem. Int. Ed. Engl. **49**, 4059 (2010).

[27] ICDD *Powder Diffraction File 2* (International Centre for Diffraction Data, Newtown Square, PA, USA, 2014).

[28] G. L. Frey, S. Elani, M. Homyonfer, Y. Feldman, and R. Tenne, Phys. Rev. B **57**, 6666 (1998).

[29] K. L. Mittal and D. O. Shah, *Adsorption and Aggregation of Surfactants in Solution* (CRC Press, New York, USA, 2002).

[30] V. Alecrim, R. Zhang, M. Hummelgård, B. Andres, C. Dahlström, M. Norgren, M. Andersson, and H. Olin, *Proc. IS&T's NIP31: 31st Int'l. Conf. on Digital Printing and Digital Fabrication 2015* (IS&T, Springfield, VA, 2015), p. 192.

[31] K. Holmberg, B. Jönsson, B. Kronberg, and B. Lindman, *Surfactants and Polymers in Aqueous Solution* (Wiley, Southern Gate, Chichester, West Sussex, England, 2003).

[32] M. Lotya, Y. Hernandez, P. J. King, R. J. Smith, V. Nicolosi, L. S. Karlsson, F. M. Blighe, S. De, Z. Wang, I. T. McGovern, G. S. Duesberg, and J. N. Coleman, J. ACS **131**, 3611 (2009).

[33] D. R. Gamota, P. Brazis, K. Kalyanasundaram, and J. Zhang, *Printed Organic and Molecular Electronics* (Springer Science & Business Media, New York, USA, 2013), p. 191.

[34] M. H. Tsai, W. S. Hwang, H. H. Chou, and P. H. Hsieh, Nanotechnology **19**, 335304 (2008).