

The Influence of pH on the Stability of Inks of Two-Dimensional Materials for Digital Fabrication

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Abstract

We aim to achieve stable printable 2D inks with environmental friendly solvents using a surfactant as a stabilizer. This study focuses on the influence of the pH on the stability of the MoS₂ dispersions in acetic acid at concentrations ranging from pH 1 to 5. The effectiveness of liquid-based exfoliation using shear exfoliation was also evaluated through SEM images and resulted in very thin nanosheets. We observed that at pH concentrations higher than 2, the dispersions were more stable.

Introduction

Printed electronics over flexible substrates is an area of significant interest due to the advantages that this technology has over traditional electronics for cheap and large-area applications [1, 2]. The low material cost, reduced material waste and simple patterning make printing technologies such as inkjet attractive and cost-effective fabrication methods [1, 3]. In order to fabricate a transistor using this technology, it is necessary to print a conductor, a dielectric and a semiconductor layer of materials. In this study, we focus on the semiconductor layer, studying one of the parameters of a good dispersion for inkjet printing [4]. We studied semiconductor dispersions for inkjet printing based on molybdenum disulfide, MoS₂, a 2D material that similar to graphene, can be exfoliated into thin nanosheets [5, 6]. We previously reported studies of dispersions of MoS₂ in water without [7] stabilizers and with stabilizers [8]; in both previous studies we used sonication energy to exfoliate the nanosheets. In this study, we used shear exfoliation, a reportedly more scalable method for liquid-based exfoliation [9]. This study complements the previous publications in achieving the ideal printable 2D material inkjet ink.

There have been previous publications focusing on the pH of MoS₂ dispersions but the solvent used was hexane [10], which is not an environmentally friendly solvent and would not be suitable for usage in printing heads. This known method of stabilization using lithium intercalation is done using hexane at pH 2 to avoid sedimentation of the particles [10], but there are several drawbacks associated with the method. We study the pH effect on the dispersion stability in acetic acid at a broader pH range of concentrations. Different than the process to stabilize the nanosheets using lithium intercalation in hexane [10], we used the surfactant sodium dodecyl sulfate (SDS) in water. The process we used was a very simple and fast exfoliation method using shear exfoliation. We observed that the stability was very low at pH 1, resulting in very clear dispersions after centrifugation, which did not occur for dispersions at higher pH concentrations. At pH concentrations higher than 2, the dispersions were stable for a few days and the nanosheets were still dispersed in the solvent after 600 days of sample preparation. Since the measurement for particle size

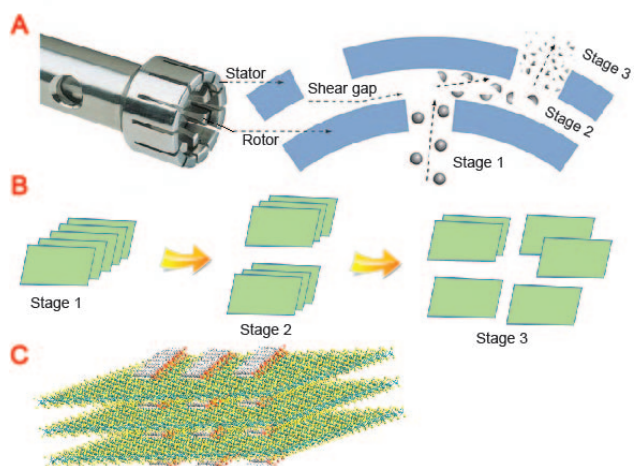


Figure 1. Mechanism of exfoliation using shear exfoliation. A) Rotor and stator illustration showing the shear gaps where the exfoliation occurs in 3 stages. B) Stages of exfoliation in detail, wherein bigger stacks of nanosheets (Stage 1) are exfoliated into smaller ones (Stage 2) and thin nanosheets are produced (Stage 3). C) Molecular representation of MoS₂ nanosheets with the adsorbed surfactant SDS within the layers acting as a stabilizing agent. It is important to notice that this adhesion is reported to be in the form of semi-micelles according to the literature [12, 13]

distribution starts to differ at pH 2, showing broader particle size distribution, we assume that the particles will be thicker and flocculate at lower pH [11]. We used shear exfoliation [9] to disperse the nanosheets and obtained thin nanosheets of MoS₂ as can be seen from the SEM image and the UV-vis absorption measurements.

Materials and Methods

In 250 mL solution of acetic acid (AnalaR Normapur) at concentrations from pH 1 to 5, 0.1 g of molybdenum disulfide (MoS₂) (SigmaAldrich) was added followed by adding 0.6 g of surfactant sodium dodecyl sulfate (SDS) (SigmaAldrich). We used shear exfoliation (IKA Ultraturrax T25 digital) to disperse the MoS₂. The medium to be processed is automatically drawn axially into the dispersion head due to the high rotation speed of the rotor and then forced radially through the slots in the rotor/stator arrangement as illustrated in Fig. 1. The high accelerations acting on the material produce extremely strong shear forces. In addition, high turbulence occurs in the shear gap between rotor and stator, which provides optimum mixing of the suspension. The processing time was 15 minutes at a rotor speed of 10,000 rpm. To evaluate the stability, the dispersions were centrifuged (Beck-

man Coulter Avanti J-20) at 800 rpm for 45 minutes. These dispersions were characterized by particle size distribution (Zetasizer, Malvern) and scanning electron microscopy (SEM) (Maia3, Triglav, Tescan) using an in-beam secondary electron detector at 5 kV acceleration voltage and a working distance of 2.5 mm.

For the SEM images of the dispersion, a 2 mL sample of a dispersion at pH 4 was diluted in 200 mL of distilled water and vacuum filtrated onto a cellulose membrane to create a film of MoS₂. The surfactant was washed away with 2 L of distilled water (although some organic material was still visible in the image). The membrane was left to dry overnight on a desiccator. 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 a UV-vis absorption measurement device (UV-1800 Shimadzu spectrophotometer).

Results and Discussion

We characterized the dispersion with UV/Vis, showing the two main characteristic MoS₂ excitonic peaks at 682 and 622 nm (see Fig. 2). These peaks called A and B respectively, represented the direct transition from the valance band to the conduction band at the K-point of the Brillouin zone [14, 15]. The peak A coincides with the monolayer emission peak [15], and as the number of layers increase the peak exhibits a slightly red shift in its wavelength compared to the literature values [15, 16], as observed here. Besides the optical properties, the concentration of the dispersions was derived from the absorption measurements [17]. The Beer-Lambert's law was employed in this case ($A/l = \alpha \cdot C$), where A is the absorption at the MoS₂ peak A at 682 nm, $l=1$ cm and α is the absorption coefficient. The value for α that was used, $\alpha = 1827 \text{ L g}^{-1} \text{ m}^{-1}$, was taken from the literature [9]. One day after sample preparation the estimated concentration of the sample at pH 4 was 33 mg L^{-1} , very close to the concentration achieved for shear exfoliated graphene dispersions [9]. After 600 days, the estimated concentration drops significantly to 7.4 mg L^{-1} , but it is still a good value considering the shelf time. The images of the dispersions at pH concentrations ranging from 1 to 5 is illustrated in Fig. 4. It is evident from this image that the concentration drops for dispersions at pH 1 and pH 2. At pH 1, the dispersions were rather clear and the concentration was so low that it was not possible to estimate it, as it would be in a range of low accuracy of the measurement (see Fig. 2). The presence of excitonic features indicate good quality of the nanosheets and successful exfoliation which is in concordance with the SEM image taken from the deposited dispersion. The image illustrated in Fig. 3 indicates some very thin and large nanosheets. At 5 kV using the in-beam detector SE during measurements, it was evident that there were very thin nanosheets, as we saw some transparency in the observed particles on top of each other. If the particles were thick (larger than 10 layers), we would not see this transparency. We evaluated the particle size distribution of the dispersions by dynamic light scattering (DLS) [7], showing that the particles were in the range of 100 to 600 nm for all pH concentrations, but the PSDs at pH 3, 4 and 5 were narrower. At pH 2, a greater number of larger particles were dispersed, showing a broad PSD, which could indicate the turning point for stability (see Fig. 5).

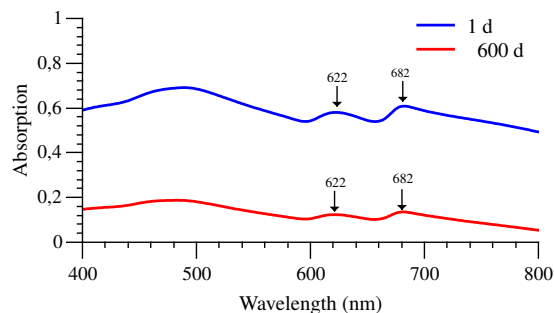


Figure 2. UV-vis absorption measurement for dispersions at pH 4, both 1 day and 600 days after sample preparation, indicating the excitonic peaks A and B at 682 and 622 nm, respectively

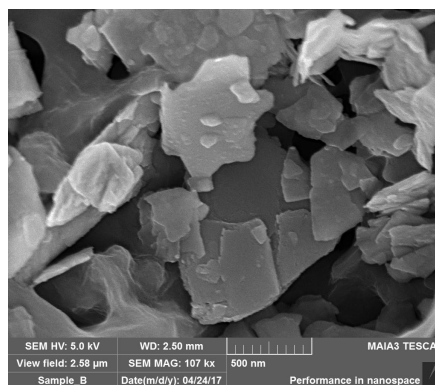


Figure 3. Scanning electron micrograph of the surface of a MoS₂ film vacuum filtered onto a cellulose membrane. This was a dispersion at pH 4. The detector used was in-beam SE (secondary electron)



Figure 4. Images of the dispersions centrifuged at 500 rpm at concentrations ranging from pH 1 to 5

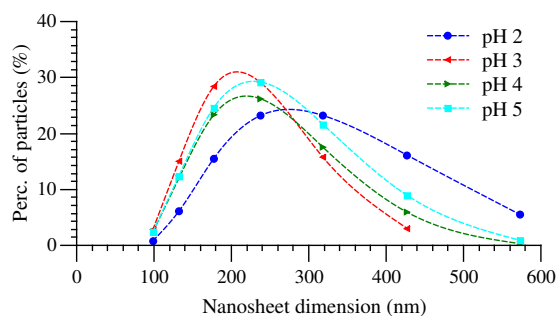


Figure 5. PSD for dispersions at varied pH concentrations

Conclusions

The dispersions of exfoliated 2D nanomaterials such as MoS₂ will be successful as long as the pH concentration is higher than 2 to avoid flocculation of the nanosheets. Even though the sedimentation occurs using acetic acid as a solvent, we measured a reasonably high concentration of nanosheets after 600 days of sample preparation at pH 4. In addition, thin nanosheets can be achieved with the shear-exfoliation method.

Acknowledgments

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Author Biography

Viviane Forsberg has a bachelor’s degree in chemical engineering from the Federal University of Sao Carlos, Brazil and a Master of Engineering in pulp and paper technology from the Munich University of Applied Sciences, Germany. She has completed her licentiate’s degree in Engineering Physics in 2016 and is finishing her doctorate degree in Engineering Physics at Mid Sweden University in Sundsvall, Sweden. She has worked previously at Oc Printing Systems (Germany), Siemens (Germany and Brazil) and Digital Printing Center (Sweden). She is a former ambassadorial scholar from Rotary International (2002-2003) and a Rotary member in Sundsvall.