Journal of Colloid and Interface Science 468 (2016) 247–252

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

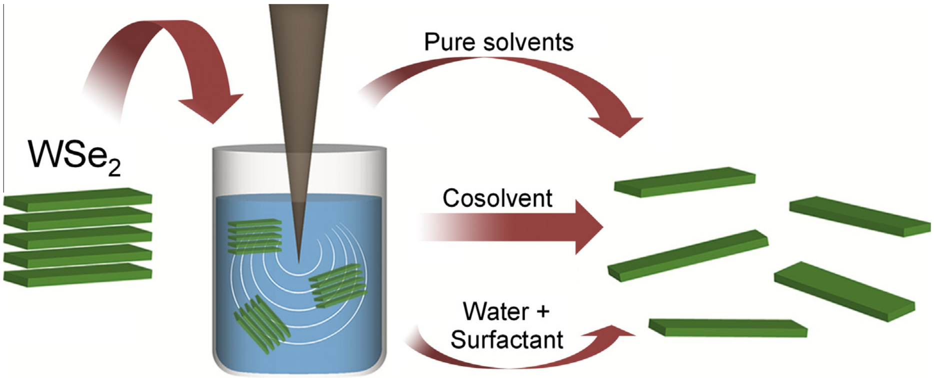
journal homepage: www.elsevier.com/locate/jcis

Solution-processable exfoliation and suspension of atomically thin WSe_2

Daniel Gerchman *, Annelise Kopp Alves

Ceramic Materials Laboratory, Federal University of Rio Grande do Sul, Osvaldo Aranha Av., 99/709, Porto Alegre 90035-190, Brazil

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 21 December 2015
Revised 26 January 2016
Accepted 28 January 2016
Available online 29 January 2016

Keywords:
WSe_2
Liquid exfoliation
Semiconductors
Layered materials
Surface properties

ABSTRACT

Hypothesis: A scalable method for the production of low-dimensional semiconductor materials, such as tungsten diselenide (WSe_2), is crucial for applications in flexible and transparent optoelectronic devices. Liquid exfoliation technique can be employed to fabricate a colloidal suspension of WSe_2 nanosheets as a low-temperature and solution-processable route.
Experiments: The production of atomically thin WSe_2 by liquid exfoliation is investigated, focusing the maximization of the concentration in the resulting suspension by selecting the most suitable solvent for this process. Three different strategies are compared: exfoliation in pure solvents, mixed solvent and aqueous solutions with surfactant.
Findings: N-methylpyrrolidone, previously reported as suitable solvent for suspension of other layered materials, results in the highest concentration among the pure solvents tested in this work; however a simple mixture of 30% of propan-2-ol in water surpasses its performance offering a low cost alternative. An optimal surface tension of 28 mN m^{-1} is proposed and the influence of the molecular size of the solvent is also considered. The use of anionic surfactant in water makes feasible the exfoliation of WSe_2 in aqueous solutions. The analysis of different exfoliation approaches under same processing conditions permits adequate comparison between different solvent systems and reveal optimal parameters for high yield liquid exfoliation of WSe_2.

1. Introduction

Tungsten diselenide (WSe_2) is a semiconductor and part of the transition metal dichalcogenide (TMDC) family. Its structure consists of triatomic layers of selenium and tungsten held together

---

* Corresponding author.
E-mail address: gerchmans@gmail.com (D. Gerchman).

http://dx.doi.org/10.1016/j.jcis.2016.01.073

by Van der Waals forces that allow the material to be exfoliated into monolayers [1,2]. Reducing its size to the sub-nanometer scale offers monolayers with distinct properties, such as transitions from 1.2 eV indirect to 1.7 eV direct bandgap [3–5], resulting in intense photoluminescence [6]. As a two-dimensional semiconductor, WSe_2 can be used in flexible solar cells and light-emitting devices [7–9], anodes of Li-ion batteries [10,11], and also in water treatment [12,13].

The most common method for obtaining TMDC monolayers is mechanical exfoliation, in which an adhesive tape is used to isolate the layers of the material [1,14,15]. Despite the high quality of the resulting monolayers, this technique is impractical in industry due to its low yield. Other routes to produce monolayers include chemical vapor deposition (CVD) [16–18], intercalation [19–22] and liquid exfoliation [23–25]. In CVD, precursors in the gas state are used for TMDC monolayer synthesis, which requires high temperatures that increase the cost of this technique. In the intercalation method, small ions [22] are introduced in between layers, weakening the binding forces, followed by a strong reaction with water that separates the layers. Despite the large amount of exfoliated material obtained with this technique, damage is caused to the structure of the material [26]. This is also a very humidity-sensitive route due to the intense reaction between water and the intercalated molecules, requiring handling precautions.

Liquid exfoliation is a simple and solution-processable method for producing TMDCs nanosheets [27]. In this process, ultrasonic waves are applied to a mixture of bulk layered material and a properly selected solvent, providing enough energy to overcome the attraction forces between layers and generating exfoliated nanosheets. After sonication, the dispersion is centrifuged to remove particles that were unsuccessfully exfoliated [28]. The result is a supernatant containing a colloidal suspension of material only a few layers thick. This can be used in a variety of applications such as composites [27], water treatment [29], batteries [30] and printed devices [31–33]. Because it is a simple, low-hazard method that is insensitive to the environment and does not require high temperatures, liquid exfoliation is ideal for large-scale production of two-dimensional materials in the industry.

In this technique, the proper selection of a solvent is critical for efficient exfoliation [27,34]. A suitable solvent should be capable of generating highly concentrated suspensions containing materials only a few layers thick while keeping the dispersion stable for long periods without precipitation. Three different solvent systems can accomplish this: pure solvents, solvent mixtures and aqueous systems stabilized with surfactants.

Exfoliation in pure solvents with certain TMDCs such as MoS_2 and WS_2 has already been studied [27,35]. According to Hernandez et al. [36], for the solvent to have a high performance in the separation of layers with minimum re-aggregation, the differences in surface energy between the two components should be minimized. Since surface energy and surface tension are related, a specific surface tension is necessary for the solvent to promote exfoliation with optimized yield. For some TMDCs, these values are in the 30–40 mJ/m^2 range, with N-methylpyrrolidone (NMP) being a prominent candidate solvent for exfoliation of these materials [27,28,34,35,37–39]. Controlling process parameters such as sonication time, initial concentration and centrifuge speed makes it possible to obtain concentrations of exfoliated TMDCs as high as 40 mg/mL [28].

It is also possible to obtain a system with ideal surface tensions by mixing different solvents [40–42]. With this method, also known as cosolvent approach, solvents that by themselves are inadequate for the exfoliation (i.e., water, ethanol) can be mixed in a defined ratio, generating the optimal surface tension for the system.

As an alternative to pure solvents and solvent mixtures, aqueous solutions with non-ionic [43] and ionic surfactants [44] can be used in the production of TMDCs nanosheets. The surfactants act as layer stabilizers in the dispersion, avoiding precipitation.

Even though there are studies with other TMDCs, such as MoS_2 and WS_2, currently there is no research in the literature on liquid exfoliation of WSe_2. Additionally, the currently reported studies concerning different approaches to liquid exfoliation are conducted under distinct processing conditions, such as sonication type, initial concentration, exfoliation time, and centrifugation speed and time. This makes any comparative study between exfoliation of TMDCs in pure solvents, mixture of solvents and aqueous solutions with surfactants impracticable. Selecting the most suitable solvent system for exfoliation is critical to produce monolayers of WSe_2 in high concentrations, a condition that is necessary for uses in inkjet printing and other applications.

In this work, we prepare two-dimensional WSe_2 nanosheets via liquid exfoliation. We conducted experiments with pure solvents, mixed solvents and water with surfactant in order to identify the appropriate solvents systems for this process.

2. Materials and methods

For the pure solvent survey, we used deionized water, acetone (Dinâmica, ⩾99.5%), methanol (Química Moderna, ⩾99.8%), ethanol (Dinâmica, ⩾99.5%), propan-2-ol (Nuclear, ⩾99.5%) and N-methyl-2-pyrrolidone (Sigma–Aldrich, ⩾99%). For the solvent mixture studies, methanol, ethanol and propan-2-ol were mixed with deionized water in proportions varying from 0% to 100% under constant stirring and were stored in closed flasks to avoid evaporation. The surface tension data of the mixtures were retrieved from Vazquez et al. [45]. To prepare the systems with water and surfactant, anionic surfactant sodium dodecyl sulfate (Sigma–Aldrich, ⩾98.5%) was mixed with deionized water at 2 g/L under constant stirring until complete dissolution.

The samples were prepared by adding 5 mg of bulk WSe_2 (Alfa Aesar, ⩾99.8%) in 5 mL of pure solvent, mixture of solvents or water with surfactant. The exfoliation was performed with an ultrasonicator (Ultrasonic Processor 500 W, Cole-Parmer, amplitude 20%) with a probe tip for 30 min using a cyclic program of 20 s on followed by 1 s off. During sonication, the sample was maintained in an ice bath to keep the temperature low during the process and to avoid solvent evaporation.

After 30 min of sonication, all of the volume was transferred to falcon tubes, and a centrifuge (Quimis Q-222T204) was used to isolate the exfoliated material in the supernatant and multilayers in the precipitate. Centrifugation occurred for 20 min at 7000RPM. The top 60% of the supernatant was then carefully collected using a pipette for further analysis. Samples were prepared in triplicate in order to provide data for average and standard deviation. Every experiment was conducted under identical process parameters (time, power, program, probe positioning, WSe_2 concentration, centrifugation time and speed) to enable subsequent comparison of the results.

In order to assess the amount of exfoliated material resulting from the process, absorbance was used as a study parameter. The relationship between absorbance and concentration was determined by atomic absorption spectroscopy (AAS) (PerkinElmer). For absorbance measurements, we used a Cary 7000 UV/VIS spectrophotometer (Agilent Technologies) in 1 cm optical path cuvettes at 760 nm. Morphological analysis was conducted in a JEOL JEM-2010 transmission electron microscopy (TEM) operating at 200 kV.

3. Results and discussion

The extinction coefficient at 760 nm of liquid-phase exfoliated WSe_2 was determined by AAS to be 25.566 $mL\,g^{-1}\,cm^{-1}$