



A comparative study on few-layer graphene production by exfoliation of different starting materials in a low boiling point solvent



Yasemin Çelik^{a,b,*}, Emmanuel Flahaut^b, Ender Suvacı^a

^aAnadolu University, Department of Materials Science and Engineering, 26480 Eskişehir, Turkey

^bCIRIMAT, Université de Toulouse, CNRS, INPT, UPS, UMR CNRS-UPS-INP N°5085, Université Toulouse 3 Paul Sabatier, Bât. CIRIMAT, 118 route de Narbonne, 31062 Toulouse cedex 9, France

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ABSTRACT

Three different graphite-based powders (expandable graphite and two different nano-graphite powders) were investigated as starting materials for an effective liquid phase exfoliation process in isopropyl alcohol (IPA). The prepared dispersions were analyzed and compared in terms of their graphene concentration, stability, number of graphene layers and quality, as well as the electrical conductivity of the prepared graphene-based materials. Good quality graphene dispersions ($I_D/I_G < 0.3$) with a relatively high concentration (~ 1.1 mg/ml) were prepared in IPA within 90 min sonication time by utilizing a high specific surface area (~ 175 m²/g) nano-graphite powder derived from natural graphite. Transmission electron microscope analyses of this sample revealed mostly folded and scrolled few layer graphene (FLG) sheets (<5 layers) entangled each other. The electrical conductivity of the thin film prepared from this dispersion was ~ 15 and 86 S/m, before and after annealing, respectively. FLG prepared from expanded graphite, obtained by thermal treatment of expandable graphite, exhibited both much higher quality ($I_D/I_G < 0.09$) and electrical conductivity (~ 2104 and $19,200$ S/m before and after annealing, respectively) when dispersed in IPA for 90 min. However, the graphene-based material concentration of the prepared dispersion was relatively low (~ 0.06 mg/ml).

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Introduction

Graphite is an inexpensive and readily available precursor for production of graphene-based materials (single layer, few-layer or multi-layer graphene sheets, graphene oxide, reduced-graphene oxide, etc.). The main challenge of graphene production from graphite is to overcome van der Waals forces which hold graphene sheets together. Liquid phase exfoliation is a promising method to exfoliate graphite into graphene sheets, dispersed as a colloidal suspension in a solvent with or without surfactant. This process eliminates the need of using a substrate. Since there is no graphene transfer step, the produced graphene-based materials can be readily incorporated into other materials such as ceramics or polymers to form composites. The critical point in liquid phase exfoliation is to be able to increase graphene concentration as much as possible while maintaining the quality of the flakes and keeping their lateral size large enough.

* Corresponding author at: Anadolu University, Department of Materials Science and Engineering, 26480 Eskişehir, Turkey.

E-mail address: ybozkaya@anadolu.edu.tr (Y. Çelik).

Comprehensive reviews were published on exfoliation of graphite powders into single- and few-layer graphene sheets in various liquids, including organic solvents, ionic liquids, and water/surfactant solutions [1–4]. The qualities, yields and electrical properties of exfoliated graphene samples are also reviewed in these papers. Zhong et al. [5] have recently reviewed wet chemical graphite exfoliation routes highlighting their progress and challenges in terms of graphene commercialization. There have been several attempts to produce graphene-based materials at a large-scale. Exfoliation of graphite in aqueous solutions with aid of surfactants yielded graphene concentrations of mostly < 1 mg/ml [6]. Concentration was further increased up to 15 mg/ml by continuous addition of surfactant throughout the sonication process [7]. Ager et al. [8] demonstrated complete exfoliation of up to 5 wt% graphene in water by using triblock copolymers and copolymeric nanolatexes based on a reactive ionic liquid acrylate surfactant for extended time periods of sonication. Ayán-Varela et al. [9] recently reported very high graphene concentrations (up to ~ 50 mg ml⁻¹) in aqueous dispersions by using the sodium salt of flavin mononucleotide biomolecule as a surfactant in an exfoliation process which was carried out in an ultrasonic bath for 5 h. However, most surfactants are insulating compounds that should

be removed from the system by an additional washing step for further applications; moreover, using relatively high amount of surfactants may bring additional cost [5]. Chlorosulphonic acid was also reported as a highly efficient solvent for graphene production with concentration values up to 2 mg/ml [10]; however, it is toxic, highly corrosive and reactive which prevents its use for further processing. Graphite can also be exfoliated into high-quality graphene sheets (with <5 layers) in 1-methyl-2-pyrrolidone (NMP, C₅H₉NO) due to well matched surface energy between graphene and the solvent [11]. Therefore, it is one of the most widely preferred organic solvent for sonication assisted liquid-phase exfoliation of graphene from graphite. Initial studies of direct exfoliation of graphene in organic solvents resulted in graphene dispersions at very low concentrations of 0.01 mg/ml [11]. Khan et al. [12] showed that the concentration of graphene dispersed in NMP can be increased dramatically (up to 1.2 mg/ml) by sonicating at low power for very long times (~460 h). Recently, Khan et al. [13] increased graphene concentration up to 2 mg/ml by simple tip sonication of graphite for 6 h in NMP, followed by centrifugation. The authors further increased graphene concentration up to 63 mg/ml at a yield of 19% (percentage of graphite exfoliated as few-layer graphene) by re-dispersing the exfoliated material after centrifugation [13]. Catheline et al. [14] reported that graphite intercalation compound KC₈ spontaneously dissolves in NMP, yielding solutions of negatively charged graphene layers with a concentration of 0.7 mg/ml after stirring overnight and centrifugation to remove insoluble material.

Although these studies have shown that NMP is an effective solvent to exfoliate graphite, its high boiling point (~204 °C at 760 mmHg) makes it difficult to be completely removed from the system and the residual solvent can be detrimental for composites. Moreover, this may cause problems during flake deposition onto a substrate, since agglomeration tends to occur during slow solvent evaporation [15]. Hence, exfoliating graphite in a low boiling point solvent to achieve graphene-based dispersions with a concentration as high as possible would facilitate applicability of these materials into composites and deposition onto substrates. O'Neill et al. [15] demonstrated graphene concentrations of up to 0.5 mg/ml in isopropyl alcohol (IPA), whose boiling point is 82.5 °C, by a low power sonication of graphite for 48 h followed by a centrifugation at 500 rpm, showing that it is possible to produce graphene dispersions with a relatively high concentration in low boiling point solvents. However, long process times make the method impractical for realizing the potential applications. Therefore, this process needs to be improved so as to achieve a higher graphene concentration within a shorter time.

The choice of starting materials, as well as the use of an appropriate solvent, is critical for liquid phase exfoliation process. The most commonly used starting material for the production of graphene-based materials by liquid phase exfoliation is natural graphite. The number of studies which use expandable/expanded graphite and nano-graphite powders as precursors is limited [14,16]. Kozhemyakina et al. [17] have recently published a comprehensive study in which they investigated the dispersibility of several types of graphite with different morphological and structural characteristics in two high boiling point organic solvents (including NMP) and in one surfactant-water solution. The authors followed an uncommon way to prepare their dispersions: they stirred graphite in the corresponding solvent over a period of two-days. The carbon uptake of the graphite materials into solvents was determined by absorption measurements on the decanted part after leaving them for 1 day of sedimentation. It was observed that the dispersibility of graphite materials with small grain size is better than that of large grain sized graphite materials, and this depends not only on the nature of the graphite but also on the viscosity of the solvent used [17].

The objective of this study was to investigate three different graphite materials (expandable graphite, nano-graphite powder derived from natural graphite and nano-graphite powder derived from synthetic graphite) as starting powders for liquid phase exfoliation in a low boiling point solvent (IPA) in order to produce good quality graphene-based materials at a large-scale within relatively short sonication times (<120 min). The prepared graphene-based dispersions were characterized and compared in terms of their concentration and stability, and number of layers, quality and electrical conductivity of the obtained graphene-based materials.

Methods

Starting materials and exfoliation process

Three different graphite-based materials, expandable graphite, surface enhanced flake graphite (SEFG) and primary artificial (PA) were used as starting powders for the exfoliation studies. The expandable graphite (Expansion ratio: 307, Grade 3772), SEFG (Grade 3725) and the PA (Grade TC307) were kindly provided by Asbury Carbons Inc. The SEFG, which was derived from natural flake graphite and the PA, which was derived from synthetic graphite are nano-graphite powders, the specific surface area (SSA) of which are 175 and 350 m²/g, respectively. These two powders were used as-received for further exfoliation studies, while expandable graphite was subjected to an abrupt heating in a pre-heated furnace at 900 °C for 2 min in air to prepare expanded graphite (EG) prior to exfoliation. Before thermal expansion, the expandable graphite was first dried in a vacuum oven and then a small amount of dried powder was put at the bottom of an alumina crucible and placed in the furnace.

The SEFG and PA powders were dispersed in IPA (Merck-Emsure) and also in NMP (Merck-Emplura) at an initial concentration of 3 mg/ml by sonicating in an ultrasonic bath (Kudos, 35 kHz, 100 W) for 10–120 min. The EG was dispersed in IPA at an initial concentration of 0.2 mg/ml by bath sonication (100 W), as well as using tip sonication (Cole Parmer, CP750, 20 kHz, running at 250 W) in order to observe the effect of sonication power on graphene concentration. Large graphitic flakes were removed from the dispersions of the SEFG and PA by a subsequent centrifugation at 500 rpm for 45 min unless otherwise stated. The dispersions prepared from the EG powder were centrifuged at 900 rpm for 45 min. After centrifugation, the top ~90% of the supernatant was removed by pipetting for further use. Prepared dispersions were denoted as 'Precursor-Solvent-Sonication time'. This is valid for the dispersions which were prepared in ultrasonic bath and centrifuged at 500 rpm for 45 min. For the tip sonicated samples, the abbreviation 'TS' was added at the end; likewise, for the samples centrifuged at 900 rpm for 45 min, the term of '900 rpm' was added at the end.

Characterization of the starting powders and the exfoliated materials

Field emission gun-scanning electron microscopy (FEG-SEM) analyses of the precursor powders and the dispersed graphene/graphite sheets were performed using Zeiss Supra 50VP. FEG-SEM samples were prepared by dropping some dispersion onto a Si substrate with an oxide layer thickness of 300 nm and subsequently drying in an oven (at ~80 °C in air). Lateral size distribution of exfoliated graphene/graphite flakes and zeta potential of dispersions were measured by dynamic light scattering (DLS) and electrophoretic light scattering (ELS), respectively, using Malvern Zetasizer Nano ZS system with a 633 nm laser. The stability of the prepared graphene-based dispersions was investigated by observing their sedimentation behavior. The sedimentation study

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