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Estimation of graphene layers number and defectiveness of few-layered graphene particles by Raman spectroscopy

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Abstract: The purpose of the present work is to develop methods for assessing the quality of aqueous suspensions of few-layered graphenes using Raman spectroscopy technique. Aqueous suspensions of few-layered graphene particles were manufactured by direct exfoliation of natural graphite under with ultrasound in the presence of surfactants. An experimental assessment of the effectiveness of different methods of Raman spectroscopy data analysis in order to determine the average number of graphene layers and the defectiveness of few-layered graphene particles was carried out. It is concluded that it is possible to determine the average number of graphene layers in aqueous suspensions of few-layer graphene particles based on the ratio of integral intensities and the position of the G and $2D$ peaks. Additionally, it is proposed to use the ratio of the peaks of the integrated intensities of peaks D and G as a parameter characterizing the defectiveness of particles of few-layered graphenes. Examples are given of using this approach to assess the quality of graphene samples obtained using various technologies via averaged distribution functions of the number of layers in particles and the I_D/I_G ratio. It was shown that samples with minimal amount of layers had minimal particle size and high defectivity, while samples with higher number of layers had larger particle size with low defectivity.

Keywords: graphene; graphene suspensions; few-layered graphene; Raman spectroscopy; colloidal solutions; graphene structure.

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Определение количества графеновых слоев и дефектности частиц малослойных графенов методом рамановской спектроскопии

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Аннотация: Цель работы – разработка способов оценки качества водных суспензий малослойных графенов с применением метода рамановской спектроскопии. Водные суспензии частиц малослойных графенов получены путем прямой эксфолиации природного графита под воздействием ультразвука в присутствии поверхностно-активных веществ. Проведена экспериментальная оценка эффективности некоторых методик анализа данных рамановской спектроскопии для определения среднего количества слоев графена и дефектности частиц малослойных графенов. Сделан вывод о возможности определения среднего количества слоев графена в водных суспензиях частиц малослойных графенов по соотношению интегральных интенсивностей и положению пиков G и $2D$. Дополнительно предложено использовать параметр соотношения интегральных интенсивностей пиков D и G в качестве параметра, характеризующего дефектность частиц малослойных графенов. Приведены примеры использования данного подхода для оценки качества графеновых препаратов, полученных по различным технологиям с использованием усредненных функций распределения количества слоев в частицах и соотношения

I_D/I_G. Показано, что препараты с минимальным количеством слоев имели минимальный размер частиц и высокую дефектность, в то время как препараты с более высоким количеством слоев – больший размер частиц при низкой дефектности.

Ключевые слова: графен; графеновые суспензии; малослойный графен; рамановская спектроскопия; коллоидные растворы; структура графена.

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1. Introduction

50 years ago, the British researchers Tuinstra and Koenig first linked the parameters of Raman spectroscopy of soot and pyrocarbon with the diameter of crystallites [1], as determined by X-ray diffraction. This marked the beginning of the development of Raman spectroscopy as a structure-sensitive method in relation to all classes of carbon materials without exception. Among the "pioneers" one cannot fail to mention the Brazilian researcher Luis Conchado, who established the relationship between the parameters of Raman spectroscopy and the parameters of the crystal structure of graphite-like materials determined by X-ray phase analysis [2].

Back in the 2000s, European scientists undertook extensive research into a wide variety of classes of carbon materials. In the studies by Ferrari and his coworkers, the data from [1, 2] were confirmed and refined, and the possibility of determining not only the size of crystallites, but also the concentration of defects in graphene layers was established [3, 4]. Raman spectroscopy has become one of the main methods for identifying graphene [3–11], and a recognized method for studying carbon nanostructures such as fullerenes [12, 13] and carbon nanotubes [14, 15].

However, the main advantage of Raman spectroscopy remains the possibility of non-destructive testing of two-dimensional nanomaterials and in particular graphenes, while intensive research is aimed at finding ways to use Raman spectroscopy for quality control of ready-to-use structures [3–10].

The most important figure of merit for the quality of graphene structures, in addition to defectiveness, is the number of graphene layers. The aim of this study was to develop methods for estimating the number of layers in particles of few-layer graphenes using Raman spectroscopy.

2. Materials and Methods

2.1. Materials preparation

In order to develop a technique for determining the number of layers in particles of few-layer graphenes and studying them, liquid-phase exfoliated samples were used. The initial raw material was natural graphite of the GSM-2 or GE-2 grades, which had previously undergone gas-thermal refining in a Freon atmosphere at a temperature of 2000 °C and processing on a cup vibrating grinder for 30–240 min. An aqueous suspension was prepared from a sample of natural graphite (300 mg), distilled water (50 mL) and a surfactant (polyglycidyl ether 1H,1H,11H-eicosofluoro-1-undecanol with a gross formula of $C_{26}H_{34}O_{11}F_{20}$) (30 mg).

The resulting suspension in a container was treated with ultrasound with a submersible (horn-type) concentrator on a MELFIZ MEF 391 installation with a frequency of 22.5 kHz and an acoustic power of 200 W for 6 hours.

After removing the container from the ultrasonic unit, a sample (at least 0.1 mL) was taken and placed in liquid form on a single-crystalline silicon wafer, then dried with hot air and submitted for Raman assessment (series 1). Series 2 was obtained in a similar way, with a sonication time of 4 hours.

Series 3 and 4 of suspension samples of few-layered graphenes were obtained using a similar method, however, before ultrasonic treatment, the samples were crushed on a roller vibrating grinder with a predominant abrasion-crushing action for 30 minutes (series 3) and 2 hours (series 4).

Samples of series 5 and 6, provided by GoldKG, Bishkek (Kyrgyzstan), were obtained by circulating a water-alcohol graphite-containing suspension in a disintegrator with a rotor diameter of 200 mm, at different speeds and process durations.

2.2. Raman spectroscopy

Raman spectroscopy is based on inelastic scattering of photons. Light scattering occurs when an electromagnetic wave interacts as it passes through a crystal lattice. When a light wave interacts with the surface of a material, the vast majority of photons (> 99.999 %) are elastically scattered without changing wavelength (Rayleigh scattering), but a small fraction of photons (< 0.001 %) undergo inelastic (Raman) scattering with respective change in energy and wavelength photons. The resulting photon spectrum is passed through a filter that separates the inelastically scattered photons. Said scattered photons are amplified and directed to a detector, which records their frequency change with respect to incident photons (Raman shift) [16].

A Renishaw inVia Reflex confocal Raman microspectrometer was used to study samples of aqueous graphene suspensions. Suspensions were applied onto a silicon wafer substrate with 300 nm thermal oxide layer. The microspectrometer is equipped with an optical microscope and a cooled CCD detector. The laser radiation power did not exceed 1 mW, and the laser spot had a diameter of approximately 0.55 μm.

3. Results and Discussion

Figure 1 shows optical microphotographs and Raman spectra of the studied samples of suspensions of few-layered graphenes. It is obvious that the applied coatings were very heterogeneous in their particle size distributions (see Figs. 1*a*–*e*). The Raman spectra of few-layered graphene samples contained three main lines: *D*, *G* and 2*D* (see Figs. 1*f*–*l*). In addition, the intense line (1000 cm^{-1}) inherent to silicon was clearly visible in the spectra. The intensity of this line varied, decreasing as the amount of graphene in the applied coating increased. In this case (see Figs. 1*f*–*l*), it is obvious that the high variation of the line intensity (1000 cm^{-1}) indicated the inhomogeneity of the applied coating.

As a rule, two characteristic bands are observed in graphene, like many other carbon materials, in the first-order Raman spectrum (1000–2000 cm^{-1}) (see Fig. 1). One of them is the Raman-allowed band at 1580 cm^{-1}, corresponding to the ideal graphite vibrational mode with E_{2g} symmetry, often referred to as the *G*-mode or *G* band, which is determined by the vibrations of carbon atoms in the plane of the “graphene” layers and is associated with carbon atoms in the state of sp^2 hybridization [2–4]. Another active Raman band at 1360 cm^{-1} is induced by disordered carbon atoms, corresponds to lattice vibrations with A_{1g} symmetry, and is called the *D*-mode. Band *D* is associated with carbon atoms also in the state of both sp^2 and sp^3 hybridization, localized in the area of defects and the periphery of “graphene” layers [2–8]. The *D* band may be absent in highly perfect graphites: single-crystalline graphite, highly oriented samples of pyrolytic graphite (HOPG), some samples of natural graphite, and an increase in its intensity is considered to be the result of an increase in the amount of disordered carbon or peripheral atoms [2–6].

In this regard, discussions continue on the origin of the main second-order spectrum feature, the 2*D* line [4], since it was initially assumed that it is a 2nd order mode with respect to the *D* line. However, recent theoretical research has indicated a different nature of the generation of this line associated with the crystal structure of the material under study, in particular with the influence of graphene layers located under the main layer [3–5].

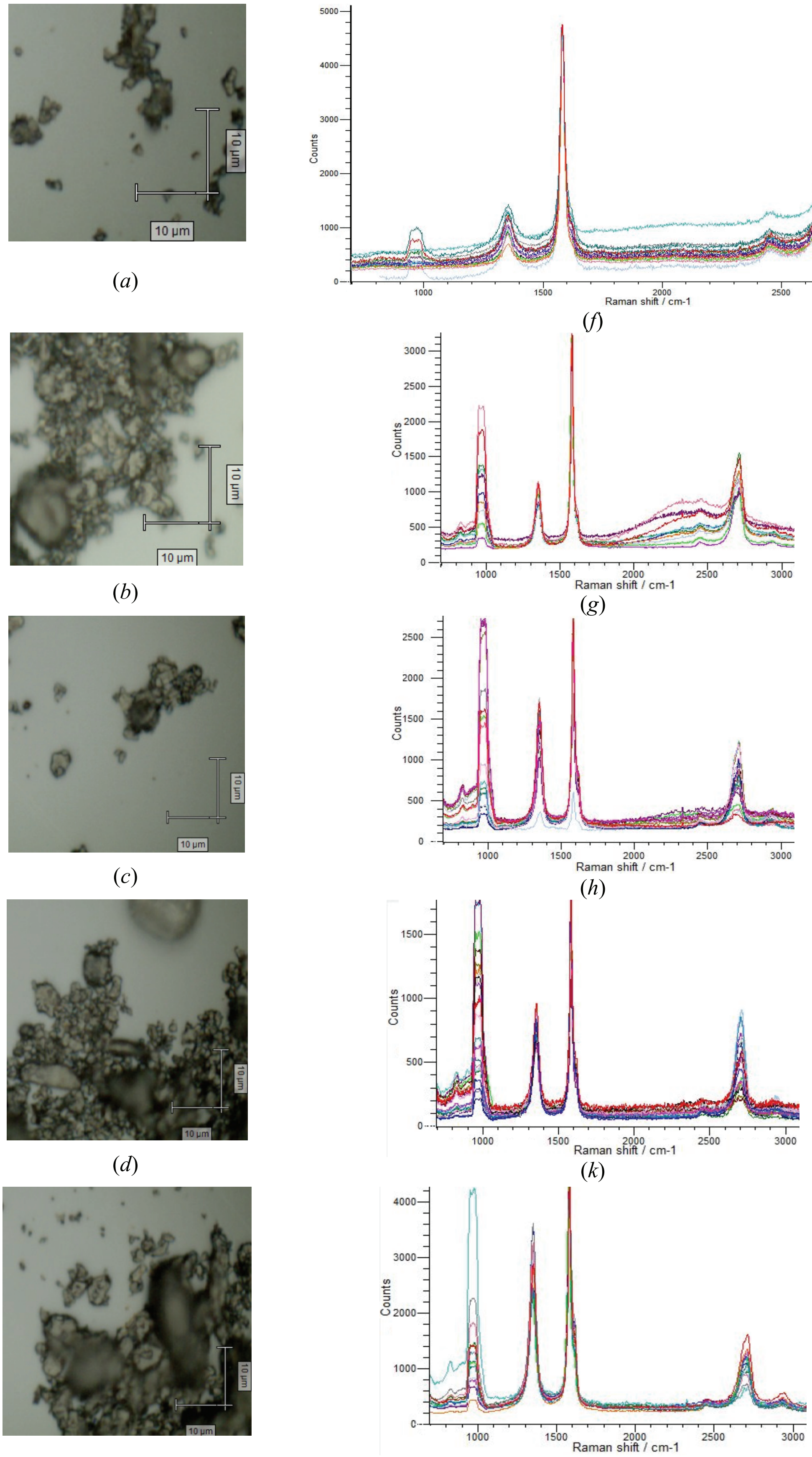
According to the results of numerous works [2–10], the ratio of the integral intensities of these bands, the I_D/I_G parameter is determined by the average distances between defects in the case of amorphized, in particular irradiated, graphene-like structures, and the sizes of L_a crystallites for natural graphites and various carbon materials after high-temperature processing at the graphitization stage [3–5]. For graphitized materials, the parameters of Raman spectroscopy can be used to determine other parameters of the crystal structure, such as the interlayer distance d_{002} and the height of crystallites L_c [2]. Numerous studies have shown the applicability of Raman spectroscopy for determining the number of graphene layers in various graphene like structures [3–11].

The most sensitive to the number of graphene layers is the I_{2D}/I_G parameter. This parameter that was used in works [4–11] for demonstrating the spectral differences between graphite and graphene. Figure 2 shows experimental data obtained by Holmi [10], who performed more than 2000 measurements on graphene samples (see Fig. 1*a*) obtained by the CVD method, and the calibration dependence for determining the average number of layers, *n*, proposed based on the results of work [10], is as follows (see Fig. 2*b*):

$$n = \sqrt{\frac{b}{(I_{2D}/I_G) - a}},$$

where $b = 1.667$, $a = 0.238$. Subsequently, this dependence was used to determine the number of graphene layers on samples of dried suspensions.

Figure 3 shows the distribution functions by the number of graphene layers for the studied suspensions of few-layered graphenes, calculated using the I_{2D}/I_G ratio.



(*a*) (*f*)

(*b*) (*g*)

(*c*) (*h*)

(*d*) (*k*)

(*e*) (*l*)

Fig. 1. Optical micrographs (*a*–*e*) and Raman spectra (*f*–*l*) of the studied few-layered graphenes suspensions

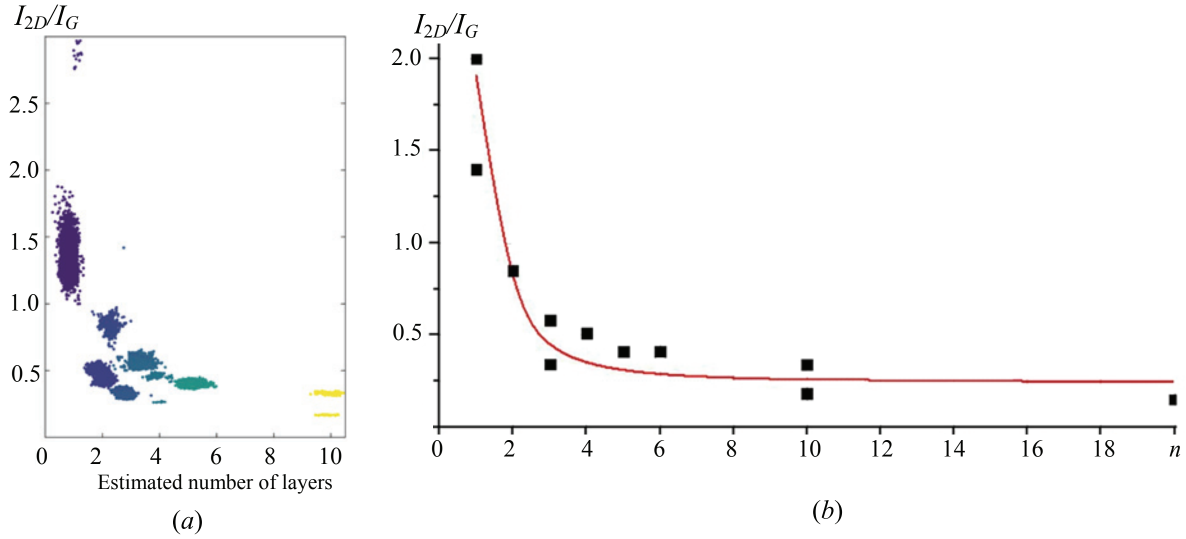


Fig. 2. Experimental data from [10] (*a*) and approximation of the I_{2D}/I_G parameter dependence on graphene layers number of low-layer graphene according to experimental data from [10] (*b*)

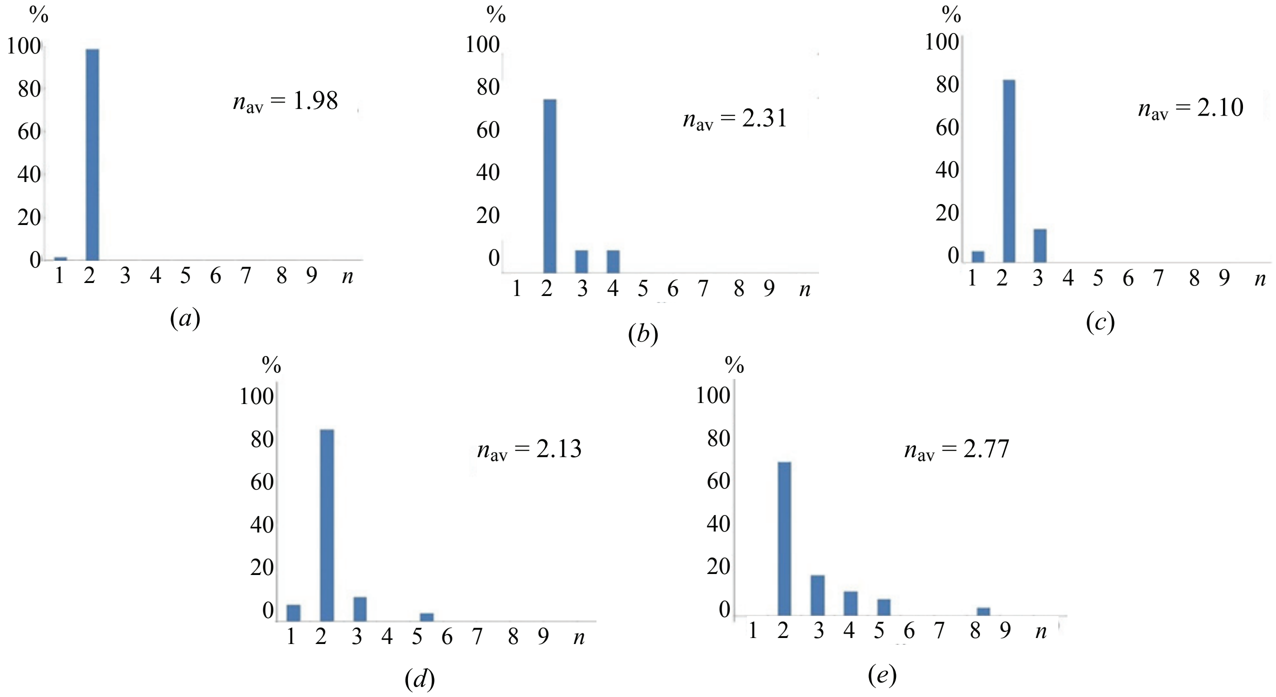
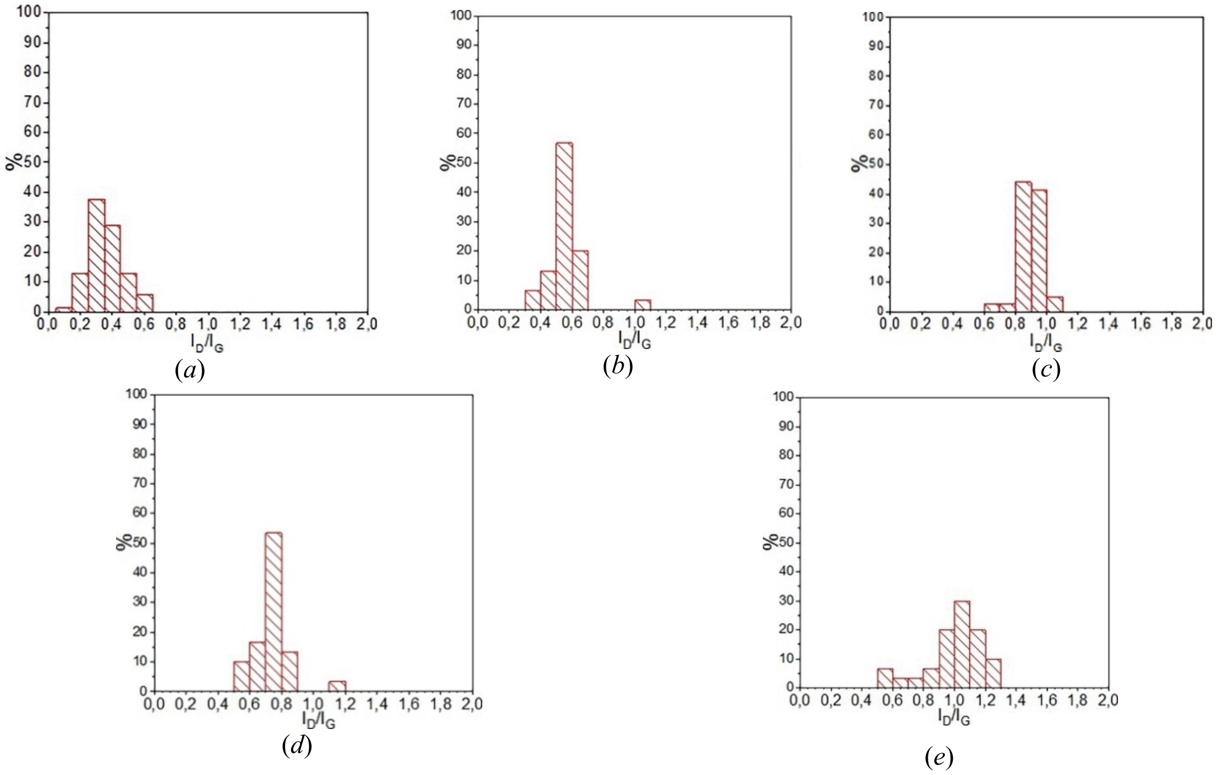


Fig. 3. Distribution functions by the graphene layers number for studied few-layered graphene suspensions calculated using the I_{2D}/I_G parameter

Additionally, the I_D/I_G parameter was used to characterize the quality of suspensions. Since the degree of graphitization of all starting materials – natural graphites – is almost the same, an increase in the intensity of the I_D peak relative to the intensity of the I_G peak shows a change in the degree of defectiveness of the material during the exfoliation process. The results representing the distribution functions of the I_D/I_G parameter for the studied suspensions are presented in Fig. 4.

4. Conclusion

Based on the data obtained, it should be concluded that exfoliation under the effect of ultrasound in the presence of a surfactant makes it possible to obtain suspensions of few-layered graphenes with a minimum number of layers, while the graphene layers have minimal defects. Reducing the ultrasonic treatment time leads to an increase in the average number of layers. The use of preliminary mechanical treatment does not lead to a decrease in the number of layers in the resulting suspensions, but the defectiveness of the layers greatly increases.



(*a*) (*b*) (*c*)

(*d*) (*e*)

Fig. 4. I_D/I_G distribution functions for investigated suspensions

When using a disintegrator, it was not possible to obtain suspensions with very few graphene layers, but the defectiveness of graphene layers in the suspensions remained quite low. It should be noted that the latter method for producing few-layered graphenes has an undoubted advantage, since it has a productivity of about 0.5–1.0 kg of dry powder of few-layer graphene per hour, while the productivity of an ultrasonic installation, even at a power of 1 kW, does not exceed 0. 3–0.5 $g \cdot h^{-1}$.

In general, the study results are consistent with the results of the extensive study of various commercial graphene samples performed by the authors of [17], where a general trend was established: samples with a minimal number of layers had a minimal particle size and maximum defectiveness, while preparations with a higher number of layers had a larger particle size with low defectiveness.

Thus, the results obtained will allow further research in the development of effective technologies for producing few-layered graphenes in the form of suspensions using Raman spectroscopy parameters, striving to obtain materials with maximum valuesof the I_{2D}/I_G parameter and minimum values of the I_D/I_G parameter, in parallel using other developed we previously described control methods.

5. Funding

This study received no external funding.

6. Conflict of interests

The authors declare no conflict of interest.

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