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Research Article

Fast high-shear exfoliation of natural flake graphite with temperature control and high yield

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Abstract

High-shear exfoliation of graphite is a cost-effective liquid-phase exfoliation (LPE) method for producing few-layer graphene dispersions. However, the drawbacks of LPE such as low graphene concentrations, long processing times and solvent residuals hamper the scalability of the process and applicability of the dispersions. Here, we demonstrate a fast graphene synthesis where concentrations as high as 3 mg/ml with a 3% yield are produced only after 2 h of shear exfoliation in environmentally friendly aqueous medium using sodium cholate as surfactant. The produced graphene is of high quality and mostly less than 5 layers thick. The high concentration is attributed to a proper choice of effective mixing parameters, low exfoliation temperature (10 °C) and an appropriate surfactant concentration. In addition, we noticed that larger graphite flakes (250 μm-1 mm) increased the lateral dimensions of the exfoliated sheets while the yield and concentration were independent of the flake size. Furthermore, using larger graphite flakes improved the conductivity of the subsequent graphene films. Prior to film fabrication, dialysis removed excess surfactant from the dispersions improving the film conductivity (17 000 S/m) by ca 40%.

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1. Introduction

Since the first successful exfoliation of graphite to produce freestanding graphene in 2004 [1], graphene-based nanomaterials have been a subject of extensive research [2]. Micromechanical cleavage, a process where monolayers of carbon are peeled from graphite crystals, was the first reported method for the isolation of graphene and it is still applied in the preparation of high-quality monolayer graphene [1–3]. Since then, various growth methods such as heteroepitaxial growth on SiC substrates [4,5], growth on metal substrates [6,7] and chemical vapor deposition [8–10] have also been developed. However, none of these methods has shown potential for scalability as the growth methods are often complex, costly, and require harsh synthesis conditions. Additionally, while a range of techniques can produce graphene, many of the potential applications demand graphene to be dispersed in liquids [11]. Graphene dispersions can be introduced into various processes such as blending, casting or functionalization, and it can find use in several application areas such as composites, energy storage, bio-applications, and transparent conductive layers [2,11]. Exfoliating graphite oxide in water is a widely used method which produces dispersions of electrically non-conducting graphene oxide (GO) in high concentration [12–15]. However, even after reduction of GO to its conducting form (RGO), the carbon lattice contains defects [12,14]. The strong oxidizing and reducing agents causing the defects are also a safety and environmental risk [16].

In order to circumvent the issues related to GO and RGO, liquid-phase exfoliation (LPE) techniques such as sonication [17,18] and high-shear exfoliation [19–21] have been developed. With these techniques, defect-free and unoxidized graphene can be produced. In LPE, pristine graphite is directly exfoliated in a liquid to produce dispersions of few-layer graphene. The first reported LPE technique was based on sonication where stable dispersions of few-layer
graphene were obtained with concentrations up to 0.01 mg/ml after 30 min bath sonication in N-methylpyrrolidone (NMP). The method is based on creating shock waves with ultrasound that has high enough energy to break the inter-layer van der Waals bonds in graphite [17]. However, sonication has shown little potential for scalability due to its high energy consumption, long processing time and low concentration of the exfoliated material. In high-shear exfoliation, a shear force is applied to separate the graphene sheets. Chen et al. initially introduced this technique by exfoliating graphite in a vortex fluidic device where the shearing arose from the interplay between centrifugal and gravitational forces [19]. After that, Paton et al. demonstrated a shear exfoliation method based on a laboratory mixer with a rotor-stator combination that created shear force. They showed that high-shear exfoliation has the potential for being used at industrial scale [20].

An important parameter affecting the exfoliation efficiency in LPE is the dispersing medium. The dispersing medium should provide non-covalent stabilization for the hydrophobic graphene to avoid re-aggregation. A large variety of organic solvents has been explored for this purpose and it has been proposed that exfoliation occurs most optimally when the surface energies of the solid and the solvent match, i.e., when the net energetic cost for exfoliation is minimal. In the case of graphite, this occurs when the surface tension of the solvent is ranges from 35 to 50 mN/m [17]. In particular, the surface tension around 40 mN/m has been noticed to be the most optimal in many reports [22–24]. Although many organic solvents meet this criterion, environmental issues caused by their high boiling points and toxicity limit their applicability as a dispersing medium. In addition, many of the solvents are expensive which also reduces the number of suitable solvents. It is possible to overcome these issues by using water-based surfactant solutions, which also allows the use of the produced graphene in biological applications [16]. The surfactant is considered to have a dual role; it promotes exfoliation by reducing the surface tension of water and it prevents re-aggregation [24,25] by electrostatic repulsion (ionic surfactants) or steric hindrance (mainly non-ionic surfactants) [26]. Some ionic surfactants, such as the bie salt sodium cholate (SC) can provide stabilization both via steric hindrance and electrostatic repulsion [27].

In order to utilize the full potential of graphene, there is a need to develop a commercially viable and environmentally friendly method for mass production of high-quality graphene. At the moment, the drawbacks of LPE methodologies are lengthy exfoliations which typically result in low graphene concentrations. For example, sonication-induced LPE typically results in graphene concentrations under 1 mg/ml [17,28–31]. A few exceptions with higher concentrations of 1.2 mg/ml [18] and 7.1 mg/ml [32] have been reported with long sonication times of 460 h and 24 h, respectively. The scalable high-shear exfoliation method has not yet been fully explored and there are only a few reports focusing on shear mixing in environmentally friendly aqueous media to produce dispersions of few-layer graphene [20,21,33–36]. The highest concentrations reported in these papers are about 1 mg/ml [21,33,34] using processing times up to 4 h [21]. As such, LPE and especially high-shear exfoliation are still rather new techniques, and albeit the apparent simplicity, there are many possible aspects that affect the exfoliation outcome in terms of quantity and quality. Such aspects include the properties of the graphite source material such as the flake size, the surfactant type and its concentration, as well as the mixing parameters (such as rotor speed and mixing time). Some of these aspects, such as the mixing parameters, have been studied more extensively [20,21], while some other parameters have gained less attention. Particularly, the effect of the flake size on the exfoliation outcome has not achieved much attention and its effect is unclear. It is of interest to study this, since typically, large graphite flakes with high crystallinity are used to obtain high-quality few-layer graphene. Additionally, reducing the amount of solvent and surfactant residuals is of great interest since they limit the applicability of the produced material for example by decreasing the conductivity of the subsequent films.

In this paper, we present a fast method for preparing highly concentrated and defect-free graphene dispersions with high yield. The high concentration and yield are achieved by shear exfoliation in aqueous media without using any costly and hazardous chemicals. Furthermore, this environmentally friendly process does not require a lengthy exfoliation making it more compatible with environmental requirements. To the best of our knowledge, the method presented here is one of the fastest methods reported offering a high graphene concentration using shear mixing in aqueous media. We obtain high concentrations by carefully controlling the experimental conditions such as surfactant (SC) concentration and temperature during exfoliation. The amount of residual surfactant in the spray-coated few-layer graphene films was reduced by dialyzing the graphene dispersions after exfoliation. With the help of dialysis, we achieve high film conductivities comparable with values obtained using high-temperature annealing. Since we used self-produced natural flake graphite, we were also able to study the effect of the graphite flake size on the concentration and quality of the exfoliated sheets. This has not been previously reported using a single graphite source. The quality of the exfoliated sheets was analyzed with atomic force microscopy (AFM) and Raman spectroscopy.

2. Experimental

2.1. Materials

Natural flake graphite from Haapamäki, Finland was used for most of the experiments in this work. The graphite ore was enriched in an in-house process to a concentrate containing 99.3 ± 0.5% (m/m) carbon and a portion of the purified graphite was sieved into 6 different size fractions (<45 μm, 45–63 μm, 63–125 μm, 125–150 μm, 150–250 μm and 250 μm–1 mm). The carbon content of the final product was determined using a Flash 2000 Elemental Analyzer (ThermoFisher Scientific). A more detailed description of the graphite purification process and material characterization can be found in the Supplementary Information material S1 and S2, respectively. Commercial graphite from Alfa Aesar (<45 μm) was used for studying the effect of surfactant concentration and temperature during exfoliation on the exfoliation efficiency. It was also used as a reference material in graphite characterization together with graphite from Sigma-Aldrich (>150 μm).

Sodium cholate (SC) powder used for the preparation of the surfactant solutions was received from Acros Organics and it was dried overnight in oven at 100 °C prior to use. Deionized MilliQ water (resistivity 18 MΩ cm) was used throughout this work.

2.2. Preparation of graphene dispersions

In the liquid-phase exfoliation of graphite, we used two different POLYTRON® immersion dispersers (Kinematica AG, Switzerland) based on the rotor-stator technique. The effect of the surfactant concentration was investigated with a PT 1200E drive unit coupled with a PT-DA 07 dispersing aggregate. A PT 10–35 GT drive unit coupled with a PT-DA 20 dispersing aggregate was used in the rest of the experiments. Technical data about these mixers with calculated maximum shear rates can be found in Supplementary material S3. In a typical experiment, 10.0 ml of 5.0 mM SC solution was first combined with a known amount of graphite
determined to be 6600 ml mg value at 660 nm. The value of the extinction coefficient (ε) was 6800 ml mg⁻¹ cm⁻¹ after exfoliation (1:4 mixture of 30% H₂O₂ and concentrated H₂SO₄) for 1 h. After this, the dispersions were centrifuged for 1 h to separate and remove any unexfoliated graphite. A Herml Z 200 laboratory centrifuge was used with a rotor speed of 1500 rpm corresponding to a relative centrifugal force (RCF) of 270 G.

UV–vis spectra were recorded with a Shimadzu UV-2501PC spectrophotometer to determine the concentration of the resultant dispersions. The concentration was calculated according to Beer and Lambert’s law, A( absorbance) = εbC using the absorbance value at 660 nm. The value of the extinction coefficient, ε, was determined to be 6800 ml mg⁻¹ cm⁻¹ (see Supplementary material S4) which is the same value as two other independent research groups have obtained [28,31].

To decrease the amount of the surfactant in the dispersions, the dispersions were dialyzed for 24 h under magnetic stirring using Spectra/Por® 3 dialysis membranes with a molecular weight cut-off of 3500 Da. The volume ratio of the sample and the dialysate (water) was 1:100.

2.3. Characterization

2.3.1. Atomic force microscopy (AFM)

The AFM samples used in the size determination of exfoliated sheets were prepared by immersing silanated silicon wafer plates in dilute graphene dispersions (C = 0.1 mg/ml) for 15 min followed by rinsing with water to remove any weakly attached particles (including free surfactant molecules). The Si wafers were first cleaned by immersing them in a Piranha solution (1:4 mixture of 30% H₂O₂ and concentrated H₂SO₄) for 1 h. After this, the platelets were silanated by coating them with a 5% dilution of N-trimethoxysilylpropyl-N,N,N-trimethylammonium chloride (50% in methanol; Abcr) for 2–5 min after which the plates were rinsed with ethanol and water and dried with compressed air. Silanitation increases the number of binding sites for graphene on the surface of the Si wafer. It also helps to avoid aggregation of particles on the sample surface since the graphene sheets are attached by electrostatic interactions between negatively charged cholate anions and the positively charged silane moieties. This method should enable the attachment of only one layer of the material from the dispersion. AFM images were captured with an NTegra PRIMA (NT-MDT, Moscow, Russia) AFM instrument. 5.0 μm × 5.0 μm images (1024 × 1024 pixels) were captured in tapping mode under ambient conditions (T = 24 ± 1 °C, RH% = 36 ± 4) using silicon cantilevers with a nominal tip radius of curvature of 8 nm (Model: HQ:NSC18/Al BS) and with a scanning rate of 1.30–1.56 Hz. The SPIP™ image analysis software (Image Metrology, Lyngby, Denmark) was used for image post-processing and particle size determination (Particle&Lore Analysis program).

2.3.2. Raman spectroscopy

Raman spectra were recorded with a Renishaw Ramascope imaging microscope (with the WireTM v1.3 Raman software). The spectra were recorded using an Ar-ion laser with an excitation wavelength of 514 nm and a laser power of 20 mW in the wave-number region from 4000 to 500 cm⁻¹. The spectrometer was calibrated against a Si standard (520 cm⁻¹). The Raman spectra were collected directly from the graphite flakes without any pretreatment. For the measurement of the dispersions, ca 10 μl of liquid was deposited on a glass plate after which it was dried in an oven at 60 °C for about 15 min. At least 5 spectra of each sample were recorded.

2.3.3. Thermogravimetric analysis

Thermogravimetric analysis (TGA) of the samples was performed with a TA Instruments SDT Q600. The analysis was conducted under nitrogen gas in an oxygen-free environment up to 1300 °C with a heating rate of 10 K/min. Dialedyzed and non-dialedyzed dispersions prepared from the in-house graphite containing all size fractions were analyzed. The dispersions were dried prior to the analysis. For comparison, TGA was also performed on pure sodium cholate powder.

2.4. Film preparation and electrical conductivity measurements

A standard airbrush pen was used to manually spray-coat the dispersions on thin glass substrates. Spray coating was performed on a heating plate with an electronic contact thermometer (IAK ETS-DS) which maintained a temperature between 150 and 200 °C to speed up the evaporation of water from the dispersions. The prepared films were ca 500–1000 nm thick as measured with AFM. The film thickness was calculated based on three 80 × 80 μm AFM images (512 × 512 pixels).

The electrical conductivity of the films was determined using the four-probe technique in a linear configuration with a tip spacing of 1.82 mm. A bias current of 1 mA was applied over the films with a Keithley 2400 SourceMeter® until a stable and reproducible voltage was obtained. The measurements were conducted both in a glovebox under nitrogen gas after 4 days of drying and in ambient conditions (T = 21.0 °C and RH% = 21.5) 1 month after their removal from the glovebox. The film conductivities were calculated using correction factors for finite size [37].

3. Results and discussion

3.1. Preparation of graphene dispersions

In our task of optimizing the exfoliation process to produce highly concentrated graphene dispersions, we started by investigating the effect of the surfactant concentration on the concentration of graphene dispersions. Previously, graphene has been stabilized in a variety of SC concentrations, such as 5 mg/ml (shearing) [20], 20 mg/ml (sonication) [38], and 40 mg/ml (sonication) [39]. These papers report rather low graphene concentrations (<0.1 mg/ml) and one reason for this could be a non-optimal SC concentration. Different factors have been speculated to affect the graphene-surfactant interaction such as the surface tension of the solution [17], the critical micelle concentration (CMC) of the surfactant [29] and the concentration ratio between graphene and the surfactant [24]. Here, we used a broad SC concentration range from 0.075 to 200 mM (0.032–86 mg/ml) with two initial concentrations of graphite, namely C(t) = 20 mg/ml and 100 mg/ml in order to analyze the graphene-SC interaction from the aforementioned point of view. It was assumed that the optimal graphene production is dependent on the ratio of C(t) and SC concentration since at high graphite concentrations, a large amount of surfactant molecules are adsorbed on the formed graphene sheets which could result in depletion of free SC molecules after some critical point. The depletion of free surfactant molecules through adsorption also increases the surface tension of the solution, which would affect the dispersability [24].
As can be seen in Fig. 1, there is an SC concentration region between 1 and 10 mM (0.43–4.3 mg/ml) where graphene is most effectively dispersed. It is evident from this result that the surfactant concentration is a key factor affecting the final graphene concentration as above and below the optimal concentration region, the graphene concentration is almost one order of magnitude lower. Interestingly, the optimum SC concentration range is the same for both initial graphite concentrations, although the graphene concentration with C(i) = 100 mg/ml increases more slowly in the beginning. Above 10 mM, there is a clear drop in the graphene concentration. We note that the peak maximum is located just below the CMC of SC, which was determined to be ca 11 mM at room temperature [40]. The surface tension of the SC solution close to the CMC is about 48 mN/m (measured with KSV Sigma 70 Tensiometer). Since the surface tension of the solution still was in the “optimal” region (i.e., 35–50 mN/m) after reaching the CMC, the drop in the graphene concentration at higher SC concentrations cannot be explained by a non-optimal surface tension. However, the vicinity of CMC could explain the location of the peak maximum. Previously, it has been noticed in a simulation study that the stability of colloidal surfactant mixtures is the highest close to the CMC of the surfactant [41]. After reaching the CMC, a micelle depletion mechanism destabilizes the surfactant-coated colloidal particles. This micelle depletion mechanism [41,42] results in an attractive interaction between the colloidal particles causing them to aggregate. The more surfactant is added, the more micelles are formed and the stronger the destabilizing effect. This kind of interaction has also been suggested for the destabilization of carbon nanotubes (CNTs) [43]. Thus, we speculate that the graphene-SC interaction is affected by the same micelle depletion mechanism explaining the gradual decrease of graphene concentration with increasing SC concentration beyond the CMC. It should be noted that all graphene surfaces are still expected to be fully covered with surfactant molecules. The micelle depletion mechanism also explains that the peak maximum is at the same SC concentration for both initial concentrations of graphite.

After finding the optimal surfactant concentration for exfoliation, we investigated the effect of mixing parameters, i.e. rotor speed (N), mixing time (t) and initial graphite concentration (C(i)) on the concentration of graphene dispersions in 5.0 mM SC solutions. As expected, the concentration of the exfoliated sheets increases with increasing N, t and C(i) (see Supplementary material S5). We also calculated the scaling exponents for each of these parameters which show how much they affect the exfoliation outcome. The scaling exponents are dependent on the experimental conditions such as the equipment used (i.e., the rotor-stator geometry). We chose the highest possible rotor speed (N = 16 500 rpm) for our set-up with the PT 10–35 GT laboratory mixer and a high initial graphite concentration (C(i) = 100 mg/ml) as we aimed to prepare as highly concentrated dispersions as possible in a relatively short time (2 h). In this manner, we prepared few-layer graphene dispersions from size-fractioned graphite and from graphite containing all particle sizes (d < 1 mm).

We obtained dispersions with concentrations of ca 3 mg/ml with 3% yields both for the size-fractioned graphite and for the graphite containing all particle sizes (Fig. 2). That is, the final graphene concentration was independent of the original flake size of graphite. In a previous study, Mori et al. found that concentration increased more than 10 times if smaller graphite flakes were used [44]. However, their flake size range (from 2.2 to 71 μm average flake diameter) and the applied exfoliation method (pressure homogenizer) was different from ours. In addition, Mori et al. investigated the effect of the flake size using commercial graphite from different sources. In our study, we had the benefit of using the same graphite source to ensure that the flake size is the only variable. This is important since graphite from different locations might have different qualities that can also affect the exfoliation efficiency and the quality of the exfoliated sheets. As we found that the final graphene concentration is indifferent of the original flake size of graphite when producing highly concentrated dispersions, it can be stated that it is not necessary to use the usually more expensive larger flakes for this purpose.

Table 1 shows exfoliation results obtained with shearing in aqueous media. The results listed in Table 1 use dispersing agents that are environmentally friendly (mostly water-soluble polymers and surfactants), and they were used as such without any tedious pre-treatment steps. Among these, the concentration we have obtained is the highest. That is, we have demonstrated a simple and effective method for producing highly concentrated dispersions in a short time. Our results also underline the efficiency of shear exfoliation compared to sonication as we obtained a concentration of 3 mg/ml after just 2 h of mixing and sonication typically gives values under 1 mg/ml after several hours of mixing. It should also be pointed out that the 2 h mixing time was chosen due to practical reasons and that by prolonging the mixing time, the concentration and yield would be even higher as can be deduced from Fig. S5.1C. The high concentrations reported here can be attributed to the

Fig. 1. The concentration of the exfoliated sheets as a function of SC concentration with C(i) = 20 mg/ml (red squares, left scale) and 100 mg/ml (blue triangles, right scale) graphite from Alfa Aesar with N = 22 500 rpm after 15 min of mixing using PT 1200E drive unit coupled with a PT-DA 07 dispersing aggregate. The vertical dashed line represents the critical micelle concentration (CMC) of SC [40]. (A colour version of this figure can be viewed online.)

Fig. 2. The concentration of the exfoliated sheets as a function of the graphite flake size after 2 h of mixing with C(i) = 100 mg/ml and N = 16 500 rpm using in-house graphite and PT 10–35 GT laboratory mixer. The results are an average of four experiments for the size-fractioned graphite samples and an average of eight experiments for graphite containing all fractions. The temperature during exfoliation was 10 °C.
proper choice of mixing parameters and surfactant concentration regime. In addition, we exfoliated the samples at T = 10 °C since we found that graphene concentration increased with decreasing temperature during exfoliation. The graphene concentration is about 2 times higher at T = 10 °C than at T = 50 °C after just 15 min of mixing (see Fig. S6.1). While the temperature affects many properties of a surfactant solution such as surface tension and CMC, we speculate that the enhanced adsorption of SC molecules on the surface of graphene particles observed at T = 10 °C is the reason for the increase in the graphene concentration [45]. In literature, the interaction of SC with CNTs has been studied in detail and it was verified with molecular dynamics simulation that the SC-CNT interaction is hydrophobic [46]. The amphiphilic surfactant adsorbs on CNTs through hydrophobic bonding which is a typical mechanism for surfactant-solid interaction in liquids [45]. It is expected that this kind of physical adsorption [47] through hydrophobic bonding also applies with graphene-SC interaction. Since adsorption is an exothermic process, low temperature favors adsorption according to Le Chatelier’s principle meaning that physical adsorption is inversely proportional to the temperature. In addition to this, the mobility of the graphene particles and free surfactant molecules decreases with decreasing temperature, which may have a positive effect on the stability of graphene-SC particles. Since the temperature of the dispersions tends to increase with increasing mixing time, a temperature-controlled exfoliation is even more important when using prolonged mixing times.

3.2. Characterization

In addition to concentration determination, it is crucial to assess the quality of the exfoliated sheets. We used both Raman spectroscopy and AFM to analyze the exfoliation degree of the highly concentrated dispersions prepared from the in-house graphite. Raman spectroscopy was also used for the analysis of the defect content and AFM for the lateral size determination of the exfoliated sheets. Fig. 3A shows an AFM image of a sample exfoliated from the in-house graphite (d < 1 nm) and some examples of individual few-layer graphene sheets are shown in Fig. 3B and C. We conducted a detailed analysis on this sample as we calculated the dimensions of ca 10 000 particles in three AFM images captured from separate spots. As can be seen in Figs. 3A and 4, the sample contains flakes of different sizes. The majority of sheets are relatively small, under 100 nm in diameter but larger particles are also present (Fig. 4A). We also conducted an AFM analysis on the dispersions prepared from the different size fractions of graphite. The average diameters of the exfoliated sheets can be seen in the inset of Fig. 4A. Although the size differences between the different size fractions are rather small, the results indicate that the average size of the exfoliated sheets increases with increasing graphite flake size. One could also expect that if the difference in the original particle size was larger, we would also see a clearer difference in the size of the exfoliated sheets.

When analyzing the thickness of the exfoliated sheets from the AFM images, it is worth noting that there is a layer of surfactant molecules on both sides of every particle. This means that the measured height of the particles is larger than the theoretical thickness of graphene layers. It has also been shown that the apparent AFM height in tapping mode is dependent on the scanning parameters. Using high setpoints corresponding to low damping leads to a weak interaction between the tip and the substrate. Such weak interaction is typically dominated by attractive interactions, which may lead in distorted height data [48]. We used low setpoints during AFM tapping imaging in order to minimize the error in height. Paton et al. have considered the apparent AFM height of a surfactant-stabilized graphene monolayer to be ca. 2 nm and that each additional layer contributes to the height by 0.95 nm [19]. In another study, Novoselov et al. observed that the apparent AFM thickness of a monolayer was ca 1 nm and that each additional layer contributes to the thickness by 0.34 nm [1]. The thinnest flakes that we could find were ca. 1 nm in thickness. To this end, we can state that the sheets were well exfoliated; the AFM height of a vast majority of the sheets (ca 76%) was under 3 nm which corresponds to a maximum of 5 layers of graphene (i.e., few-layer graphene).

Fig. 5 shows the averaged Raman spectra of the few-layer graphene sheets exfoliated from graphite containing all size fractions (shown as well) and from the smallest and the largest fraction of graphite. The spectra of the exfoliated sheets contain three major peaks: the G band (≈ 1580 cm\(^{-1}\)), D band (≈ 1350 cm\(^{-1}\)) and the 2D band (≈ 2700 cm\(^{-1}\)), which are typical for solution-processed few-layer graphene [18,20,21,28,49]. The G band and the 2D band are always present in graphic materials whereas the D band stands for defects and depends on the quality of the material. The 2D band gives an indication about the number of graphene layers. A graphene monolayer would have a sharp 2D band roughly four times more intense than the G band [50]. In the spectra of the exfoliated sheets, the shape of the 2D band has become more symmetric and it has shifted to a lower wavenumber compared to the starting material (the spectra of the <45 μm and 250 μm–1 mm graphene fractions are shown in Fig. S2.2). Both factors indicate that the number of layers has decreased after exfoliation [50,51]. Furthermore, the 2D band of graphene with five or more layers is very similar to that of graphite [50–52] and since the 2D band of our dispersion is clearly distinguishable from that and resembles typical few-layer graphene, it can be stated that the dispersion mostly contains graphene with less than five layers. This result is in agreement with the AFM results. The Raman results also indicate that the exfoliation degree was the same regardless of the flake size of the starting material.

The relative D band intensity increased in all the spectra compared to the graphite spectrum (Fig. 5 and Table 2). The defects associated with the D band can be edges including grain boundaries and flake edges or topological (basal plane) defects in the sheet [53]. The D/G intensity ratio for the exfoliated sheets prepared

<table>
<thead>
<tr>
<th>Dispersing agent</th>
<th>Exfoliation time (h)</th>
<th>Concentration (mg/ml)</th>
<th>Yield (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>SC</td>
<td>4</td>
<td>0.07</td>
<td>0.07</td>
<td>[20]</td>
</tr>
<tr>
<td>Fairy dish washer</td>
<td>4</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>[21]</td>
</tr>
<tr>
<td>SC</td>
<td>2</td>
<td>0.7</td>
<td>1.8</td>
<td>[33]</td>
</tr>
<tr>
<td>Polyvinylpyrrolidone (PVP)</td>
<td>2</td>
<td>1.1</td>
<td>2.8</td>
<td>[33]</td>
</tr>
<tr>
<td>Ethanol + sodium dodecyl sulphate (SDS)</td>
<td>14</td>
<td>0.26</td>
<td>0.26</td>
<td>[36]</td>
</tr>
<tr>
<td>Black tea</td>
<td>0.25</td>
<td>0.032</td>
<td>0.19</td>
<td>[35]</td>
</tr>
<tr>
<td>Modified polyvinyl alcohol (mPVOH)</td>
<td>1.66</td>
<td>1.04</td>
<td>4.2</td>
<td>[34]</td>
</tr>
<tr>
<td>SC</td>
<td>2</td>
<td>3.0</td>
<td>3.0</td>
<td>This work</td>
</tr>
</tbody>
</table>

Table 1: A comparison of the exfoliation results obtained by shear exfoliation of graphite using different dispersing agents in water solutions.
The average Raman D/G intensity ratios (n = 5) of graphite and exfoliated sheets prepared from all size fractions and from the smallest (<45 μm) and the largest (250 μm–1 mm) size fraction of graphite. The intensity ratios are calculated from the peak amplitudes (n = 5).

<table>
<thead>
<tr>
<th>Graphite particle size</th>
<th>Raman D/G intensity ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Starting material</strong></td>
<td><strong>Exfoliated sheets</strong></td>
</tr>
<tr>
<td>All fractions (&lt;1 mm)</td>
<td>0.06 ± 0.02</td>
</tr>
<tr>
<td>&lt;45 μm fraction</td>
<td>0.05 ± 0.02</td>
</tr>
<tr>
<td>250 μm–1 mm fraction</td>
<td>0.06 ± 0.02</td>
</tr>
</tbody>
</table>

using all size fractions is 0.46 ± 0.20. This value is in the same range as reported in other similar studies that use shear exfoliation [21,33,54]. The increase in the D/G intensity ratio is most likely due to the formation of new edges since the flakes become smaller during exfoliation and the Raman excitation beam spot size (ca 2 μm) is larger than the exfoliated sheets. We can also note that the D/G intensity ratio of the sheets exfoliated from the <45 μm fraction was somewhat higher than of the sheets exfoliated from the 250 μm – 1 mm fraction (see Table 2). The I(D)/I(G) ratios of the middle fractions were between these two values (not shown here). These results indicate that the average size of the sheets exfoliated...
from the <45 μm fraction is smaller than from the 250 μm−1 mm fraction. Since the AFM results also indicated that the particle size is smaller in the dispersions prepared from the <45 μm fraction than from the 250 μm−1 mm fraction, it is more likely that the higher intensity ratio is caused by a smaller flake size than basal plane defects.

To further confirm that the defects were of edge type, we analyzed the D/D’ intensity ratio of the exfoliated sheets. According to Eckmann et al., the D/D’ intensity ratio reveals the defect type as the boundary and edge defects give rise to D/D’ ≈ 3.5, vacancy basal plane defects to D/D’ ≈ 7 and sp² defects to D/D’ ≈ 13 calculated from the peak amplitudes [55]. The D/D’ intensity ratio for our starting material containing all the size fractions and for the subsequent graphene dispersion was 3.7 ± 0.5 and 4.4 ± 0.6, respectively. The D/D’ intensity ratio is somewhat higher for the exfoliated sheets than for the starting material, but both of these values are closer to the value for boundary type defects than vacancy type basal plane defects confirming that no other defects than new edges were most probably not introduced during the shear exfoliation process.

3.3. Dialysis, thin film fabrication and conductivity

Finally, after assessing the quality of the highly concentrated few-layer graphene dispersions, we prepared electrically conductive films by spray-coating on thin glass substrates. Prior to the film fabrication step, the dispersions were dialyzed to remove excess surfactant. To verify that dialysis removes surfactant from the dispersions, we performed TGA on the dialyzed and the non-dialyzed samples. According to the TGA results, the dialyzed and the non-dialyzed dispersions contained 22% m/m and 27% m/m SC, respectively. It is assumed that dialysis only removes the free SC molecules from the dispersions and not the ones adsorbed on the surface of graphene by hydrophobic interactions. If the adsorbed SC molecules were also removed, the exfoliated sheets would restack in the hydrophilic environment. Nevertheless, we expect that dialysis removes the SC molecules which otherwise would be trapped between the layers of the exfoliated sheets during film preparation where they would decrease the conductivity of the films. To investigate the impact of dialysis on the conductivity of the films, we prepared films both from dialyzed and non-dialyzed dispersions. The average conductivities of the films from the dialyzed and non-dialyzed dispersions were 13 000 S/m and 8000 S/m, respectively (Fig. 6). That is, dialysis improved the conductivity of the films by 40%.

We also fabricated films from the dispersions prepared from the size-fractioned graphite. As can be seen in Fig. 6, the average conductivity of the films prepared from the smallest (d < 45 μm) and the largest fraction (d = 250 μm−1 mm) was 11 000 ± 1000 S/m and 15 000 ± 2000 S/m, respectively. The difference in conductivity could be attributed to the size difference of the exfoliated sheets. That is, the average particle size is somewhat larger in the dispersions prepared from the larger flakes than in the dispersions prepared from the smaller flakes as indicated by AFM and Raman D/G intensity ratio results (see Table 2). The porosity (the size and number of inter-flake junctions) of a graphene nanosheet network has been linked with its conductivity [56,57] and we speculate that when the film is composed of larger sheets, there will be less inter-flake junctions (or they will be smaller) than in a film that is composed of smaller sheets. The inter-flake junctions decrease the mobility in the nanosheet network thereby increasing the resistance in the system.

Conductivities as high as 17 300 S/m (the highest measured value for an individual film) were measured, which is higher than previously reported values for materials prepared in a similar manner. This value was achieved without any additional heating/annealing step, which in many reports has increased the film conductivity significantly [17,28,33,49,58]. For example, after annealing/heat at 250 °C, the conductivity of vacuum-filtrated few-layer graphene films increased from 5 to 6500 S/m [17]. Graphene electrodes prepared by spray-coating have displayed a conductivity of 859 S/m before annealing and 4095 S/m after annealing [58]. To the best of our knowledge, the highest reported value without any heat treatment is 6600 S/m [49], which is slightly lower than the values observed here using the non-dialyzed dispersions (ca 8000 S/m). The high conductivities in this study can be attributed to the usage of dialysis to remove the excess SC and to the absence of basal plane defects in the exfoliated sheets as verified by the Raman analysis. In some reports, the films were washed afterwards to remove some of the dispersing agent [20,33]. However, with this method, only the outermost surface is washed since it is impossible to remove the dispersant trapped between the layers after the film fabrication step. Washing the films after fabrication also limits their applicability.

4. Conclusions

A successful preparation of highly concentrated graphene
dispersions is a complex process with many different factors affecting the outcome. In this paper, we present a fast graphene synthesis showing that highly concentrated and defect-free few-layer graphene dispersions can be prepared in aqueous-based medium using the high-shear exfoliation method. We studied several aspects of the process from the properties of the starting material to the dialysis of the prepared dispersions in order to increase the concentration of the dispersions and thereby improve the applicability of the material. The concentration (3 mg/ml) and yield (3%) reported here are significantly higher than in previous reports using environmentally friendly water-based exfoliation medium. In addition to the choice of right processing parameters, the surfactant concentration and temperature during exfoliation affect the resultant graphene concentration significantly. The graphene concentration was found to be indifferent of the flake size rendering it unnecessary to use the usually more expensive larger flakes for this purpose. However, we concluded from AFM, Raman conductivity (up to 17 300 S/m) were achieved with the sheets dimensions of the exfoliated sheets. The highest individual flake graphite. The main benefit of using environmentally friendly water-based surfactant solutions is that the excess surfactant can be removed from the dispersions by dialysis. Dialysis is a useful method for removing extra surfactant since it does not limit the applicability of the subsequent films and it also improves the electrical conductivity of the films with about 40% (8000 S/m vs 13 000 S/m).

CRediT authorship contribution statement
Sara Lund: Conceptualization, Methodology, Investigation, Formal analysis, Visualization, Writing - original draft. Jussi Kauppila: Conceptualization, Methodology, Investigation, Writing - review & editing, Supervision. Saara Sirkia: Investigation. Jenny Palosaari: Writing - review & editing, Resources. Olav Eklund: Writing - review & editing, Project administration, Funding acquisition, Resources. Rose-Marie Latonen: Writing - review & editing, Supervision, Funding acquisition. Jan-Henrik Smått: Conceptualization, Methodology, Writing - review & editing, Supervision, Funding acquisition. Jouko Peltonen: Writing - review & editing, Supervision, Funding acquisition. Tom Lindfors: Conceptualization, Writing - review & editing, Supervision, Funding acquisition.

Declaration of competing interest
The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data
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