Establishing the applicability of the laser diffraction technique for the graphene oxide platelets lateral size measurements

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Abstract. In this paper, basing on the thorough comparison of the size measurement results obtained by Laser Diffraction (LD) and microscopic methods, we demonstrate the LD method to provide reliable and accurate data on the lateral size of two-dimensional graphene oxide (GO) platelets. Taking cue from the experimental study and theoretical calculations of scattering patterns, model accounting for arising of diffraction pattern that can be correctly processed with common LD instrumentation is suggested.

1. Introduction
Graphene oxide (GO) synthesis nowadays is regarded as one of the most prominent approaches for graphene-based materials large-scale production [1,2]. This is due to the method’s simplicity, low-cost, and high yield along with the hydrophilic nature of the synthesized GO [3]. The latter fact is a key advantage since it allows one to form GO films on the surface of various substrates using facile spin-coating, aerosol deposition, or Langmuir-Blodgett technique [4]. Once formed, GO film can be easily converted into graphene by so-called reduction techniques [5], resulting in fabrication of graphene coating with the desired thickness and morphology, which is a substantial issue addressed to overcome within the frame of other methods of graphene synthesis [6]. Obviously, the obtained reduced GO (rGO) film will be composed of an array of partially overlapping rGO platelets, which mean lateral size will define the physical and chemical properties of the film. In particular, the reduction of the GO platelets’ lateral size would induce the diminishing of the film’s electrical conductivity due to the increase of the total boundaries length, providing scattering of charge carriers [7]. Furthermore, the smaller GO platelets are the higher is the concentration of edge-located oxygen moieties, which are more stable to the elimination during the reduction process and, thus, require application of the more sophisticated reduction methods [8]. On the other hand, the excessively large lateral size of GO platelets complicates their deposition using spin-coating or spray coating techniques owing to the high tendency of the formation of wrinkles and folds [9]. As a net result, the analysis of the GO platelets lateral size in the used aqueous or organic suspensions is one of the crucial stages for their further studying and application.

Several methods are commonly used for this purpose, mainly presented by the direct imaging applying microscopic techniques, such as optical microscopy with the use of specially designed substrates [10], scanning electron microscopy (SEM) and atomic force microscopy (AFM). However, the analysis of GO size distribution through the processing of the SEM or AFM images is a rather complicated, time-consuming, and statistically unreliable method. Furthermore, it can be applied only to the GO platelets deposited onto the surface of the suitable substrate. Oppositely, light scattering techniques, namely dynamic light scattering (DLS) and laser diffraction (LD) methods are widely used, simple, rapid and
effective methods for the particle size analysis that can be applied to liquid samples [11,12]. However, these methods are considered to be applied exclusively for the suspensions, containing spherical or approximately particles, not for two-dimensional structures, such as GO platelets. Recently, Lotya et al. and Andryushina et al. both demonstrated that despite the high anisotropy of the GO and rGO platelets their mean diameter and size distribution can be diagnosed using DLS with the relevant accuracy (the relative error is estimated to be around 40%) [13,14]. However, the application of the LD method, which has wider measurement range and provides the geometrical size of particles, not their hydrodynamic radius as DLS does, for the studies of GO suspensions has not been analyzed yet.

In the presented work, on the base of a comparative study using LD method and SEM imaging we analyze the applicability and accuracy of the GO platelets size distribution measurements via the Laser Diffraction method. We also have performed both theoretical and experimental studies of the light scattering on the GO two-dimensional particles, giving a hint on the optical properties of GO suspensions.

2. Materials and Methods

2.1 Studied materials
The set of four GO suspensions with different lateral sizes of GO plates, hereinafter designated as GO#1, GO#2, GO#3, GO#4, were investigated. GO#1 and GO#2 suspensions were purchased from GraphOx (Russia, www.graphox.ru), being synthesized by a modified Hammer’s method using GSM-1 and GO350 graphite, respectively. GO#3 and GO#4 samples were obtained by treating the GO#1 suspension in an ultrasonic bath (PSB-Gals, Russia; 60 kHz, 75 W) for 120 seconds and then centrifuging (Sigma S-16 centrifuge, Germany) of the obtained slurry (19200, 15 minutes). The GO#3 sample corresponds to supernatant after the centrifugations, while the GO#4 sample is a sediment rinsed with the deionized water. GO films were manufactured using the Langmuir-Blodgett method on the surface of silicon wafers according to the conventional procedure [15].

2.2 Characterization
The LD size distribution was measured using the Mastersizer 2000 (Malvern, United Kingdom). The SEM images were collected using JSM-7001F microscope (Jeol, Japan). The morphology of GO layers was analyzed by the Veeco Dimension 3100 tapping atomic force microscope using RTESP probes. The ultraviolet-visible (UV-Vis) absorption spectra of the GO suspensions were recorded both with and without integrating sphere using Shimadzu-2450 (Shimadzu, Japan) and Unico-2100 (Unico, USA) spectrophotometers, respectively. The spectra were measured in the range of 210-1000 nm, 1 nm step.

To analyze the scattering patterns of GO suspensions, an original setup was designed, consisting of a CCD detector (IMX249 Matrix, Sony, Japan) fixed on a rotating platform, sample holder with a quartz cuvette, Fourier lens, and a fiber-coupled diode laser (650 nm, 5 mW. Hamamatsu, Japan). The photo (Figure 1a). To verify the accuracy of the designed optical scheme, the scattering pattern of the aqueous suspension of the standardized 3.2 μm latex spheres (provided by the D.I. Mendeleev All-Russian Institute for Metrology (VNIIM), Russia) was measured using the designed setup and compared to the theoretical one (Figure 1b). Both the measured and theoretical scattering patterns coincided well, thus demonstrating the correctness of the measurements provided by the designed setup.

2.3 Theoretical calculations
For the theoretical modeling of the GO scattering patterns, MiePlot v4503 software package was used. The following parameters were chosen to perform calculations: monochromatic radiation; wavelength – 650 nm; real and imaginary refractive indexes of GO – 2.1 and 0.01, respectively [25]; refractive index of medium – 1.33 (water); angular resolution – 0.05; angle scale – from 0 to 80 degrees. Mie and Fraunhofer models were applied with the calculations performed for the polydisperse suspensions with the size distribution, modeling the experimental ones obtained via Laser Diffraction method (Multimodal distribution, N=5000)

3. Results and discussion

Laser diffraction was used to measure the size of the studied GO#1-GO#4 suspensions. As seen, GO#1 sample exhibits a single modal size distribution with the maximum centered at ca. ~2.2 μm with a descending slope extending up to 50 μm. At the same time, GO#2 suspension synthesized using graphite having a larger mean size of crystallites is demonstrated to contain platelets with the utmost lateral size. The mean measured diameter is about 19 μm, whereas the largest platelets are measured to be 130-140 μm. These values correspond to the highest ones being reported [16]. After the sonication and centrifugation (GO#3 and GO#4 samples) this distribution substantially changes. Particularly, LD size distribution of GO#3 sample, presenting the supernatant of the resulting mixture, has narrow size distribution with the maximum at about 0.7 μm and absence of any GO platelets with the lateral size exceeding 10 μm. On the other hand, the fraction of GO platelets in the sediment after the centrifugation demonstrate the LD sized distribution of the same character as the GO#2 one, although the mean size has reduced to ~7 μm. Apparently, these changes are due to the disruption of the initial GO platelets upon the sonication treatment and subsequent centrifugation cycle. Thus, the use of LD measurements allows us to separate the GO suspensions having distinct size distributions in the range of 0.5 – 200 μm.

Figure 2. (a-d) Size distribution obtained via Laser Diffraction method. (e-h) Size distributions obtained by the analysis of a set of the SEM images. (i-l) Representative SEM images of the GO#1-GO#4 platelets deposited on the surface of silica wafers.

To further analyze the correctness and accuracy of the LD size distribution measurements, the results obtained for the studied GO suspensions were compared to the one acquired from the straightforward analysis of the SEM images of the arrays GO#1-GO#4 suspensions deposited on the silica wafers (Figure
The calculated size distributions are presented in Figure 2 (e-h). One can see that both LD measurements and SEM imaging demonstrate almost equal mean lateral size with a maximum deviation of about 7-9%. Moreover, the LD size distribution of GO#4 sample almost perfectly fits the one obtained from the SEM images. In comparison, for all the other samples (GO#1-GO#3), the SEM analysis demonstrates the presence of a large number of particles with the lateral sizes smaller than the mean one. These particles are not diagnosed via LD measurements, where the collected size distributions demonstrate a sharp decrease at the small particles’ sizes. We attribute this to the features of the diffraction pattern processing within the frame of the mathematical model used in the laser diffraction particle analysis. The smaller particles are the less resolved scattering pattern with broadband maximums it causes in the range of 0-90° angles [17]. In the range of lateral sizes of less than 1 μm the scattering pattern becomes a smoothed curve without any detectable features. Hence, in the diffraction patterns of polydisperse systems such as GO suspensions it is extremely difficult to detect the presence of small particles, even in the multimodal model. As a result, the performed comparative analysis of the size distribution obtained from LD measurements and processing of the SEM images does demonstrate that despite LD measurements underestimates the presence of small particles, this method can be quite well applied to analyze the distribution of two-dimensional GO particles in the aqueous suspensions.

Such a descent accuracy of the LD measurements of two-dimensional GO platelets is quite surprising since this method is limited to the analysis of the spherical or almost spherical particles. This is due to the independence of the spherical particles’ scattering cross-section and, thus, the scattering pattern on their spatial orientation. At the same time, highly anisotropic two-dimensional monolayer GO particles exhibit a drastic dependence of the scattering cross-section on their orientation against the propagating laser radiation. Hence, the coincidence of the GO particles’ lateral size and scattering cross-section must be achieved to obtain the relevant size distributions via laser diffraction. This proceeds only if several conditions are met, particularly: i) GO particles must be planar and not crumpled in the aqueous medium; ii) GO particles must be aligned orthogonally to the laser beam; iii) the light scattering on the GO particles is determined mainly by the laser diffraction at their boundaries, i.e. corresponds to Fraunhofer diffraction, not the Mie scattering.

The planar configuration of GO platelets in the aqueous suspensions was demonstrated earlier for the case of monolayer GO platelets using both polarized light microscopy and neutron scattering [18,19]. The linearization and orientation of GO platelets in the aqueous media orthogonally to the laser radiation was studied and discussed by Wu et al. According to the performed experiments, the reorientation of GO platelets arises from the electron motion associated with the oscillating electric field of the incident light. In detail, absorption of light leads to the formation of electrons and holes which move in opposite directions under the external electric field from the incident laser radiation and result in the dipole formation. In the case of the chaotic orientation of GO platelets, there will be an angle between the dipole and the electric field, inducing the increase of the interaction energy between the radiation and a particle. Apparently, to minimize the interaction energy the reorientation of GO to align the vectors of external electric field and arising dipole proceeds, making them orthogonal to the laser beam.

To analyze the light scattering mechanism in the aqueous suspensions of GO platelets we performed additional experimental and theoretical studies. Using the designed optical setup, the diffraction patterns of the GO#2 and GO#3 aqueous suspensions were measured in the range of 0-100 degrees. The obtained scattering patterns are presented in Figure 3.
Figure 3. Comparison of experimental data (red line) with Mie (blue line) and Fraunhofer (green line) theories for GO#2 (a) and GO#3 (b) samples.

To further estimate whether the measured scattering pattern corresponds to the Fraunhofer diffraction or the Mie scattering, we also calculated the theoretical scattering patterns using both of these scattering models applying the MiePlot software. Note that the calculations were performed for the polydisperse systems with the size distributions mimicking the ones obtained via LD measurements to provide the correct scattering pattern. Comparing the experimental and theoretical scattering patterns for both samples, one can see that the light scattering in GO suspensions is governed by the Fraunhofer diffraction. The Mie scattering pattern substantially differs from the experimentally measured ones, while the Fraunhofer pattern almost perfectly fits the experimental curve in the whole range of angles, until the detection limit of the used CCD camera is reached. This means that light scattering is only due to the radiation diffraction at the edges of GO platelets with the absence or negligible impact of the other effects, such as light refraction upon its propagation through the GO platelet.

Interestingly, the fact that light scattering on GO platelets is determined mainly by the light diffraction on the edges is also demonstrated by the UV-Vis spectroscopy.

Figure 4 demonstrates the UV-Vis spectra of GO#2 and GO#3 suspensions of the same mass concentrations measured with (red curve) and without (black curve) integrating sphere. In the former case, the measured optical density spectra refers only to the absorbed light, while in the latter case it corresponds to both the absorbed and scattered radiation.

Figure 4. UV-vis spectra of samples GO#2 (a) and GO#3 (b) with an integrating sphere (red curve) and without an integrating sphere (black curve).

Hence, the difference between these spectra resembles the scattered part of light. Comparing the GO#2 and GO#3 pairs of UV-Vis spectra, one can see that the variance within the spectra pairs is substantially higher in the case of GO#3 sample, even though the mean lateral size of GO platelets in this suspension is more than one order of magnitude lower smaller than in the GO#2 suspension. This contradicts to the...
conventional rule that the scattering efficiency is proportional to the \(-r^4\), where \(r\) is particle radius, but perfectly fits to the model that light scattering at GO is determined by the diffraction on the platelets edges. With the reduction of GO platelets’ lateral size and retention of their mass concentration in the suspension the overall extent of the edges substantially increases with the corresponding rise of the light scattering. Thus, the UV-Vis spectroscopy measurements of different GO suspensions independently confirm the assertion that light scattering in GO suspensions is mainly governed by the diffraction on the edges of platelets.

4. Conclusions
As a net result, for the first time we analyze the applicability of laser diffraction method for the measurements of size distribution of GO platelets in aqueous suspensions. We demonstrate that LD method provides a relevant data on the size distribution of GO suspensions and allows one to determine the mean lateral size of GO platelets with high accuracy. At the same time, the data obtained via this method underestimates the presence of the particles of the small size, most possibly due to the features in the data processing within the frame of the mathematical model applied in the used setup. On the base of both experimental and theoretical studies we also point out that the applicability of the LD method developed to study the spherical particles and conventionally not applicable for the anisotropic two-dimensional platelets arises from the fact that i) GO particles align and orthogonally orients under the propagating radiation, ii) light scattering on GO particles is determined by the diffraction on their edges according to the Fraunhofer model of the light diffraction. Owing to these facts, laser diffraction appears to be an efficient tool for the express analysis of the size distributions of GO.

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