



TAMPEREEN TEKNILLINEN YLIOPISTO
TAMPERE UNIVERSITY OF TECHNOLOGY

MUSTAFA NURULLAH YURTSEVER
AQUEOUS DISPERSIONS OF GRAPHENE

Master of Science Thesis

Examiners: Professor Jurkka Kuusipalo
and Senior Research Fellow Johanna
Lahti
Examiners and topic approved on 01
March 2017

ABSTRACT

MUSTAFA NURULLAH YURTSEVER: Aqueous Dispersions of Graphene

Tampere University of Technology

Master of Science Thesis, 38 pages

September 2017

Master's Degree Programme in Materials Science and Engineering

Major: Materials Technology

Examiners: Professor Jurkka Kuusipalo, Senior Research Fellow Johanna Lahti

Keywords: graphene, aqueous dispersions, graphene dispersions, graphene colloids, non-covalent functionalization, surfactant stabilization.

Unprecedented properties of graphene continue to incite a great deal of interest for its prospective applications. Graphene is still at its early stages of utilization, and one big challenge is to overcome the strong attraction of graphene flakes and obtain a stable aqueous graphene dispersion at concentration.

To cope with challenge, this study investigates the colloidal stability of aqueous graphene dispersions stabilized by three different stabilizers. It has been identified that one of the stabilizers, the one denoted stabilizer 1, is suitable for the stabilization of commercial graphene flakes in water. Dispersions of graphene stabilized by stabilizer 1 in water has also been characterized by UV-VIS and TGA. As a result, aqueous graphene dispersions of stable for 12 weeks, up to 0,3 wt% graphene concentration as well as a 0,32 surfactant/graphene ratio were achieved.

PREFACE

This research is performed in order to fulfill the course of OPN-9006 Master's Thesis (equivalent 30 ECTS) in Materials Engineering Department of Tampere University of Technology.

The work presented in this thesis was also carried out as a contract work for BillerudKorsnäs. Due to IPR related issues, some details are left out. E.g. the names of the stabilizers are concealed – instead they are denoted as stabilizer 1, 2 and 3.

This thesis work is planned and carried out as a continuation of another thesis work which was done by Felix Lundkvist in March 2017 with the title of “Characterization of commercial graphene powders”. The substantial part of the research was conducted at Chemistry, Materials and Surfaces unit of RISE Bioscience and Materials Division, Drottning Kristinas väg 45, Stockholm, Sweden, during the period between 2017-02-01 – 2017-08-30.

I would like to express my gratitude everyone who supported me during the thesis work in particular to my supervisors Anwar Ahniyaz at RISE, Jurkka Kuusipalo and Johanna Lahti at the Tampere University of Technology. I would also like to thank Thomas Gillgren and Johan A Larsson at BillerudKorsnäs AB for their help. Without their support, it is not possible to finish the project successfully. I owe a huge debt of gratitude to my family, my fellow diploma workers and the staff of RISE for their bottomless support.

Stockholm, 20.09.2017

M. Nurullah Yurtsever

CONTENTS

1.	INTRODUCTION	1
1.1	Aim and Structure of Thesis	2
2.	LITERATURE REVIEW.....	3
2.1	Graphene	3
2.2	Surfactants.....	3
2.2.1	Adsorption of Surfactant at the Surface	4
2.3	Colloidal System	4
2.3.1	Electrical Double Layer	5
2.3.2	Electrostatic Stabilization.....	7
2.3.3	Steric Stabilization.....	7
2.3.4	Electrosteric Stabilization	7
3.	EXPERIMENTAL.....	8
3.1	Materials	8
3.1.1	Graphene Types.....	8
3.2	Methods	9
3.2.1	Preparation of Unpurified Graphene Dispersions (AGD).....	9
3.2.2	Preparation of Purified Aqueous Graphene Dispersion.....	9
3.3	Application Instruments.....	13
3.3.1	Sonication.....	13
3.3.2	Centrifugation.....	13
3.3.3	Ultracentrifugation.....	14
3.4	Characterization Instruments	14
3.4.1	UV-vis Spectrophotometry	14
3.4.2	Thermogravimetric Analysis (TGA)	15
4.	RESULTS AND DISCUSSION.....	17
4.1	The Stabilization Capacity of Different Surfactants Types	17
4.1.1	Visual Examinations	17
4.2	Presence of Graphene Reflecting on UV-vis	19
4.2.1	Interpretation	19
4.3	Investigation into varying parameters of Unpurified Dispersions	21
4.3.1	Determination of the ideal initial concentration.....	21
4.3.2	Effect of time.....	22
4.4	UV-visible spectrophotometry characterization of the purified stabilizer 1- Graphene dispersions.....	23
4.5	TGA MEASUREMENTS.....	25
4.5.1	Initial TGA measurements	25
4.5.2	TGA measurements of the dispersion.....	27
5.	CONCLUSIONS	28
5.1	Future Work	28
	REFERENCES.....	30

LIST OF FIGURES

Figure 1.	<i>Surfactant adsorption mechanism on graphene surface [25].....</i>	<i>4</i>
Figure 2.	<i>Depiction of electrical double layer formation and surface potential [29].....</i>	<i>6</i>
Figure 3.	<i>a) Electrostatic Stabilization, b)Steric Stabilization, c) Electrosteric Stabilization</i>	<i>6</i>
Figure 4.	<i>SEM images of selected flakes, graphene A and B (adopted from the master's thesis of Felix Lundkvist) [42]......</i>	<i>9</i>
Figure 5.	<i>The schematic illustration of the process making unpurified graphene dispersion AGD. (1) Blending of ingredients, water, surfactant, and graphene. (2) Ultrasonication. (3) Centrifugation. (4) Removal of sediment.....</i>	<i>9</i>
Figure 6.	<i>The schematic illustration of the process making one-time purified aqueous graphene dispersion. (1) First ultracentrifugation of the unpurified aqueous graphene dispersion (2) Removal of excess surfactant by decantation (3) Re-suspension of residual wet cake of graphene in water via ultrasonication.</i>	<i>10</i>
Figure 7.	<i>Thermal stability of graphite (a), rGO (b) and XGO (c). (The plot is directly adopted from the given reference) [63]......</i>	<i>15</i>
Figure 8.	<i>Demonstration of aqueous graphene dispersions stabilized by different surfactants, and a surfactant-free aqueous graphene solution (Image A, left-to-right: surfactant-free graphene, stabilizer 2, stabilizer 3 and stabilizer 1 graphene dispersions. Image B, left-to-right: stabilizer 3 and stabilizer 1).....</i>	<i>17</i>
Figure 9.	<i>Unpurified and purified graphene dispersion along with the diluted versions. (From left to right: Unpurified aqueous graphene dispersion stabilized by stabilizer 3, stabilizer 1, and Dilutions-stabilizer 1).....</i>	<i>18</i>
Figure 10.	<i>Pictures of stabilizer 1-stabilized graphene without any visible agglomeration or sedimentation.....</i>	<i>19</i>
Figure 11.	<i>The demonstration of the differentiation in absorbance curve by the addition of graphene in different surfactant concentrations (from top-to-down; dashed blue: Unpurified aqueous graphene dispersion stabilized at 0,5 wt% stabilizer 1 (S1), dashed orange: Unpurified aqueous graphene dispersion stabilized at 1 wt% stabilizer 1, solid orange: 1 wt% aqueous stabilizer 1 dispersion without graphene, solid blue: 0,5 wt% aqueous stabilizer 1 dispersion without graphene. All dilutions are of 1:100 ratio).....</i>	<i>20</i>
Figure 12.	<i>The absorbance of aqueous graphene dispersions at the same dilutions in which surfactant concentration is fixed. The legend on the right denotes the initial amounts of the surfactant and graphene</i>	

	<i>in milligrams. For instance, 50/20 represents 50 mg surfactant and 20 mg graphene.</i>	<i>21</i>
Figure 13.	<i>The absorbance value of aqueous graphene dispersions at the same dilutions of stock solutions in which surfactant concentration is fixed. The legend on the right indicates the amount initial additions of surfactant and graphene in milligrams. For instance, 50/45 represents 50 mg surfactant and 45 mg graphene.....</i>	<i>22</i>
Figure 14.	<i>The sedimentation behavior of stabilizer 1-stabilized graphene by time (from left-right: after 48 hours, two weeks and a month)</i>	<i>23</i>
Figure 15.	<i>The absorbance behaviors of graphene-stabilizer 1 dispersions in varying concentrations by time.....</i>	<i>23</i>
Figure 16.	<i>The absorption behavior of purified, unpurified and graphene-free stabilizer 1 (S1) dispersions (From top-down: 1XP signifies one-time ultracentrifugated graphene, 2XP signifies two-times ultracentrifugated graphene, GF-100mg is graphene free 0,01 wt% stabilizer 1, and G-stabilizer 1 is unpurified 0,01 wt% stabilizer 1-graphene dispersion).....</i>	<i>24</i>
Figure 17.	<i>Purified graphene after 8 weeks without any sedimentation and agglomerate</i>	<i>24</i>
Figure 18.	<i>The TGA plot of the first initial measurement (run under nitrogen gas flow).</i>	<i>25</i>
Figure 19.	<i>The TGA plot of the first initial measurement (run under oxygen gas flow).</i>	<i>26</i>
Figure 20.	<i>The TGA plot of the first initial measurement (run under oxygen gas flow).</i>	<i>27</i>

LIST OF SYMBOLS AND ABBREVIATIONS

AGD	Aqueous Graphene Dispersion
C	Carbon
DLVO	Derjaguin, Landau, Vervey, and Overbeek
GO	Graphene Oxide
L/W	Length to Width Ratio
nm	Nanometer
OFET	Organic field effect transistor
PLA	Polylactic Acid
RCF	Relative Centrifugal Force
rGO	Reduced Graphene Oxide
S	Order Parameter
SEM	Scanning Electron Microscopy
S/G	Surfactant to Graphene Ratio
TGA	Thermogravimetric Analysis
TUT	Tampere University of Technology
UV	Ultraviolet
UV-vis	Ultraviolet visible
vdW	van der Waals
XGO	Exfoliated graphene oxide
2D	Two-dimensional

1. INTRODUCTION

Over the course of the last decade, graphene has attracted a tremendous amount of attention from scientific community due to its superior properties. Such that, in 8 years (2005-2013) over 8.000 articles have been published in the pursuit of what graphene can bring about and how would it be utilized in both conventional and state-of-the-art products [1]. Although convenient manufacturing methods for bulk graphene quantities have not yet been established, so far, exfoliation of graphite to graphene oxide (GO), and following reduction from GO to reduced graphene oxide (rGO) have widely been researched. However, pristine graphene flakes with a minimum amount of oxygen residuals are of much greater importance, since residual oxygen deteriorates the final properties of products in which graphene is applied [2].

In 2008, Coleman and his research group showed how graphite could be directly exfoliated to graphene, using solvents whose surface energies match with that of graphite. However, solvents that are used in Coleman's work do not fulfill both the practical and environmental requirements because they are high boiling point solvents and toxic. Therefore, being able to stabilize graphene flakes in water is crucial [2-4].

Graphene is inherently hydrophobic; therefore, having graphene stabilized in water without any surface modification is not possible, as long as the surface energy of water stays the same. In this respect, surface modification of graphene is essential. Surface modification of graphene being made by either covalent functionalization or non-covalent functionalization. Covalent functionalization of graphene requires chemical reactions in which electronic configuration of graphene is substantially disrupted. That is to say that the sp^2 hybridization of graphene, the property by which graphene is endowed to be a wonder material, is deteriorated. However, current methods are not scalable. Hence, non-covalent functionalization has become more prominent [5] [6].

Non-covalent functionalization of graphene can be realized by two means: surfactants and polymers. While surfactants electrostatically stabilize graphene flakes, whereas the latter sterically blocks agglomeration of graphene particles. For both methods, however, graphene dispersions must be agitated in order to separate the stacked graphene flakes. In the case of graphene dispersions, the shear force has popularly been exerted by sonication, more dominantly, by ultrasonication. Ultrasonication has been found to be superior over bath sonication due to the fact that 100 times more power can be inserted into dispersion without damaging flakes providing considerably higher graphene yields [7]. Another way of applying shear is microfluidization. However, practicality issues and the presence of

more experience with ultrasonication have led many have to come to the conclusion that, so far, ultrasonication is the best alternative amongst all [5, 8, 9].

Obtaining aqueous graphene dispersions enables its use in many categories. In the stable aqueous form, graphene can innocuously be incorporated into polymers, functional inks, as well as it can be deposited as a thin film by itself. Therefore, the commercial interest in graphene particularly drawn by the industries which focused on organic photovoltaics, sensor applications, and organic field effect transistors (OFETs) as well as polymer-composite and flexible packaging [10].

1.1 Aim and Structure of Thesis

The study starts off with the investigation of obtaining aqueous dispersions of graphene using three different kinds of surfactant, here designated stabilizer 1, 2 and 3. The study continues surveying the degree of stabilization afterward. The aim is to find out the method and the surfactant by which highest concentration of graphene along with the lowest surfactant to graphene ratio (S/G ratio) is achieved.

2. LITERATURE REVIEW

2.1 Graphene

“Monocrystalline graphitic films”, this is how graphene was defined when it was first isolated in 2004 [16]. After a period of time through which the spectacular properties of graphene have emerged, it has been given a nickname of ‘wonder material’. Properties of a single-layer graphene as follows:

- High intrinsic electron mobility ($200,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at electron densities of $\sim 2 \times 10^{11} \text{ cm}^{-2}$) [17]
- Superior thermal conductivity (up to $5.30 \pm 0.48 \times 10^3 \text{ W/mK}$) [18]
- Impermeable to all gases including Helium [19]
- Young's modulus of $E = 1.0$ terapascals, “strongest material ever measured” [20]
- Strong light absorbance by $2.3\% \pi a$ [21]

Before delving deeper more about the molecular structure of graphene, see section 2.4.1. It is noteworthy to mention about a serious confusion regarding the nomenclature of graphene. Currently, ‘graphene’ is being overused due to the absence of a convention concerning the distinction of a defect-free single-layer graphene from that of multilayer and defective versions. In this matter, Alberto Bianco has conducted an extensive research and proposed a convention [22]. Despite that it is not universally accepted, Bianco’s work classifies graphene according to six principles which are based on the number of layers, lateral dimension, imperfection and crystallinity of graphene. While ‘Graphene’ is reserved only for sp^2 hybridized one-atom-thick sheet; between 2-10 sheets of a stack, it is named ‘Multilayer graphene’. Below the lateral size of 100 nm, ‘nano’ is suffixed after the notation. Unfortunately, in this work, Bianco’s proposal has not been put into action.

2.2 Surfactants

Surface active agents, more widely known as surfactants are amphiphiles consisting of soluble and insoluble parts. They have two fundamental duties: Adsorption at Interfaces and aggregation into supramolecular structures, namely micelle formations. Depending on the characteristics, surfactants decrease the surface energy of organic or inorganic systems by being adsorbed onto these bodies [23, 24].

In the context of water, surfactants are divided into two parts: the hydrophilic head group and the hydrophobic tail group. Furthermore, surfactants are classified according to the polar head groups as anionic, cationic, non-ionic and zwitterionic. The vast majority of surfactants are anionic. Among the anionic surfactants, sodium and potassium have been

the preferred counterions in head groups due to their strong electronegativity. In addition to that their effortless manufacturing and low-cost paved the way anionic surfactants, to be the best option especially in the household detergent industry [23].

2.2.1 Adsorption of Surfactant at the Surface

Adsorption of surfactant at the surface is particularly important for detergent applications and aqueous dispersions of solid particles. Surfactant adsorption is determined by the nature of the surface to be adsorbed and the nature of the surfactant. Within the context of this study, in hydrophobic surfaces, adsorption is mainly governed by the by the $\pi - \pi$ interactions between the aromatic rings of surfactant and hexagonal carbon array of graphene, as it is depicted in **Figure 1**. Therefore, the surfactant adsorption on a hydrophobic surface is projected to take place in such a way that while the hydrophilic head groups are attracted to water molecules, hydrophobic tails are attached to the graphene surface.

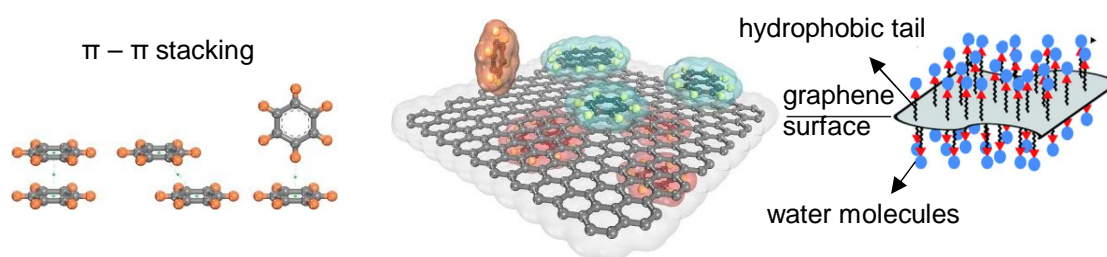


Figure 1. Surfactant adsorption mechanism on graphene surface [25]

2.3 Colloidal System

Colloidal systems are most properly defined by Munday as “A system consisting of one substance (the dispersed phase: a solid, liquid, or gas) finely divided and evenly distributed (relatively speaking) throughout a second substance (the dispersion medium or continuous phase: a solid, liquid, or gas).” Defined particle size limitations of colloids in the literature can be arbitrary and may bring many controversies along with it. Therefore, it is better to define a system as a colloid, if it behaves in the manner of colloids [26].

A colloidal system contains a lot of solid particles which constitute a substantially high area of surface; thus, a tremendous amount of interfacial energy. Particles tend to minimize the interfacial energy by forming aggregates. This is primarily caused due to the instantaneous dipoles called London-van der Waals Forces. In addition to that other type of forces such as electrostatic forces, hydrogen bonding, and permanent dipoles can accelerate the interactions between the particles [24]. However, particle aggregation is an

undesired phenomenon which prevents stable colloids to be obtained. To cope with this challenge, an energy barrier must be built around the particles.

$$V_X = \frac{1}{H_0} x \frac{Aa}{12} \quad (1)$$

Hugo Christian Hamaker was the first scientist who explained the attraction phenomena as the interaction energy is inversely dependent on the distance between the particles as it is shown in equation 1[27]. A more comprehensive explanation has later been developed by Derjaguin, Landau, Vervey, and Overbeek in understanding the particle interactions [28]. The DLVO theory explains the particle interaction by combining electrostatic repulsive forces with attraction forces. Besides elucidating the interaction forces, the DLVO theory also sheds light on the aggregation behaviors of particles [29].

2.3.1 Electrical Double Layer

The combination of charged surface and the scattered distribution of counter and co-ions in the vicinity of the surface called electrical double layer. When a solid substance is introduced into water, a certain tension takes place at the solid-liquid interface. Solid substances are intrinsically charged with anions. This is caused due to the higher dielectric constant of water. Closely packed anions attract counter-ions which form a layer of cations around the particle which is called 'stern layer'. Subsequently, another layer of electron cloud which is rather loose and moveable is built up around the stern layer because of the residual anionic attraction, see **Figure 2**.

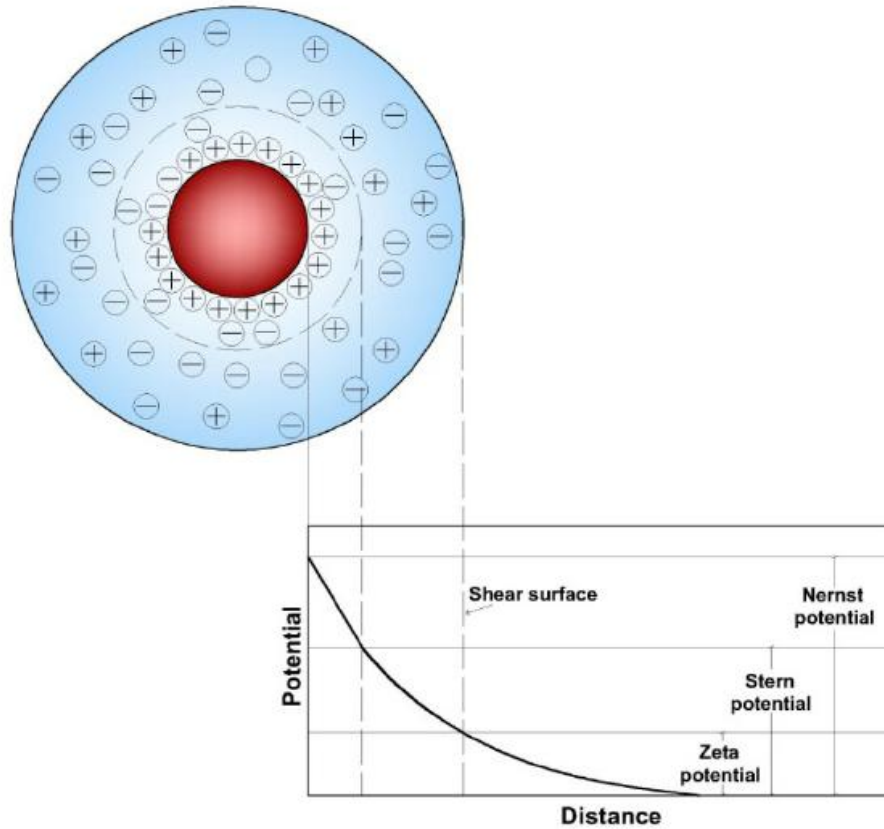


Figure 2. Depiction of electrical double layer formation and surface potential [30]

Moreover, there are two principal mechanisms by which solid particles kept apart and suspended in a medium. These mechanisms are electrostatic stabilization—where electrical double layer formation plays the main role—and steric stabilization. In addition to that electrosteric stabilization, electro-steric stabilization is also considered a way of stabilization which combines both electrostatic and steric repulsion forces, which are shown below. However, it is not common as the formers[23, 27].

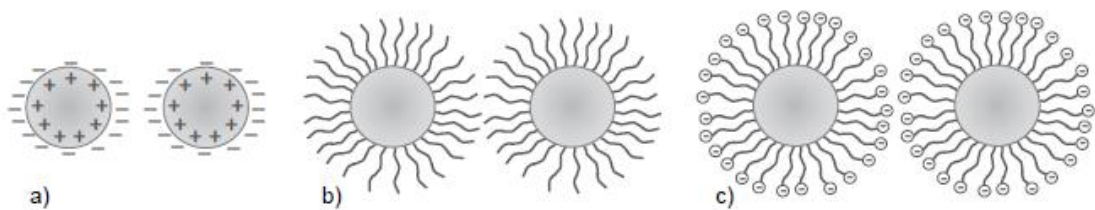


Figure 3. a) Electrostatic Stabilization, b) Steric Stabilization, c) Electrosteric Stabilization

2.3.2 Electrostatic Stabilization

Electrostatic stabilization is a way of stabilization by which the surfaces are charged, and repel each other. Electrostatic stabilization has been the driving force in keeping particles apart by withstanding London forces and other types of forces.

2.3.3 Steric Stabilization

Although, it is the most potent particle de-agglomeration mechanism, electrostatic stabilization, in some cases, could be insufficient or undesired. Commonly, a thin electrical double layer as a result of an inadequate surface potential is seen in the cases which electrostatic stabilization lacks. As it is shown in **Figure 3**, steric stabilization works based on the mode by which surfactants or polymer flock on particles, introduces a physical barrier; hence, cripples particle agglomeration. On the other hand, apart from the polymer which actively blocks particle conglomerates, redundant polymers constitute a depletion region. In this respect, it is rather important to choose the optimal polymer-surfactant content. Otherwise, free polymer cause destabilizations in the system. Furthermore, the thickness of the adsorbed layer is another vital property, which determines the quality of stabilization since there is only limited room on each particle's surface. Therefore, the longer the polymer chains, the higher the stabilization. On top of that, it is important to keep in mind that the type of suspended material does not affect whatsoever in the stabilization system[23, 31].

2.3.4 Electrosteric Stabilization

As the name indicates, this stabilization mechanism combines both above-presented stabilization systems by which sufficient energy for particle separation is built [3].

3. EXPERIMENTAL

At the beginning of the study, three different kinds of surfactant were experimented and evaluated for their capability of graphene stabilization in the aqueous medium. Ultrasonication and subsequent centrifugation steps were used as a dispersing technique. Furthermore, Ultraviolet-visible spectrophotometry (UV-vis) measurements were taken place at regular intervals to monitor the degree of stabilized graphene concentration by time.

Depending on the results obtained from the initial stabilization study (where the aqueous graphene dispersions are unpurified), a further purification study was carried out with the surfactant type which exhibited more promising outcomes than the other types. In this stage, In addition to standard centrifugation, ultracentrifugation steps were added to the initial method. Thermogravimetric Analysis (TGA) measurements were also carried out in order to get more reliable data regarding both the graphene and surfactant concentration.

3.1 Materials

3.1.1 Graphene Types

Prior to the study, a comprehensive investigation on the characterization of 17 different graphene powders has been carried out. As a result, two kinds of graphene flake which have exhibited more consistent graphene-like characteristics than the other powders were selected for the purpose of this study. In addition to that, a coarser type of powder was also added to the selection as the third type [41].

Due to the objectivity reasons, the origins of graphene platelets have not been revealed in this work. They have been numbered according to their qualitative gradation as Graphene A, Graphene B, and Graphene C.

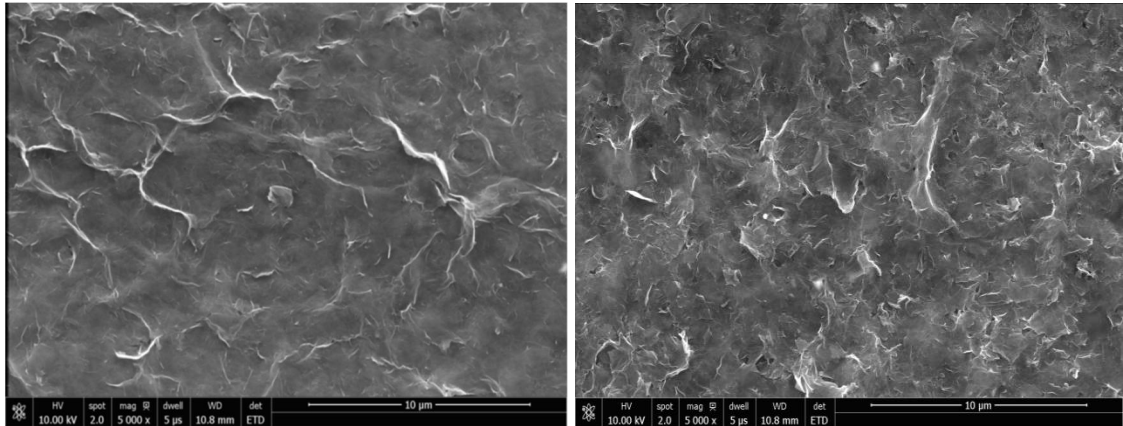


Figure 4. SEM images of selected flakes, graphene A and B (adopted from the master's thesis of Felix Lundkvist) [41].

3.2 Methods

3.2.1 Preparation of Unpurified Graphene Dispersions (AGD)

A simple screening method was applied to determine whether the chosen surfactants are capable of stabilizing graphene. After screening, we made a rough aqueous graphene dispersion (AGD), which is called 'Unpurified aqueous graphene dispersion' in this thesis. In this respect, each sample of unpurified AGD was prepared as described below, **Figure 5**.

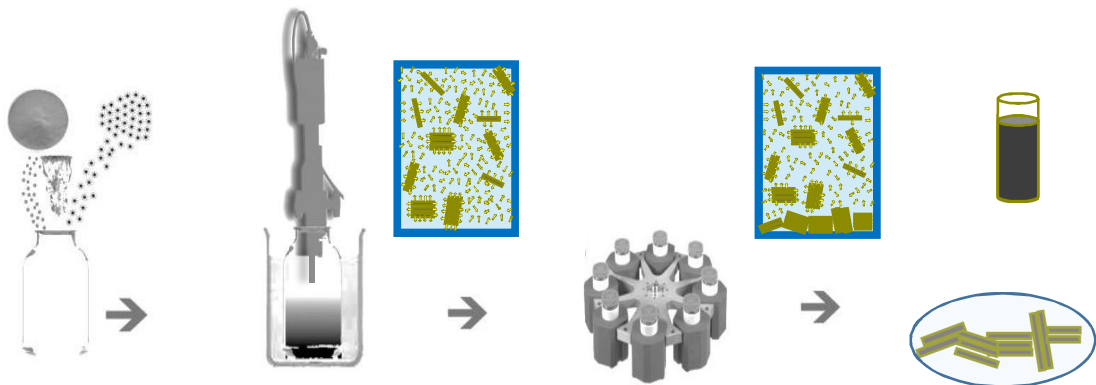


Figure 5. The schematic illustration of the process making unpurified graphene dispersion AGD. (1) Blending of ingredients, water, surfactant, and graphene. (2) Ultrasonication. (3) Centrifugation. (4) Removal of sediment.

3.2.2 Preparation of Purified Aqueous Graphene Dispersion

As the excess amount of surfactant was used in the preparation of 'Unpurified aqueous graphene dispersion' above, ultracentrifugation steps were added to the process to purify the aqueous graphene dispersion further. At this point, it is noteworthy to mention that in

this context, purification connotes getting rid of the bulk free-surfactant content from the dispersion while keeping the sediment, the wet cake of stabilized graphene, see **Figure 6**.

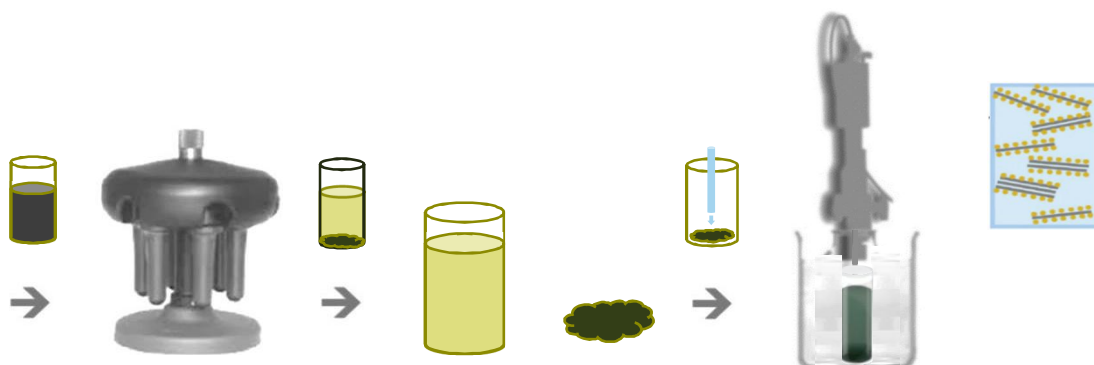












Figure 6. The schematic illustration of the process making one-time purified aqueous graphene dispersion. (1) First ultracentrifugation of the unpurified aqueous graphene dispersion (2) Removal of excess surfactant by decantation (3) Re-suspension of residual wet cake of graphene in water via ultrasonication.

In the study, aqueous graphene dispersions (AGDs) were produced in three different ways. They were also named according to the method applied. Below, **Table 1** demonstrates the processing steps and conditions.

Table 1. Preparation steps of Unpurified, One-time-purified, and Two-time-purified aqueous graphene dispersions.

	Unpurified Graphene Dispersions	One-time-purified Graphene Dispersions	Two-time-purified Graphene Dispersions
	Blending of ingredients	Blending of ingredients	Blending of ingredients
	Ultrasonication (7 minutes, 40% power)	Ultrasonication (7 minutes, 40% power)	Ultrasonication (7 minutes, 40% power)
	Centrifugation (2000 rpm, 30 minutes)	Centrifugation (2000 rpm, 30 minutes)	Centrifugation (2000 rpm, 30 minutes)
	Collection of the supernatant and removal of sediment	Collection of the supernatant and removal of sediment	Collection of the supernatant and removal of sediment
		Ultracentrifugation (14.600 rpm, 20 mins)	Ultracentrifugation (14.600 rpm, 20 mins)
		Collection of the first sediment and removal of supernatant from the first ultracentrifugation	Collection of the first sediment and removal of supernatant from the first ultracentrifugation
		Re-suspension of the first sediment (40 – 65 secs, 30% power)	Re-suspension of the first sediment (40 – 65 secs, 30% power)
			Ultracentrifugation (20.000 rpm, 20 mins)
			Collection of the second sediment and removal of supernatant from the second ultracentrifugation
			Re-suspension of the second sediment (40 – 65 secs, 30% power)

Over the course of the study, over 100 vials of AGD were produced. Those of which were subjected to further quantitative analysis instruments are described in **Table 2**.

Table 2. Sample names and their compositions

Unpurified Graphene Dispersions									
Dispersion Name		Unpurified Gr-stabilizer 1 1wt%	50/20	50/30	50/40	50/45	50/60	50/75	50/90
Composition	Surfactant type-Initial weight (mg)	stabilizer 1-100	stabilizer 1-50	stabilizer 1-50	stabilizer 1-50	stabilizer 1-50	stabilizer 1-50	stabilizer 1-50	stabilizer 1-50
	Graphene type-Initial weight (mg)	Graphene B-40	Graphene B-20	Graphene B-30	Graphene B-40	Graphene A-45	Graphene A-60	Graphene A-75	Graphene A-90
	Water (ml)	10	10	10	10	10	10	10	10
One-time Purified Aqueous Graphene Dispersion				Two-time Purified Aqueous Graphene Dispersion			Graphene-Free Surfactant Solution		
Dispersion Name		1XPur-Gr-stabilizer 1	2XPur-Gr-stabilizer 1			Gr-free 1 wt%			
Composition	Surfactant type-Initial weight (mg)	stabilizer 1-100	stabilizer 1-100			stabilizer 1-100			
	Graphene type-Initial weight (mg)	Graphene A-40	Graphene A-40			---			
	Water (ml)	10	10			10			

3.3 Application Instruments

3.3.1 Sonication

Sonication is a very effective way of obtaining homogeneous dispersions, in which cavitation is attained by means of ultrasound energy, alternating low and high-pressure cycles. Sonication is a common practice in dispersion preparations and can be done in two ways: Bath sonication and ultrasonication. It has several times been proved that ultrasonication imparts more efficient dispersions, higher in concentration, including the pristine graphene applications [8].

Over the course of the study, Vibracell VCX 750 with the regularly maintained 6 mm Stepped Microtip was used. In the majority of applications, sonication time was chosen as 7 minutes, and the sonication power was kept at the amplitude of 40%. Moreover, the sonicated compounds were often of 10 ml in volume. Since dynamically changing parameters (temperature, surface tension, viscosity, etc.) are often obscure, no preliminary calculations were made. The practice of parameter selection was relied on the previous laboratory experience and determined according to the Sonics User's Manual "maximum volume that can effectively be processed with a 3 mm probe is 15 ml" [61].

3.3.2 Centrifugation

Centrifugation was one of the main steps both for unpurified and purified AGD preparation. It is also used in tandem with the ultracentrifugation step in the purification studies. Centrifugation is a method of sedimenting both large and dense particles in suspensions by which particles are pushed from the axis via relative centrifugal force (RCF) thus, separated from the rest. In the case of graphene dispersions, it was used to separate the unattached graphene particles from the dispersion.

$$v = \frac{d^2 (p-L) x g}{18 n} \quad (6)$$

Although it is seemingly possible to predict the size group of sedimented graphene flakes through the Stokes Equation as it is presented in Equation 6 (where v is sedimentation rate, d is sphere diameter, p is particle density, L is medium density, n is viscosity of medium and g is gravitational force), the equation requires more thorough and preliminary size selection processes for graphene powders. Therefore, this stays beyond the scope of this work.

Moreover, Jonathan L. Coleman and his research groups have many times unveiled practical ways for accurate speed selection of the centrifugation of graphene dispersions [62, 63]. In this respect, sedimentation of unanchored graphene flakes via centrifugation

was predominantly made between 2000 - 4400 rpm. Rotina 420, with the 4-placed Swing-out rotor (radius: 160 mm) was conducted over the course of the thesis work.

3.3.3 Ultracentrifugation

Same in principle, ultracentrifuge separates the particles differing in size and density at even faster rotational speeds than a regular centrifuge. However, on the contrary of its former purpose, in this stage, it was used to precipitate the anchored surfactant-graphene to the bottom whereas free surfactants were kept on the surface.

Optima L-90K ultracentrifuge was employed throughout the purification steps of the aqueous graphene dispersions. Disposable PLA tubes and titanium capsules were used as inner and outer carriers respectively. Chosen rotational speeds were at 14.600 rpm and 20.000 rpm attributing the study of Jonathan L. Coleman [63].

3.4 Characterization Instruments

3.4.1 UV-vis Spectrophotometry

UV-visible spectrophotometry functions based on the principle of electron excitation by which incident light is absorbed in a certain range of wavelength. The quantitative analysis made on the amount of transmitted or absorbed atoms.

$$T = I/I_0 \quad \text{and,} \quad A = -\log_{10}(T) \quad (7)$$

The Beer-Lambert law defines that the absorption of light is directly proportional to the concentration of the medium (mol/cm^3), the path that light traveled through the medium (cm), and the molar absorptivity ($\text{L}/\text{mol}\cdot\text{cm}$), see Equation 7 and 8.

$$A = \epsilon lc \quad (8)$$

Absorption is a characteristic value for every material since each material has its unique color. UV-visible spectrophotometry is particularly important for organic conductive materials because by detecting the absorption range of materials it is possible to determine their bandgaps which allow one to array an organic device. Although organic electronics and graphene are closely related, in the case of this study, UV-vis spectrophotometry was utilized to get an idea about the concentration degree of the aqueous graphene dispersions.

To elucidate the degree of graphene concentration in dispersions, it is common practice to draw a calibration curve. However, the calibration curve can only be drawn out a stock solution with known graphene concentration so that the Beer's Law can be applied. However, since we are investigating the dispersibility of graphene in stabilizer 1 as a function of time without knowing the absolute concentration of graphene, the

measurements have been done and evaluated relative to each other; comparing the absorption deviance by time for a given solution, and monitoring the characteristic peak behavior of graphene-free aqueous dispersion in a way that how this peak is being differentiated by the addition of graphene.

In this study, Lambda 650 UV/vis spectrophotometer was used to implement the concentration study. Scanning was taken place in the wavelength range of 200 – 800 nm at 2 nm slid width.

3.4.2 Thermogravimetric Analysis (TGA)

As a thermal analysis method, the thermogravimetric analysis determines chemical and physical changes in material composition as a function of temperature and time. In this research, Mettler Toledo TGA 2 Thermogravimetric Analyzer was employed to probe the mass concentration of the graphene and the surfactant in the AGDs. On the other hand, thermal degradation of the surfactants and the graphene was monitored under both nitrogen and oxygen flow.

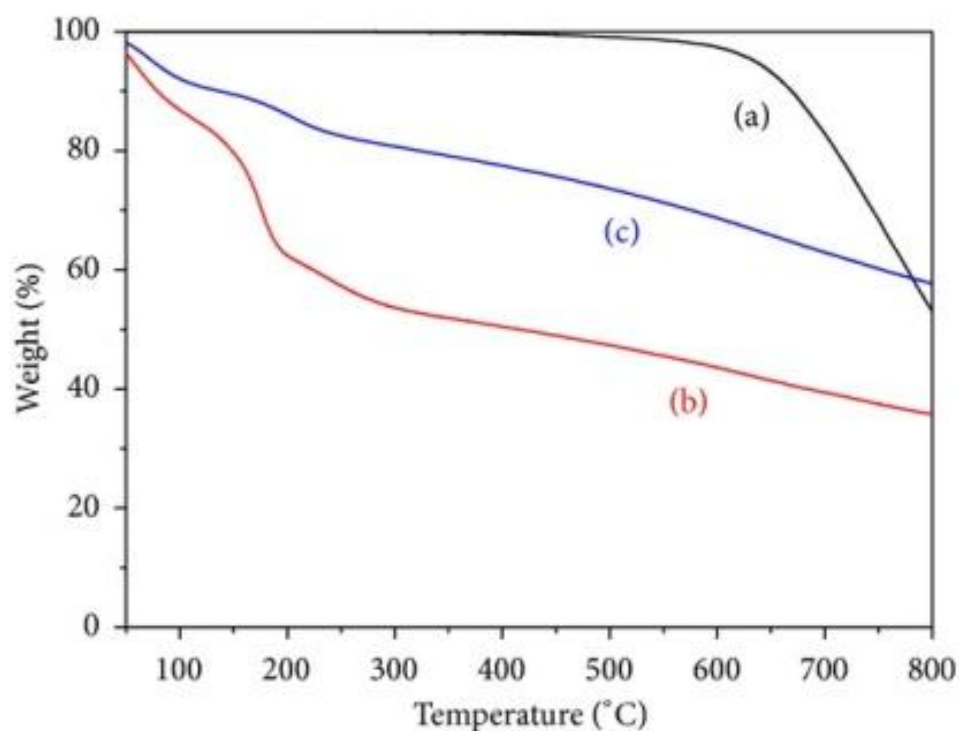


Figure 7. Thermal stability of graphite (a), rGO (b) and XGO (c). (The plot is directly adopted from the given reference) [64].

To get a better understanding of ‘Results and Discussion’ section of this thesis, it is essential to acquaint oneself with how carbon-based materials behave when they are

exposed to a gradual temperature increase. The shown plot in **Figure 7** represents the chemical decomposition behaviors of few-layer graphene-oxide (XGO), reduced graphene oxide (rGO), and graphite under the nitrogen flow. According to the plot, while graphite is quite stable up to 600°C, XGO and rGO lose a reasonably large amount of weight in the temperature range of 50-600°C. First significant weight loss of XGO and rGO is attributed to the water loss which takes place over 50-120°C. The difference between XGO and rGO is the labile oxygen groups which are heavily present in XGO. The presence of the labile oxygen groups results in another significant weight loss for XGO from 120°C to 440°C. Moreover, following weight loss, over 440°C, both for XGO and rGO, is referred to the pyrolysis of functional groups. Although all the carbon-based materials are exfoliated in water in the absence of stabilizers; the TGA result sheds light for the purpose of this study [64, 65].

4. RESULTS AND DISCUSSION

4.1 The Stabilization Capacity of Different Surfactants Types

4.1.1 Visual Examinations

Three different kinds of anionic surfactant were subjected to an identical preparation method by which unpurified AGDs are obtained. The initial graphene and surfactant concentrations were kept same for all the AGDs experimented (the initial concentrations of stabilizer 2 were unknown).

When dispersions were diluted, it was evident that only stabilizer 2 seemed incapable of stabilizing the graphene flakes whereas stabilizer 3 and stabilizer 1 exhibited a rather dispersed display.

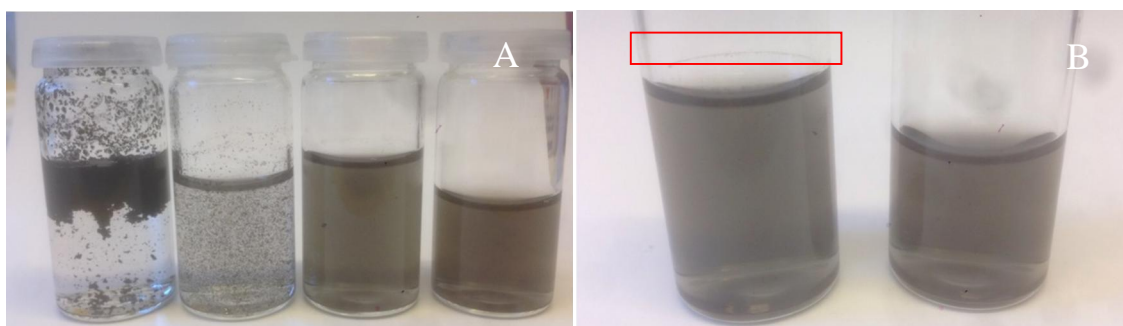


Figure 8. Demonstration of aqueous graphene dispersions stabilized by different surfactants, and a surfactant-free aqueous graphene solution (Image A, left-to-right: surfactant-free graphene, stabilizer 2, stabilizer 3 and stabilizer 1 graphene dispersions. Image B, left-to-right: stabilizer 3 and stabilizer 1).

Stabilizer 2, was synthesized in-house. It has shown no prospect to stabilize graphene. This might as well can be attributed to the conditions of synthesis process in which possible impurities might have left in the solution which deteriorate the properties of stabilizer 2.

On the other hand, phase separation was one of the main characteristics of stabilizer 2-stabilized AGDs. The recurrence of phase separation allows us to infer that thermodynamically favorable positioning of different phases might accelerate the aggregation of graphene flakes since the majority graphene flakes roam at a limited space. This is an undesired phenomenon for the purpose for aqueous graphene dispersions.

The blackness of aqueous graphene dispersions does not allow one to precisely determine, whether the dispersions are dispersed as desired. The aggregation of graphene was examined in a way that vials are revolved around and subsequently observed if any

aggregate left on the top of the glass when the liquid moved toward the bottom. By doing so, both in the stabilizer 1 and stabilizer 3 stabilized AGDs, neither considerable sedimentation nor aggregate formation was seen on the glass indicating that both surfactants are capable of stabilizing graphene at given initial concentrations. However, when the AGDs of stabilizer 1 and stabilizer 3 were diluted, it became visible that in the stabilizer 3 dispersions, there were many particles (aggregates); swirling in Brownian Motion, as it is shown in **Figure 8**. Nevertheless, the overbearing yellow color of the dispersion was partially faded pointing out that a part of the surfactant molecules was adsorbed on the graphene surface. This insufficient stabilization of stabilizer 3 might be for the reasons that either some graphene flakes were not thoroughly agitated or the stabilizer 3 was not capable enough to stabilize the exfoliated graphene flakes those of which rapidly ended up aggregating. The former should indeed be considered highly unlikely because the level of agitation (applied shear force) was consistently sufficient for the stabilizer 1-stabilized AGDs as well as poorly agitated graphene clusters were already sedimented in the centrifugation step

Moreover, a course of purification was held for the stabilizer 3-stabilized AGD to eliminate the excess stabilizer 3 content and to apply even more shear stress. At the end, however, the particles remained the same as in the unpurified case. As a result, the stabilizer 3 has been ruled out for further in-depth studies.



Figure 9. Unpurified and purified graphene dispersion along with the diluted versions. (From left to right: Unpurified aqueous graphene dispersion stabilized by stabilizer 3, stabilizer 1, and Dilutions-stabilizer 1).

Stabilizer 1, on the other hand, has been observed to be the most successful surfactant amongst all samples which are made in a unpurified manner. The stabilizer 1-stabilized unpurified AGDs have shown neither agglomerations nor considerable sedimentation up to two months, see **Figure 9** and **Figure 10**.



Figure 10. Pictures of stabilizer 1-stabilized graphene without any visible agglomeration or sedimentation.

Ultimately, the initial observations were found to be enough of a promising AGD, to merit stabilizer 1. Therefore, stabilizer 1 has been selected as the surfactant type to carry on in following studies.

4.2 Presence of Graphene Reflecting on UV-vis

4.2.1 Interpretation

The idea is here to highlight the difference between the characteristic pattern of surfactant and graphene which reflected as the absorbance of an incident light at a spectrum of wavelength. Hence, one can accurately comment on the dominance of one material over another. The authentic character in UV-vis is being displayed as curves. Therefore, significance in the differentiation of the curve pattern does indicate the graphene dominance over surfactant in mass which is what actually is desired in the first place.

By the introduction of graphene powder into Gr-free stabilizer 1 (water solution of stabilizer 1 without graphene), a considerable shift has taken place along the y-axis compared to that of graphene-free versions of aqueous stabilizer 1. Firstly, the plateau of the non-absorption region (550 -800 nm) of Gr-free stabilizer 1 elevated along the y-axis without compromising from its characteristic shape as it is demonstrated in **Figure 11**. This is the starting evidence of graphene presence in the dispersions since graphene absorbs the incident light over visible to near infrared spectrum.

On the other hand, as the concentration of stabilizer 1 goes up, the shape of its characteristic peak becomes more distinct. As it is mentioned earlier, the key aspect here is the alteration of this character toward that of graphene, which is unknown until now. In the Unpur Gr-stabilizer 1 1 wt%, this character seemed to remain the same (graphene character is not visible). However, when the stabilizer 1 concentration cut half from 1 wt% to 0,5 wt%, the characteristic peak started to differentiate subtly and reflected as the peak loses it's beaked shaped, and the slope between 260 -280 nm becomes wider and convexial. This signifies that the characteristic curve of graphene starts to be uncovered,

and understood that it should be at a similar wavelength range with that of stabilizer 1, edging out toward near ultraviolet region.

Moreover, in the unpurified aqueous graphene dispersions, the absorbance over the near ultraviolet region has shifted upwards by over two and five-fold. However, in the absence of a precise calibration curve wherein all the graphene flakes 100% concentrated, and a mathematical model by which graphene content could be extracted by means of UV-vis, no earthly speculation can be made with regard to the graphene concentration.

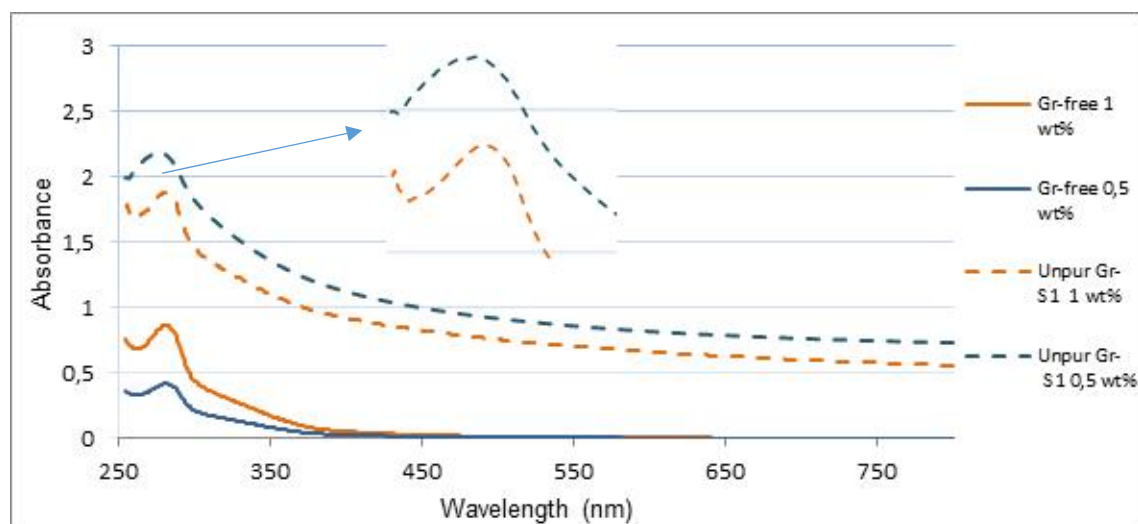


Figure 11. The demonstration of the differentiation in absorbance curve by the addition of graphene in different surfactant concentrations (from top-to-down; dashed blue: Unpurified aqueous graphene dispersion stabilized at 0,5 wt% stabilizer 1 (S1), dashed orange: Unpurified aqueous graphene dispersion stabilized at 1 wt% stabilizer 1, solid orange: 1 wt% aqueous stabilizer 1 dispersion without graphene, solid blue: 0,5 wt% aqueous stabilizer 1 dispersion without graphene. All dilutions are of 1:100 ratio).

The plot shown in **Figure 11** does provide information about the graphene existence in the unpurified stabilizer 1–stabilized AGD. However, it is not possible to purport what is the exact peak range of graphene alone. On top of all, the plot indicates that the mass fraction of surfactant is still excessive since the peak of the graphene-free stabilizer 1 curve is only partially swept by the graphene addition.

4.3 Investigation into varying parameters of Unpurified Dispersions

4.3.1 Determination of the ideal initial concentration

Prior to the quantitative analysis of graphene dispersions, a selected portion of surfactant and graphene content in 10 ml water was 100 mg and 20 mg respectively. After stabilizer 1 seemed to be successful at stabilizing graphene, different experiments have taken place in which surfactant content was gradually decreased to 50, 25, 20 and 10 mg while graphene content kept same. As a result, it was found that surfactant addition below 50 mg in 10 ml water (0,5 wt%) was not sufficient. Therefore, studies went on focusing mainly on the increment of graphene content at a particular surfactant concentration which is 0,5 wt%. Moreover, aqueous graphene dispersions in varying initial amounts at a fixed concentration of stabilizer 1 were exposed to UV-vis spectrophotometer, see **Figure 11**. At this point, it is noteworthy to mention that in the absence of a true calibration curve, interpreting is still valid since we draw a comparison among the dispersions, instead of determining their precise concentrations.

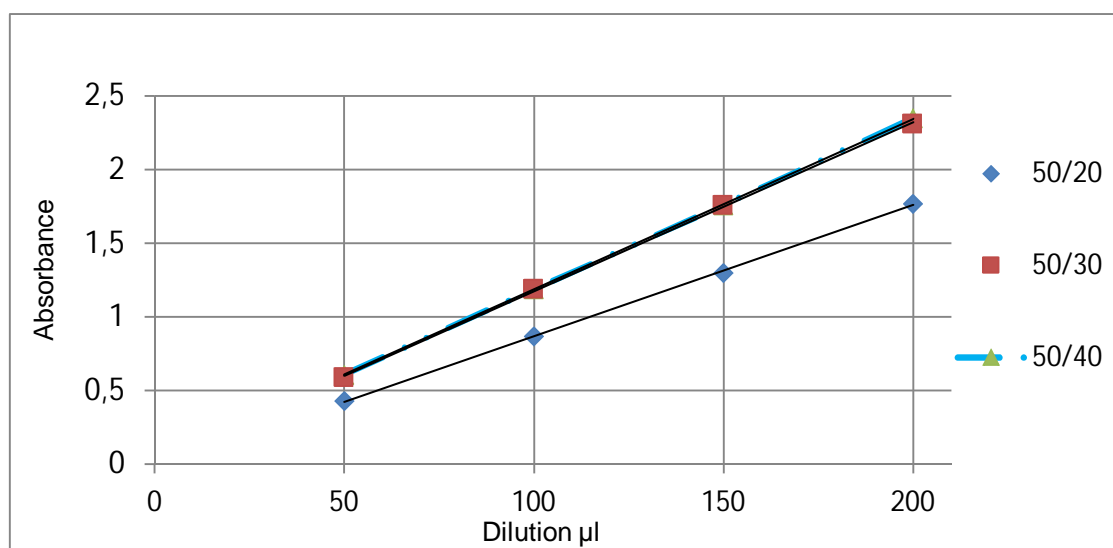


Figure 12. The absorbance of aqueous graphene dispersions at the same dilutions in which surfactant concentration is fixed. The legend on the right denotes the initial amounts of the surfactant and graphene in milligrams. For instance, 50/20 represents 50 mg surfactant and 20 mg graphene.

According to the plot, represented in **Figure 12**, by increasing the initial mass of graphene from 20 to 30 mg, approximately 36% higher absorbance, thus, a higher yield of graphene in an aqueous dispersion is achieved. However, above 30 mg the increment seemed to be almost negligible. Therefore, it was found that initial amount of graphene should be between 30 – 40 mg in a 10 ml aqueous medium.

Furthermore, more effort has later been put in the pursuit of discovering a sweet spot, a particular graphene amount, by which highest graphene yield could be possible. Therefore, in the same manner as before, keeping the surfactant concentration same, even more graphene added to see pushing limits would bring out any valuable information for initial concentration study of unpurified aqueous graphene dispersions.

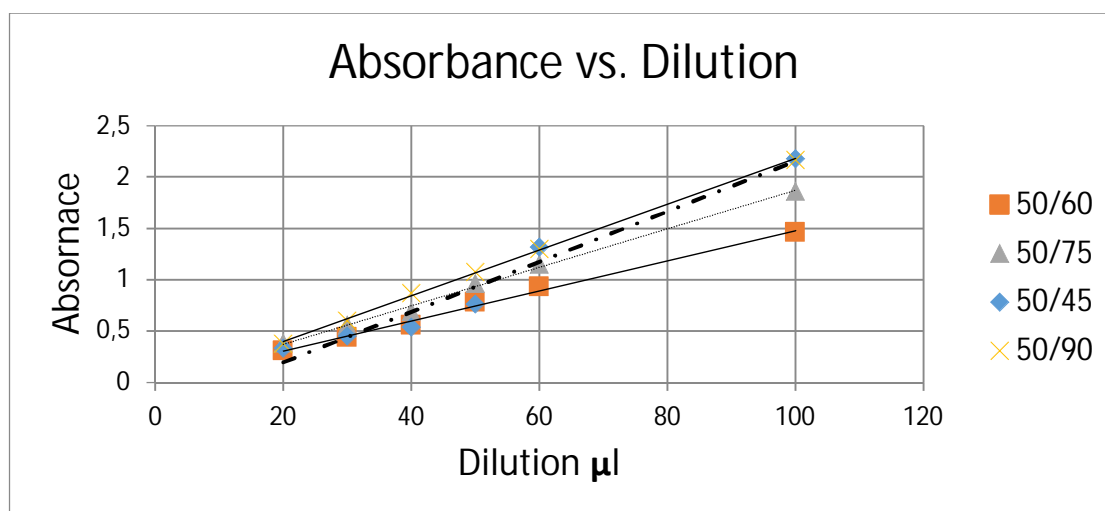


Figure 13. The absorbance value of aqueous graphene dispersions at the same dilutions of stock solutions in which surfactant concentration is fixed. The legend on the right indicates the amount initial additions of surfactant and graphene in milligrams. For instance, 50/45 represents 50 mg surfactant and 45 mg graphene.

As it is shown above in **Figure 13**, having a higher amount of graphene added in the mixing stage - over 45 mg graphene - does not yield a higher graphene concentration at the given surfactant concentration. On the contrary, the dispersion of 50/45 mg surpasses others with a higher slope.

Hence, to avoid from a large amount of graphene loss, and to keep the harvested graphene at its highest, 35 mg graphene addition was found to be suitable with 50 mg stabilizer 1 in 10 ml water.

4.3.2 Effect of time

After two weeks, the majority of the unpurified AGDs of stabilizer 1 have exhibited only a negligible sedimentation to an eye without any agglomerations. Apart from the visible examinations, UV-vis measurements have shown that there is not any trace of a considerable absorbance drop, which means that dispersions are stable after two weeks. Although the sedimentation became more apparent to an eye after a month, this did not reflect on UV-vis measurements as a considerable decrease in absorbance, see **Figure 14** and **15**.



Figure 14. The sedimentation behavior of stabilizer 1-stabilized graphene by time (from left-right: after 48 hours, two weeks and a month)

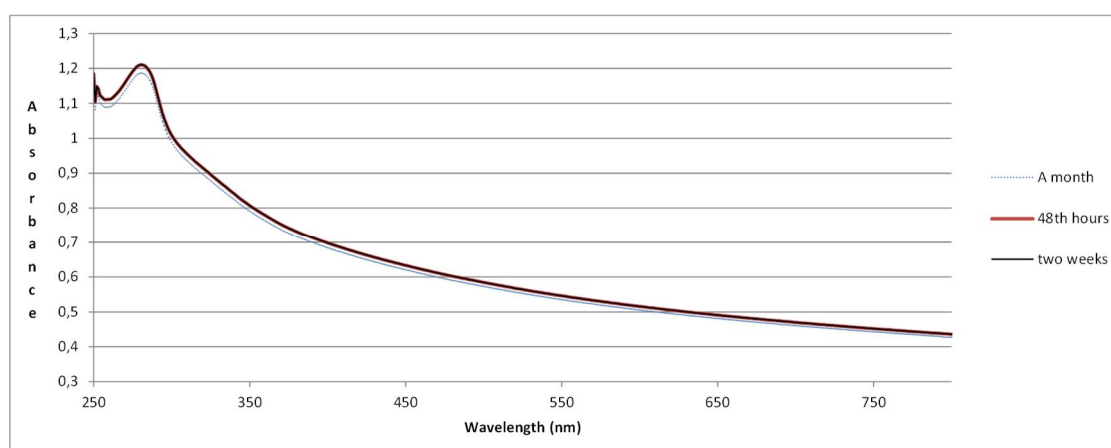


Figure 15. The absorbance behaviors of graphene-stabilizer 1 dispersions in varying concentrations by time.

4.4 UV-visible spectrophotometry characterization of the purified stabilizer 1-Graphene dispersions

By the purification of stabilizer 1-stabilized aqueous graphene dispersions, the characteristic curves of the unpurified AGDs have substantially changed. This change has reflected as a planar extension of the unpurified curve in the range of 250-280 nm wavelength over which the mound-like shape of the characteristic peak is being smoothed out, and the peak point is shifted from 281 nm to 277,5 nm (blue shift). It is now clear that the graphene has its peak at between 275-278 nm, and the peak is consistent over the spectrum of 265 to 285 nm, see **Figure 16**. In addition to that, although the precise concentration of purified AGD has not yet been identified, the plot strongly suggests that purified graphene dispersions have a lot more mass fraction of graphene than a surfactant. Moreover, initial assumptions concerning the graphene dominance over surfactant can be interpreted in relation to the curve's proximity to the ultraviolet region has been confirmed.

On the other hand, it has been found that one-time purification of is successful enough removing the majority of excess surfactant since there isn't any difference in the characteristic peaks of between the one-time-purified and two-time-purified AGD.

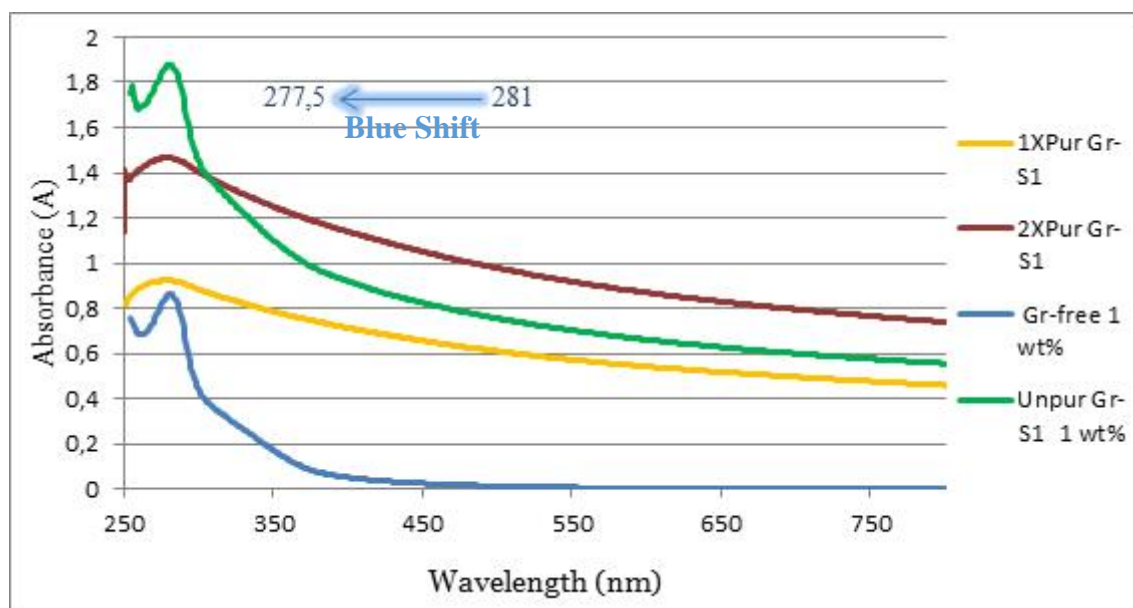


Figure 16. The absorption behavior of purified, unpurified and graphene-free stabilizer 1 (S1) dispersions (From top-down: 1XP signifies one-time ultracentrifugated graphene, 2XP signifies two-times ultracentrifugated graphene, GF-100mg is graphene free 0,01 wt% stabilizer 1, and G-stabilizer 1 is unpurified 0,01 wt% stabilizer 1-graphene dispersion).

Unpurified stabilizer 1-stabilized AGD is a lot like graphene-free stabilizer 1, rather than purified graphene; therefore, purification is an indispensable step in the production of aqueous graphene dispersion stabilized by stabilizer 1. Thus, it was decided the following production of aqueous graphene-stabilizer 1 dispersions must be purified.



Figure 17. Purified graphene after 8 weeks without any sedimentation and agglomerate

Moreover, the purified graphene-stabilizer 1 dispersions have exhibited neither sedimentation nor agglomeration up to 8-12 weeks, see **Figure 17**. This indicates that

considerable amount of graphene could be stabilized along with a reasonably low surfactant amount.

4.5 TGA MEASUREMENTS

So far, it has been stressed that how graphene dominance over surfactant in mass could manifest itself by UV-visible spectrophotometric characterization. It is now well-discerned that stabilizer 1-stabilized purified AGDs predominantly consist of graphene. However, as it is mentioned earlier, having AGDs be the subject of UV-vis does not bring any concrete result regarding their graphene concentrations, which is of great importance. Therefore, thermogravimetric analysis (TGA) of stabilizer 1-stabilized purified AGDs is imperative to elucidate to which extent the dispersions contain graphene.

4.5.1 Initial TGA measurements

First two measurements were held with the wet cake forms of a stabilizer 1-stabilized AGD dispersion.

According to the first initial TGA measurement which was run under nitrogen gas flow, significant weight loss was taken place in the midst of 180°C - 520°. This weight loss ascribed to the decomposition a moiety of stabilizer 1's, see **Figure 18**. Based on the molar weight of the moiety of stabilizer 1 in proportion to the total molar weight of stabilizer 1, it could be calculated that the overall surfactant content was 0,30 wt%.

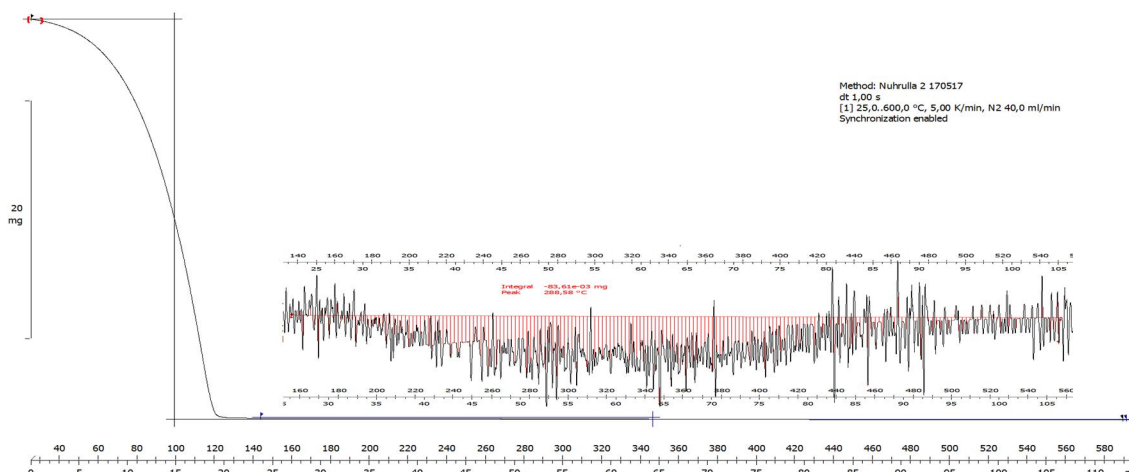


Figure 18. The TGA plot of the first initial measurement (run under nitrogen gas flow).

Ideally, in the first initial TGA measurement, under inert nitrogen gas flow, the measurement ought to run without any reaction taking place. Therefore, in the end, only a few elements should be left as a residue in the crucible. Having said one fraction of these elements constitutes 20% of stabilizer 1 in molar weight, which accounts for the 0,20 mg mass residue in the crucible; remaining residue other than these is to be one

specific element only. If so, the concentration of the graphene is estimated to 2,95-3%. This is a remarkable result but alas, might possibly be unlikely as well.

After the evaporation of water, and the subsequent decomposition of a moiety of the stabilizer molecule, one specific element is uncovered and can readily bind with another specific element, which leads to a specific chemical compound to be left in the crucible at the end of the measurement. Considering the molar weights of one element of the stabilizer and nitrogen (from the TGA instrument), and the possible binding of nitrogen on the surface of graphene, a very rough graphene concentration would be between 1,5-2 %.

To avert the possible undesired reactions of nitrogen, the second initial TGA measurement was taken place under the oxygen gas flow with the identical stabilizer 1-stabilized AGD dispersion used in the first initial TGA measurement. According to the result, as it is shown below in **Figure 19**, after all the water evaporated-by 120°C-the weight loss occurred at a steady rate through the range of 125-400°C. This is attributed to the oxidation of one specific functional group in the one moiety of stabilizer 1. The outcomes of the oxidation, should not affect the crucible weight and be outgassed immediately after being formed since they are of gaseous phase. Moreover, over 400°C, the weight loss slop has gotten steeper, indicating a greater weight loss in the range of 400°C-500°C. This is attributed predominantly to the oxidation of one specific element. Therefore, estimated graphene concentration was found to be at least 1,5-2 wt% along with 0,9-1,4 wt% concentration of the stabilizer 1.

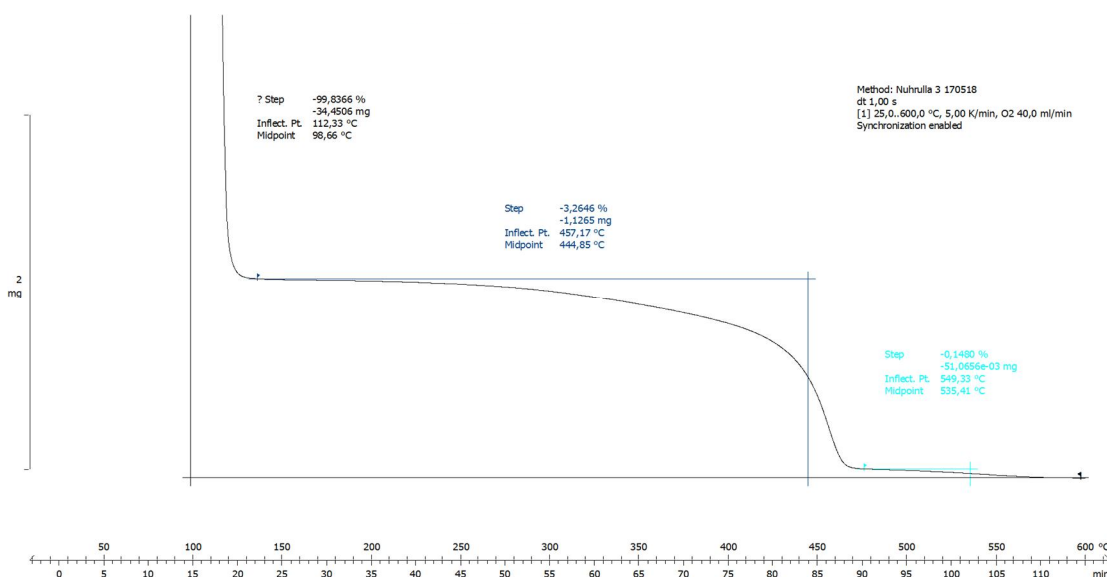


Figure 19. The TGA plot of the first initial measurement (run under oxygen gas flow).

Initial TGA results do not pose any controversy about the overall graphene-surfactant mass. At this point, however, it is rather difficult to distinguish precisely how much of

the outgassed material did consist of graphene since the weight loss pattern (400°C-500°C) of graphene and stabilizer 1 is interwoven.

4.5.2 TGA measurements of the dispersion

Following the initial TGA measurements, the samples were also exposed to thermogravimetric analysis under the oxygen gas flow. Indeed, these materials were re-suspended with distilled water, thus, contained a lot more water than the subjects of the initial TGA measurements.

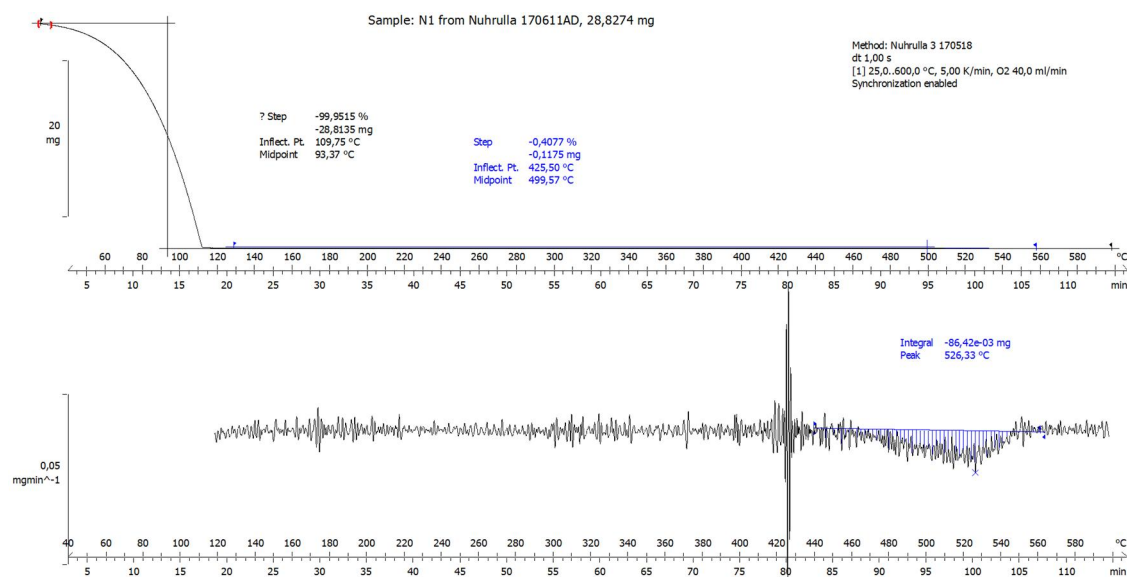


Figure 20. The TGA plot of the first initial measurement (run under oxygen gas flow).

As it is represented in **Figure 20**, similar to the second initial run under oxygen gas flow, the TGA plot of the dispersion have shown a substantial weight loss over 400°C as an indication of the carbon oxidation. This time, however, the peak point of the weight loss took place at 530°C, 70°C shift toward a higher temperature in comparison to the second initial measurement. This might have taken place for the reason that, the first TGA measurement run under oxygen was more concentrated. Therefore, the produced heat as a result of oxidation was proportionally higher than that of the former, thus, induced an earlier carbon oxidation.

Moreover, the weight loss between 420-540°C accounts for the mass graphene content, 0,30 wt% graphene concentration. And the rest, the weight loss between 120-420°C, accounts for the stabilizer 1 content, 0,10 wt% stabilizer 1 concentration. Therefore, it has been determined that the dispersion is of 0,30 wt% graphene concentration and contains three times more graphene over surfactant.

5. CONCLUSIONS

Over the course of the thesis study, over a hundred of vials of AGDs have been made. It has been identified that stabilizer 1, is capable of readily stabilizing graphene whereas stabilizer 2 is completely incapable. However, stabilizer 3 has shown peculiar formations, dissimilar to what has been observed with stabilizer 1 and stabilizer 2. Therefore, the graphene stabilizing capacity of stabilizer 3 has not been resolved at any length.

On the other hand, the dispersions made via unpurified method were an excessive amount of a surfactant. Thus, the unpurified method found to be inadequate. In this regard, an ultracentrifugation step must be employed right after the centrifugation to decant the free surfactant content.

Uv-visible spectrophotometric characterization has been of a great help throughout the study, monitoring whether the graphene or surfactant prevails over another in the dispersion. By the aid of UV-vis, the characteristic absorption curves of stabilizer 1 and graphene have been located. Hence, it has been identified by the differentiation of the characteristic absorption curve of stabilizer 1—blue shift—that free surfactant content was discarded by ultracentrifugation. However, UV-vis is indeed insufficient in determining the graphene concentration from scratch, which entails thermogravimetric analysis (TGA) to be an integral part of specifying the graphene concentration of AGDs.

TGA results of the purified dispersions have shown that the stabilizer 1-stabilized purified AGDs contained graphene at 0,3 wt% as well as three times more graphene than surfactant (1:3 surfactant/graphene) in mass. Moreover, over these dispersions were stable starting from a month, up to three months. The results indicated that stabilizer 1-stabilized AGDs are already suitable to be applied for its prospective applications.

5.1 Future Work

While the utilization of graphene at large scales yet to be understood, this study sheds light on the suspended form of graphene in an aqueous medium; thus, its future industrial implementations.

For future applications, this work suggests that the purification method comes in handy for the simple screening of surfactant-stabilized AGDs. However, in order to monitor and pinpoint the graphene and surfactant concentration: Firstly, in the very beginning, graphene powders should undergo to TGA both in powder form and as in the stabilized AGD form. Knowing that the graphene and surfactant concentration are unraveled separately, in the meantime, the sample of the AGD should be monitored by UV-vis spectrophotometry, and a calibration curve regarding the graphene concentration should

be drawn out. In this way, the various concentrations of AGD will be able to be displayed throughout the study. Moreover, to scale-up the process, a better alternative for ultracentrifugation should be sought in order for bulk quantities of purified AGDs.

REFERENCES

1. Larousserie, D., *Graphene - the new wonder material in Guardian*. 2013.
2. Hernandez, Y., et al., *High-yield production of graphene by liquid-phase exfoliation of graphite*. *Nat Nanotechnol*, 2008. **3**(9): p. 563-8.
3. Ayan-Varela, M., et al., *Achieving extremely concentrated aqueous dispersions of graphene flakes and catalytically efficient graphene-metal nanoparticle hybrids with flavin mononucleotide as a high-performance stabilizer*. *ACS Appl Mater Interfaces*, 2015. **7**(19): p. 10293-307.
4. Shih, C.J., et al., *Understanding the stabilization of liquid-phase-exfoliated graphene in polar solvents: molecular dynamics simulations and kinetic theory of colloid aggregation*. *J Am Chem Soc*, 2010. **132**(41): p. 14638-48.
5. Texter, J., *Graphene dispersions*. *Current Opinion in Colloid & Interface Science*, 2014. **19**(2): p. 163-174.
6. Georgakilas, V., et al., *Functionalization of Graphene: Covalent and Non-Covalent Approaches, Derivatives and Applications*. *Chemical Reviews*, 2012. **112**(11): p. 6156-6214.
7. *Ultrasonic Equipment*, in *Sonochemistry*. 2016, WORLD SCIENTIFIC (EUROPE). p. 41-58.
8. Durge, R., R.V. Kshirsagar, and P. Tambe, *Effect of Sonication Energy on the Yield of Graphene Nanosheets by Liquid-phase Exfoliation of Graphite*. *Procedia Engineering*, 2014. **97**: p. 1457-1465.
9. Karagiannidis, P.G., et al., *Microfluidization of Graphite and Formulation of Graphene-Based Conductive Inks*. *ACS Nano*, 2017. **11**(3): p. 2742-2755.
10. Johnson, D.W., B.P. Dobson, and K.S. Coleman, *A manufacturing perspective on graphene dispersions*. *Current Opinion in Colloid & Interface Science*, 2015. **20**(5): p. 367-382.
16. Novoselov, K.S., et al., *Electric Field Effect in Atomically Thin Carbon Films*. *Science*, 2004. **306**(5696): p. 666-669.
17. Bolotin, K.I., et al., *Ultrahigh electron mobility in suspended graphene*. *Solid State Communications*, 2008. **146**(9): p. 351-355.
18. Balandin, A.A., et al., *Superior Thermal Conductivity of Single-Layer Graphene*. *Nano Letters*, 2008. **8**(3): p. 902-907.
19. Bunch, J.S., et al., *Impermeable Atomic Membranes from Graphene Sheets*. *Nano Letters*, 2008. **8**(8): p. 2458-2462.
20. Lee, C., et al., *Measurement of the Elastic Properties and Intrinsic Strength of Monolayer Graphene*. *Science*, 2008. **321**(5887): p. 385-388.
21. Nair, R.R., et al., *Fine Structure Constant Defines Visual Transparency of Graphene*. *Science*, 2008. **320**(5881): p. 1308-1308.
22. Bianco, A., et al., *All in the graphene family – A recommended nomenclature for two-dimensional carbon materials*. *Carbon*, 2013. **65**: p. 1-6.
23. Holmberg, K., et al., *Introduction to Surfactants*, in *Surfactants and Polymers in Aqueous Solution*. 2003, John Wiley & Sons, Ltd. p. 1-37.
24. Hermel, W., *Beebhas C. Mutsuddy, Renee G. Ford. Ceramic Injection Molding (Spritzgießen von Keramik)*. Chapman & Hall, 2–6 Boundary Row, London SE1 8HN, UK First edition 1995 ISBN 0–412–53810-5 368 p. Preis: £ 75.00. Crystal Research and Technology, 1995. **30**(6): p. 774-774.
25. ; Available from:
<http://pubs.rsc.org/services/images/RSCpubs.ePlatform.Service.FreeContent.Ima>

geService.svc/ImageService/Articleimage/2016/RA/c6ra20315a/c6ra20315a-fl_hi-res.gif.

26. Munday, D.L., *Surfaces, Interfaces and Colloids — Principles and Applications, Second Edition* by D. Myers, Wiley-VCH, New York, 1999, xx+501 pp., ISBN 0-471-33060-4; £61.50. *Talanta*, 2000. **51**(3): p. 609.
27. Hamaker, H.C., *The London—van der Waals attraction between spherical particles*. *Physica*, 1937. **4**(10): p. 1058-1072.
28. Verwey, E.J.W. and Overbeek, J.Th.G. (1948) *Theory of the Stability of Lyophobic Colloids: The Interaction of Sol Particles Having an Electric Double Layer*. Elsevier, Amsterdam.
29. Trefalt, G., F.J. Ruiz-Cabello, and M. Borkovec, *Interaction forces, heteroaggregation, and deposition involving charged colloidal particles*. *J Phys Chem B*, 2014. **118**(23): p. 6346-55.
30. Rana, A., *Mesh resolution constraints with the Electrical Double Layer (EDL)*. 2017.
31. Zecha, H., *Stabilization of colloidal dispersions by polymer adsorption*. Von TATSUO SATO und RICHARD RUCH. *Surfactant Science Series*. New York/Basel: Marcel Dekker Inc. 1980. 155 S., 46 Abb., 302 Lit. SFr. 58.—. *Acta Polymerica*, 1981. **32**(9): p. 582-582.
41. Lundkvist, F., *Characterization of commercial graphene powders*, in *Center for Analysis and Synthesis*. 2017, Lund University: Sweden.
61. Inc., S.M., *Vibracell Ultrasonic Liquid Processors*. 2017.
62. Backes, C., et al., *Guidelines for Exfoliation, Characterization and Processing of Layered Materials Produced by Liquid Exfoliation*. *Chemistry of Materials*, 2017. **29**(1): p. 243-255.
63. Backes, C., et al., *Production of Highly Monolayer Enriched Dispersions of Liquid-Exfoliated Nanosheets by Liquid Cascade Centrifugation*. *ACS Nano*, 2016. **10**(1): p. 1589-601.
64. Loryuenyong, V., et al., *Preparation and Characterization of Reduced Graphene Oxide Sheets via Water-Based Exfoliation and Reduction Methods*. *Advances in Materials Science and Engineering*, 2013. **2013**: p. 5.
65. Yang, H., et al., *Covalent functionalization of polydisperse chemically-converted graphene sheets with amine-terminated ionic liquid*. *Chem Commun (Camb)*, 2009(26): p. 3880-2.