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Quantitative evaluation of delamination of graphite by wet media milling

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ABSTRACT

Surfactant-free Few-Layer-Graphene (FLG) suspensions were prepared by wet media delamination of unmodified isostatic graphite in organic solvents using a shaking plate for fast screening of favorable process parameters and a stirred media mill as a delamination tool. The achieved FLG-concentration was determined by a combination of UV/Vis and Raman spectroscopy. A study of wet delamination for different solvents reveals an analogue behavior as for ultrasound-assisted delaminated samples. In N-methylpyrrolidone as dispersing medium the influence of delamination process parameters on FLG concentration was studied and an optimal set of parameters was found. A comparison between various delamination methods shows that delamination by enhanced shear leads to largest flake structures. The highest value for the FLG production rate (produced mass/time) is obtained in a stirred media mill. The formation of FLG was also proved by measuring the flake thickness by atomic force microscopy (AFM). The FLG percentage derived from AFM agrees well with the results determined by statistical Raman spectroscopic analyses.

1. Introduction

The excellent material properties and potential applications found for graphene in the last decade triggered the development of various production methods. Since the scotch-tape method used by Geim and Novoselov in their first works [1] is not scalable and yields graphene on a "few flake scale" more feasible production methods are needed. Within the last 10 years both bottom-up and top-down approaches as production methods were established and continuously further developed [2–4]. Bottom-up processes as epitaxial growth [5–8] or chemical vapor deposition yield highly pure graphene, but on low scales, high costs and with limited scalability [9–12].

Top-down production of graphene is achieved either via wet chemical oxidation of graphite or by solvent- or surfactant-assisted mechanical graphite exfoliation to graphene monolayers and FLG [13,14]. The oxidative graphene production route, however, requires the use of aggressive chemicals [15–19]. In comparison with the oxidative route the surfactant- or solvent-assisted graphite exfoliation is much easier to handle and offers a process route for graphene production under mild conditions [20–33]. Single Layer Graphene and FLG have been produced by ultrasound-assisted graphite exfoliation in aqueous media in the presence of surfactants or in surfactant-free organic solvents [20–33]. The ultrasound-assisted wet chemical graphite exfoliation is simple and yields graphene flakes of good quality. Its scalability, however, is limited because for batches of some hundreds mL process times of up to seven days are necessary to achieve reasonable dispersed carbon concentrations [28]. Therefore, the development of scalable and cost-effective methods for

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graphene production is in the focus of current research. Recently promising methods based on shear-induced graphite exfoliation by using a rotor–stator device [34] or a kitchen blender [35] were presented. The rotor–stator method yields FLG suspensions in scale of some liters in short process times and good quality. Graphene and boron nitride monolayers were obtained in a yield of about 1% and 5%, respectively, by using a vortex fluidic device [36]. In this method sheets are exfoliated from layered materials by an interplay between centrifugal and gravitational forces [36]. Moreover, layered materials were delaminated successfully by using a hydrodynamic apparatus in which the feed materials are exposed to high pressure cycles [37].

Milling processes are known to be well scalable. Recently, planetary ball milling techniques of graphite in wet or dry state have been developed continuously for graphene production [38–46]. Dry milling of graphite in an SO_3 atmosphere and in presence of dry ice yields graphene functionalized with carboxylic and sulfonic acid groups [44,45]. These methods inherit the combination of functionalization and delamination of graphite [43–46]. A drawback for planetary ball milling techniques is the long process time (about 24 h) [43–45] and/or requirement of ultrasound-assisted post-dispersing steps [41,42,46]. Usually, high energy ball milling favors in-plane fracture in comparison with delamination which limits the yield and leads to defective sheets.

In contrast to planetary ball mills, stirred media mills operate with much smaller grinding media (bead-size: in most cases 1 mm or smaller) and allow a better temperature control during processing. Therefore, stirred media milling is a simple, but highly effective and well scalable top-down approach for the production of nanoparticles under variable mild conditions with typical process times of a few hours [47–50]. In our previous studies we could show the feasibility of FLG and few layer boron nitride production by delamination of graphite or hexagonal boron nitride in a stirred media mill [47,51]. Comparably little is known about the influence of process parameters on the delamination yield and product quality.

In this paper we present a scalable method for production of surfactant-free FLG suspensions by stirred media milling of graphite in organic solvents. The influence of process parameters (milling tool, solvent, milling bead size, stirrer rotation speed) on FLG yield is investigated systematically to provide guidelines for technology of large scale industrial graphene production. In this work the FLG concentration is determined by a combination of UV/Vis-spectroscopy and statistical Raman spectroscopic product analyses giving a deeper insight into the product quality distribution [52,53]. The FLG production rate achieved by the method presented in this paper is higher in comparison with ultrasound-assisted graphite delamination.

2. Experimental

2.1. Materials

The unmodified isostatic graphite “GSI70” (RMC Remacon GmbH) was used as feed material for preparation of FLG. It has a purity > 99.5% and a median particle size $x_{50,3}$ of 15–20 μm (measured by the supplier using a Cilas particle sizer 920). N-methylpyrrolidone (NMP), cyclohexanone (CHO) and i-propanol (IPA) were purchased from Merck and have a purity > 99.5%. All materials were used without any further purification.

2.2. Wet media delamination procedure

For all delamination experiments suspensions of 1 wt.% of graphite in one of the solvents mentioned in Section 2.1 were used. A shaking plate “LAU disperser DAS H 200-K” (LAU GmbH) or a lab-scale stirred media mill “PE 075” (Netzsch GmbH) were used as delamination tools. Both devices operate in batch mode. Yttria stabilized ZrO_2 beads (Tosho Inc., Japan) were used as delamination media. The bead size was varied from 30 to 200 μm. For a typical delamination experiment using the LAU disperser 0.2 g of graphite, 20 mL of solvent and 30 g of ZrO_2 beads were placed in 30 mL screw-cap bottles. After sealing the bottles were mounted on the shaking plate of the LAU disperser. For a typical delamination experiment using the stirred media mill “PE 075” the chamber of the mill (volume 600 mL) was loaded with 170 mL of solvent, 1.7 g of graphite and 1.5 kg of ZrO_2 beads. All the delamination experiments were performed at ambient temperature. After the desired process time samples were taken and centrifuged for 10 min with 5000 rpm (1817 g) using a table top centrifuge “Sigma 3-30KS” (Sigma GmbH) to remove not yet delaminated feed particles from the suspensions prior to further characterization. The centrifuging conditions correspond to a cut size of 361 nm for a sphere-equivalent diameter, see also Section 3.2.

2.3. Characterization methods

The concentration of dispersed carbon in the supernatant of centrifuged samples was determined by UV/Vis-spectroscopy using a “Cary 100 Scan” spectrophotometer (Varian). UV/Vis-spectra of suitable diluted suspensions were recorded in the wavelength range from 400 to 800 nm using quartz cuvettes with an optical path length of 1 cm. The absorbance at 660 nm was evaluated and the carbon concentration was calculated using the extinction coefficient of 3620 mL mg^{-1} m^{-1} determined by Khan et al. (2010) for FLG in organic solvents [27]. For Raman spectroscopy and AFM 15 μL of the supernatant of centrifuged milled samples were deposited on a silicon wafer, with a 300 nm thick SiO_2 layer on top, by spin-coating (40 rpm). The wafers have been dried at ambient temperature for 24 h. Residuals of the solvents NMP and CHO having high boiling points would disturb Raman and AFM investigations and were therefore removed by washing the wafers with absolute ethanol. Raman spectra were recorded in the wave number range from 1100 to 3000 cm^{-1} using a “LabRAM HR Evolution” Raman spectrometer (Horiba) equipped with a Nd-YAG laser (second harmonic, wavelength: 532 nm, beam diameter in focus: 0.7 μm) and a piezo-driven table (Märzhäuser) for two-dimensional maps. The FLG content in the delaminated samples was checked by statistical Raman spectroscopy. Raman maps including 500–600 different positions on the wafer were recorded from each sample (for more details see Supporting information). The full width at half maximum (FWHM) of the 2D-Raman peak was evaluated by peak fitting using a single Lorentz function. For comparison