Analysis of the structural characteristics of graphene materials obtained by electrochemical exfoliation of graphite

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Abstract. The aim of the research is to study the structural characteristics of graphene materials obtained by electrochemical exfoliation of graphite. The objects of study are prepared in electrochemical cells using alkaline and acid electrolytes with various applied voltages. Scanning electron microscopy, Raman spectroscopy, and X-ray diffraction have been used as research methods. The possibility of a theoretical calculation of the structural characteristics of nanomaterials (the defectiveness parameter, the density of the defects, the average distance between defects and average crystallite size) obtained by electrochemical exfoliation, according to Raman spectroscopy, is discovered. The results of these calculations satisfactorily correlate with the data of X-ray analysis.

1. Introduction
Electrochemical exfoliation of graphite is a promising method for the synthesis of graphene nanostructures. The availability of the source material, ease of implementation and the possibility of varying the process conditions in a wide range are significant advantages over other synthesis processes. This method allows one to obtain graphene in a short time. The electrolytic cell is filled with electrolyte solutions, which can be presented as water mixtures of the acid [1-3], inorganic salts [4-6], ionic liquids [7-10], and alkalis [11]. The bath is immersed electrodes, at least one of which is made of graphite [12]. The use of different types of graphite as the electrode, the change in the composition of the electrolyte, voltage, flow direction (constant, variable) allows you to control many parameters of the process. For example, it can be the rate of individual stages of the electrochemical process and their mechanisms, the ability to stabilize and functionalize free fragments by different groups, to modify by metal atoms [13].

For the analysis of the obtained materials, a wide range of various analytical methods are used, the most obvious of which is electron microscopy. But it permits to analyze only a small part of their surface. Therefore, this method does not give a complete understanding of the properties of the material. The method of Raman spectroscopy makes it possible to significantly supplement and expand the understanding of the structure of layered graphene materials. The degree of surface defects and the average distance between them, the crystal composition of the sample, the approximate number of layers, and the presence of certain functional groups on the area are possible to determine on the basis of the obtained spectra [14-16].

Raman spectra of carbon nanomaterials contain several characteristic peaks. The peaks D (~ 1350 cm⁻¹) and G (~ 1550 cm⁻¹) are the main ones for most materials. Peak D presents the disorder of the crystal structure of the samples, which reduces the overall symmetry of the structure. It requires
a structural defect to be activated and represents “breathing” vibrations of cyclic carbon structures. It is created by transverse optical phonons and can be associated with both interplanar and intraplanar double resonance. In the second case, a second branch appears at peak D - peak D' (~ 1600 cm⁻¹). It is important to note that the intensity of peak D depends not only on the presence of defects in the structure of carbon hexagons. It is also based on their type, depending on the scattered electrons. Peak G is associated with the vibrational mode of sp²-carbon and demonstrates the presence of a defect-free crystal structure. The ratio of peak performance D/G is used as a relative indicator of defectiveness.

The spectra also contain second-order peaks: 2D (~ 2700 cm⁻¹), D+G (~ 2900 cm⁻¹). The 2D peak demonstrates the presence of a single graphene layer and is divided into several smaller bands with an increase in the number of layers. This peak is not related to the presence of defects since it occurs when a pulse is held by two phonons with the same antiparallel wave vectors. Defects are necessary for the excitation of the D + G peak. This peak appears as a result of the interaction of phonons with various momenta [14].

The purpose of this research is to determine the structural characteristics (density of the defects, average crystallite size, average distance between defects) of graphene nanomaterials obtained by the electrochemical method using theoretical calculations based on Raman spectroscopy data.

2. Materials and methods

The object of the study was multilayer graphene materials obtained by electrochemical separation of graphite foil Graflex (sample 1). In the first case (sample 2), electrochemical exfoliation was carried out in a two-electrode cell using pulsed current. The duration of the cathode and anode pulses was 1 s, and the current density was maintained at 0.1 A/cm². The process was carried out in a 0.1 M potassium hydroxide solution. The resulting product was centrifuged and repeatedly washed with distilled water to remove electrolyte residues to pH=7, and then subjected to ultrasonic treatment for 8 hours and dried in a vacuum oven for 24 hours at a temperature of 40 °C.

In the second case (samples 3 and 4), electrochemical exfoliation was carried out in a two-electrode cell at a constant current. The current density was maintained at a level of 0.125 A/cm² (5 V, sample 3) and 0.25 A/cm² (10 V, sample 4) was applied. The platinum electrode acted as a cathode, and the graphite foil served as the anode. The process was carried out in a 0.15 M sulfuric acid solution. The resulting product was centrifuged and washed repeatedly with distilled water to remove electrolyte residues to pH=7, and then subjected to ultrasonic treatment for 8 hours and dried in a vacuum oven for 24 hours at a temperature of 40°C. Direct current with a density of 0.25 A / cm² and a voltage of 5 V and 10 V was applied to the element.

For preparing the material for diagnosis, parts of the mixtures were dried for 24 hours to obtain a dry nanographite film. Then, the film was subjected to diagnostics on a Thermo Scientific DXR Raman Microscope (USA) with a laser wavelength of 633 nm with an aperture of 50 μm of the “slit” type. The structural analysis of the samples was carried out on a X-ray diffractometer “Difrey-401” (XRD, “Scientific instruments”, St. Petersburg, Russia) with a Bragg-Bretano focus. Images of the nanomaterials were taken using scanning electron microscopy (SEM) on a Carl Zeiss “Merlin” with a resolution of up to 0.8 nanometers.

To determine the average distance between defects, the equation (1) can be used [15]:

\[
\frac{I_D}{I_G} = C_A \left( \frac{r^2_A - r^2_S}{2} \right) \left[ \frac{e^{-\frac{r^2_S}{L_D}}} {e^{-\frac{r^2_A}{L_D}}} - e^{-\frac{r^2_A - r^2_S}{L_D}} \right]
\]

where, \(L_D\) is the average distance between defects, \(r_A\) is the radius of the zone around the defect, produced by \(D\) peak, \(r_S\) is the radius of the structurally disordered space, \(C_A\) is the active surface parameter, which is taken depending on the area of the active zone, \(C_S\) is the unstructured surface parameter, which is depending on the area of the unstructured zone. In the study, \(C_S = 0\) was taken. This is due to consideration of the ideal case without complete breaking of the C – C bond, as well as the conditions of low defect density (\(L_D > 10\) nm), and is not considered in the formula. During the
experiments, the values of $r_A$, $r_S$, and $C_A$ were revealed, with the last parameter being inversely proportional to $E_L$. Formula (1) can be approximated to formula (2) with allowance for large $L_D$ values and the dependence of the $CA$ parameter on the laser energy. (2):

$$L_D^2 = \frac{(4.3 \pm 1.3) \cdot 10^3}{E_L^4} \left(\frac{I_D}{I_G}\right)^{-1}$$

In terms of the density of the defects $n_D = 10^{14}/(\pi L_D^2)$:

$$n_D = (7.3 \pm 2.2) \cdot 10^9 E^4 \left(\frac{I_D}{I_G}\right)$$

The possibility of applying this approach to the evaluation of the structural characteristics of products of electrochemical exfoliation of graphite is due to their common nature with the objects considered in [15-16].

Graphene crystallite size determination is possible with the assumption of a defect-free inner planar surface. Also in [17] separation of a polycrystalline zone into a structured crystalline and disordered around the crystallite, and the contribution of both zones to peak formation was introduced, equation (4). Crystallite is understood as a defect-free surface area. It was found that the dependence of the crystallite size is uniform for different values of the $D/G$ ratio, independently of the laser excitation energy. This allows us to use the proposed calculation to predict the size of the flat surface in the obtained samples.

$$\frac{l_D}{l_G} = \frac{l_D^4 + l_G^4}{l_D^4 + l_G^4}$$

Formula (5) allows determining the intensity of the Raman scattering of the vibrational mode $\gamma$:

$$I_{C}^{\gamma} = \frac{\omega^4}{\varepsilon_0 c^4} \int \left| G(r; \omega) \chi_C^{\gamma}(r; \omega, \omega_s)E(r; \omega_s) \right|^2 d^2r,$$

where, $C$ is a domain that includes the crystalline zone $A$ and the disordered zone $S$; $G (r; \omega_s)$ is the outgoing Green’s function, which includes the whole system; $\chi_C^{\gamma} (r; \omega, \omega_s)$ is the Raman susceptibility of the vibrational mode $\gamma$ over the domain $C$; $E (r; \omega_s)$ is the excitation of the electric field; $r$ is the position of the sample plane; $c$ and $\varepsilon_0$ are the speed of light and the dielectric constant of the medium in vacuum; $\omega$ and $\omega_s$ - the frequency of the incident and scattered light.

When equations (4) and (5) have been combined with considering the peculiarities of the $D$ and $G$ peak in the crystalline and disordered areas, the ratio (6) was obtained:

$$\frac{l_D}{l_G} = \frac{C_D^4 l_S (L_a - l_s)}{C_D^4 l_S (L_a - l_s)} + \frac{C_D^4 (L_a - 2l_S) \left[1 - e^{-2(L_a - 2l_S)/l_A}\right]}{C_G^4 l_S (L_a - l_s) + C_G^4 (L_a - 2l_S)^2}$$

where, $l_A$ and $l_S$ are the coherence lengths of electrons/holes and optical phonons; $C$-parameters are constant factors of the intensity function of Raman oscillations. The coherence lengths were obtained by approximating the experimental data. According to them, formula (7) for the crystallite size calculation was derived, which is in agreement with Tuinstra-Koenig ratio:

$$L_a \approx \frac{(490 \pm 100)}{E_L^4} \left(\frac{l_D}{l_G}\right)^{-1}$$

The formula (7) was derived experimentally. Different lasers were used in the analysis of samples. This dependence persists in spite of significant changes in the laser energy. On the one hand, this permits the application of (7) to the other graphenes. On the other hand, the parameters of the functions, which
assumes to be constant for graphenes obtained by thermal treatment of diamond-like amorphous carbon, may differ for graphenes obtained by electrochemical exfoliation method. In any case, this approach can be used to identify qualitative patterns of changes in the structure of the product.

3. Results and discussion

Figure 1 shows the SEM image of the graphene material obtained by the method of electrochemical exfoliation of graphite. It consists of two-dimensional structures with a large surface length (figure 1, left). Defects of the graphene layers are presented as some perceptible irregularities and bends. Edge plots also represent part of a disordered structure. Methods of microscopy are the most obvious and powerful but localized around a small area of the sample under study. When zooming in to cover a larger surface the accuracy of this method decreases. Even in the image with a larger scale (figure 1, right), small flexural disorders can be hardly seen. At the same time, it is not possible to determine the size of defects and the defect-free areas between them. Method for a limited time allows us to analyze only a small part of the surface, and therefore it does not give a complete picture of the properties of the material.

Figure 1. SEM images of the graphene nanostructured material obtained by the exfoliation method: general (left) and large (right) frames.

The Raman spectra of the samples (Figure 2) have typical peaks: \( D (~1350 \text{ cm}^{-1}) \); \( G (~1550 \text{ cm}^{-1}) \); \( D' (~1600 \text{ cm}^{-1}) \); \( 2D (~2700 \text{ cm}^{-1}) \) and \( D+G (~2900 \text{ cm}^{-1}) \), characterized by different intensity and width at half-height (FWHH) (table 1).

The spectrum of the starting material (sample 1) contains only peaks \( 2D \) and \( G \). For sample (2) obtained in an alkaline electrolyte, a low-intensity peak \( D \) appears. Graphite separation into fragments with the increasing of the percentage of atoms, which interacts with an environment, can be the reason. Also uprising of the surface defects, due to the aggressive influence of the alkali, contributes to peak growth. However, the value of the intensity ratio of the peaks \( D/G \), which is often used as an indicator of the defectiveness of the material [18], for sample (2) is only slightly higher than for sample 1. In this case, it is possible that the formed fragments consist of a large number of layers. The use of sulfate electrolyte during exfoliation contributes to deeper structural changes in the material. On Raman spectra of samples (3) and (4), peak \( D \) becomes intense, \( D' \) and \( D+G \) appear, and \( 2D \), on the contrary, becomes less pronounced. The \( D/G \) ratio greatly grows. This is due to the increase in intraplanar flexural defects on the surface of graphene layers and attaching of the oxygen-included functional groups. Accordingly, crystallite sizes, which can be considered as flat areas without defects, are reduced. As a result, \( D' \) peak becomes intense. The increase in the intensity of the \( D+G \) peak indicates the validity of this assumption.

Increasing the voltage from 5 (sample 3) to 10 V (sample 4) during electrochemical exfoliation helps to reduce the intensity of typical peaks and the \( D/G \) ratio. This may indicate the forming of a less defective product.
Figure 2. Raman spectra of the source material (1) and samples obtained by using KOH solution as electrolyte (2) and acidic solutions with direct current 5V (3) and 10V (4).

The XRD results of the initial graphite and materials obtained by the electrochemical exfoliation are shown in figure 3 and table 1. The diffractogram of the sample (1) (figure 3, a) contains 2 peaks of higher and lower intensity with 2θ values equal to 41.11 (100) and 85.42 (112), respectively. They indicate that the material consists of crystalline graphite [19]. For samples (2), (3) and (4) (figure 3b and 3d) the most intense peak on the diffractogram is shifted and has 2θ = 36.52 – 36.61. It is caused by the distance of the graphene planes from each other to a greater distance compared to graphite. On the diffractogram of sample (2), there is no second peak, which indicates that its volume is predominantly represented by low-layered fragments. The intensities of the peaks in the diffraction patterns of samples (3) and (4) are noticeably lower than in the first two cases, which indicates an increase in the fraction of the unstructured phase. For samples 2-3, a halo component is observed, also confirming the nanosize character of the objects.

Table 1. Characteristics of the Raman and main XRD (Intensity=100%) peaks of the source material (1) and nanographite samples obtained using KOH solution (2) and acidic electrolytes with 5V (3) and 10V (4).

|          | D   | G   | D'  | 2D  | D+G | D/G | 20  | Int. (20) | d (Å) |
|----------|-----|-----|-----|-----|-----|-----|-----|-----------|-------|
| Int., cps| ~13 | -   | 119 | 19  | -   | 48  | -   | 0.11      | 41.11 | 50900 | 3.262 |
| FWHH, cm⁻¹| 56  | 99  | 18  | -   | 40  | -   | 0.19 | 36.52     | 19159 | 3.655 |
|          | 245 | 124 | 242 | 73  | 181 | 76  | 59  | 1.01      | 36.61 | 165   | 3.647 |
|          | 114 | 114 | 137 | 41  | 66  | 42  | 26  | 0.82      | 36.52 | 613   | 3.655 |
Figure 3. XRD spectra of the source material (a) and samples obtained by using KOH solution as electrolyte (b) and acidic solutions with direct current 5V (c) and 10V (d).

Table 2 presents the results of calculating the crystallite size \( (L_a) \), the interdefect distance \( (L_D) \) and the number of defects per surface area \( (n_D) \) of the samples of materials obtained by electrochemical exfoliation of graphite, based on Raman spectroscopy using formulas (2), (3) and (7).

| Synthesis parameters | \( L_a, \text{ nm} \) | \( L_D, \text{ nm} \) | \( n_D \cdot 10^9, \text{ cm}^2 \) |
|----------------------|-----------------|-----------------|-----------------|
| Source               | 240-363         | 43-59           | 8.28-15.42      |
| KOH Solution         | 139-210         | 33-45           | 14.30-26.64     |
| \( \text{H}_2\text{SO}_4 \) Solution, 5V | 26-39           | 14-19           | 76.02-141.60    |
| \( \text{H}_2\text{SO}_4 \) Solution, 10V | 32-49           | 15-21           | 61.72-114.96    |

According to the calculations, areas of the defect-free surface of the largest size, the smallest defect density and inter-defect distance are formed when using an alkaline electrolyte. Taking into account the data of XRD and Raman spectroscopy, we can conclude that the resulting particles are nanoscale. In turn, the use of acid electrolytes permits to obtain a material with a less pronounced crystal structure and a large number of defects in graphene layers.
4. Summary
Raman spectroscopy data provide detailed characteristics of graphene nanomaterials obtained by electrochemical exfoliation of graphite: the defectiveness parameter, the average crystallite sizes, the defect density, and the average distance between them. The values of the parameters can be obtained by using D and G peaks information and experimentally determined equations. They were found by analysis of the Ar+-bombarded graphene and polycrystalline graphene, which were described by the common theoretical data with experimental correction by Raman spectroscopy, XRD, transmission electron microscopy, scanning tunneling microscopy. The results of the analysis of samples obtained using sulfuric acid correlate with XRD data.

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