X-ray diffraction analysis on layers in graphene samples obtained by electrolysis in molten salts: a new perspective

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There are several accepted methods used for X-ray diffraction analysis on graphene layers and sample's stacking height L_C. The Scherrer equation is avoided since the layers in the graphene samples are non-uniformly distributed and therefore the samples have non-uniform thickness. Instead, a model that includes thickness distribution is used to calculate the average number of layers and then the stacking height. The analysis was performed on 12 graphene samples produced by high-temperature electrolysis in molten salts. Another method that was used to calculate the number of layers and hence the samples' stacking height, was Raman spectra C-peak position method. It served as a control model for the analysed samples, since for four samples the corresponding parts of the Raman spectra were not usable due to the very low-frequency region. However, the obtained results of both methods were in agreement, and indicate that studied graphene samples are few layered.

1. Introduction: To date, several methods have been used to produce graphene, the atom thick material that is building unit of all carbon allotropes [1]. To mention some – mechanical exfoliation of graphite, chemical vapour deposition of carbon bearing gases on the surface of copper films [2], cutting open nanotubes [3], and others. Electrochemical method is a proven low-cost method for a high-yield production of carbon-based nanostructures, as is graphene [4, 5]. Depending on the production procedure, graphene can be produced as a mixture of monolayers, bi-layers, and multilayers (three to ten monolayers) in form of flakes or flat sheets [6]. Having highly unusual properties largely due to its structure makes structural characterisation of graphene a very important activity as a part of intensive graphene studies.

In this Letter, the authors focus on X-ray diffraction (XRD) analysis on graphene layers in graphene samples produced by high-temperature electrolysis in molten salts. The attention is strictly directed to the 002 peak, to calculate the mean crystallite size L_{002} or L_C. Scherrer equation has been used in some works to estimate the average number of graphene layers by XRD data [7, 8]. However, some other works have argued on the possibility of decreased accuracy level of such method, due to the non-uniform distribution of the graphene layers [9]. Therefore, the authors use two different methods to calculate the average number of layers N, and then use obtained value to calculate the stacking height. Methods that are used are Laue functions XRD model and Raman spectrum C-peak position method. Both methods' results are given and both are in high accordance, while stacking height results obtained from Scherrer equation deviate from both other methods.

2. Materials and techniques: The graphene samples that were studied here were produced by electrolysis in molten salts from various type of graphite using non-stationary current regimes. The temperature of the electrolysis was varied. So, the samples from G1 to G3 were produced at 350°C, samples G4–G6 at 370°C, G7–G9 at 330°C, and G10–G12 at 390°C. XRD spectra were recorded using a PAN-analytical X'Pert Pro diffractometer (CuKα radiation between 2 and 70 2). Raman spectra were recorded using LABRAM ARAMIS-HORIBA JOBIN YVON system with a 532 nm wavelength incident laser light, hole 250 μm, slit of 250 μm.

3. Analysis and methods: The XRD pattern is analysed by the following Laue functions model which includes graphene thickness distribution and certain parameters [10]:

$$|F|^2 \propto |f(\theta)|^2 \left| \sum_{j=0}^{N} \beta_j e^{jka_j i} \right|^2 \qquad (1)$$

where F is a structure factor, N is the number of graphene layer, $|f(\theta)|$ is an atomic scattering factor which varies from 6.00 to 6.15 e/atom with incident radiation ranging from 2 to 433 KeV. $ka_j = (4\pi d_j \sin\theta)/\lambda$, where d_j is a lattice spacing between jth and $(j–1)$th layer, θ is an angle between the incident ray and the scattering planes, $\lambda = 1.54$ nm is the wavelength of X-ray, and β_j is an occupancy of the jth graphene layer. The value of β_j is between 0 and 1. The employed equation parameters β_j make it possible to calculate the distribution of graphene layers. $B_j = 100\beta_j$ is j-layer occupancy in %, and $D_j = B_j − B_{j+1}$ is j-layer coverage in %, for each $j = 0,1,...,n$, assuming $\beta_0 = 1$, $\beta_{n+1} = 0$, where n is the total number of layers in the studied sample, regardless of the distribution. Hence, the average number N of graphene layers may be calculated by the following formula:

$$N = \sum_{i=1}^{n} i D_i / \sum_{i=1}^{n} D_i \qquad (2)$$

The number of layers calculated by (2) will be denoted by N^{XRD}, in order to be explicitly and clearly compared to calculated number of layers by other methods for the same samples. The results of the calculations are given in Table 1.

If a parallel layer group consists of N layers, then the mean dimension L_{002} or L_C of the crystallite perpendicular to the plane of graphene sample is calculated by the following equation given elsewhere [7–9]:

$$L_{002} = (N - 1)d_{002} \qquad (3)$$

where $d_{002} = \lambda/(2\sin\theta)$ is the average distance between graphene planes, $\lambda = 1.54$ nm is the wavelength of the X-ray, and θ is the angle between the incident ray and the scattering planes when the 002 peak reaches its maximum.

Table 1 Structural parameters calculated from the curves fitting of XRD spectra and values from Raman spectra

Sample	θ	d_{002}, Å	N^{XRD}	Pos(C), cm^{-1}	N^{RS}	L_C^{XRD}, Å	L_C^{RS}, Å	L_C^{Sch}, Å
G1	13.175	3.38	2.87	/	/	6.32	/	7.16
G2	12.78	3.48	2.4	35.72	2.54	4.87	5.35	14.32
G3	13.25	3.36	3.13	39.1	3.3	7.15	7.73	19.09
G4	13.26	3.36	2.55	35.2	2.46	5.21	4.91	11.46
G5	13.24	3.36	2.14	32.46	2.13	3.83	3.8	11.23
G6	13.25	3.36	2.42	34.91	2.42	4.77	4.77	13.97
G7	13.2	3.37	2.02	31.64	2.05	3.44	3.54	11.4
G8	13.26	3.36	1.96	30.81	1.98	3.23	3.3	11.15
G9	13.26	3.36	4.33	41.5	4.79	11.19	12.73	11.93
G10	13.225	3.37	5.57	/	/	15.4	/	7.34
G11	13.205	3.37	2.74	/	/	5.86	/	7.44
G12	13.215	3.37	3.27	/	/	7.65	/	7.17

Another equation relevant to N is the one related to a peak within the Raman spectrum, the C-peak, whose position Pos$(C)_N$ is the only value from Raman spectra that directly points to the number of graphene layers N, and it varies with N as in the formula [11, 12]

$$\text{Pos}(C)_N = \sqrt{\frac{2\alpha}{\mu}}\sqrt{1 + \cos\left(\frac{\pi}{N}\right)} \qquad (4)$$

where $\alpha = 12.8 \times 10^{18}$ Nm^{-3} is the interlayer coupling, and $\mu = 7.6 \times 10^{-27}$ kg Å^{-2} is the graphene mass per unit area. Hence, if Pos$(C)_N$ is known, and we denote $A = \mu/2\alpha$, N may be explicitly calculated from the following formula:

$$N = \pi / \arccos\left(A \cdot \text{Pos}^2(C)_N - 1\right) \qquad (5)$$

4. Results and discussion: There are 12 graphene samples produced by electrolysis in molten salts that were analysed: G1, G2, G3, G4, G5, G6, G7, G8, G9, G10, G11, and G12.

Although these samples are produced under different conditions (various type of graphite using non-stationary current regimes and temperatures), this Letter focuses on determination of L_C regardless of the conditions, by the two different methods mentioned in Section 3.

The calculation of theoretical XRD curves around the 002 peak is shown in Fig. 1b, whereas in Fig. 1a experimental XRD curves are shown. Their corresponding correlation coefficients are high and are given on the right side in Fig. 1b.

By model 1 and the β_j parameters, the graphene thickness distribution is calculated for the 12 graphene samples. Calculations show that each graphene sample analysed here is few layered in its dominant structure (80% or more). Based on the layers distribution, their number N^{XRD} is calculated, and the outcomes are given and shown for each studied graphene sample in Table 1. By N^{RS}, the calculated number of layers by the Raman C-peak position is denoted (Figs. 2a–h). The Raman spectra C-peak may show only within the low-frequency interval between 30 and 43 cm^{-1} [11, 12]. As it is the most expressed peak, the ones having the highest maximum intensity were used for the studied samples. This method is used to compare calculations for N^{RS} to calculations for N^{XRD}, and therefore, the obtained corresponding stacking heights L_C^{RS} to L_C^{XRD}. There are some graphene samples with no calculations for N^{RS}. Their Raman spectra were not usable at the region of low frequency, where the C-peak shows off, and such situation is sometimes possible [12]. Therefore, the C-peak method is used as a control method in this work. However, all calculations given in Table 1 show agreement between the two methods. Within Table 1 are also included calculations for stacking height L_C^{Sch} for each studied sample, obtained from Scherrer equation. The deviations in these results are obvious, as they are clearly different from the results obtained from both the presented methods. This is due to the graphenes' non-uniform thickness distribution
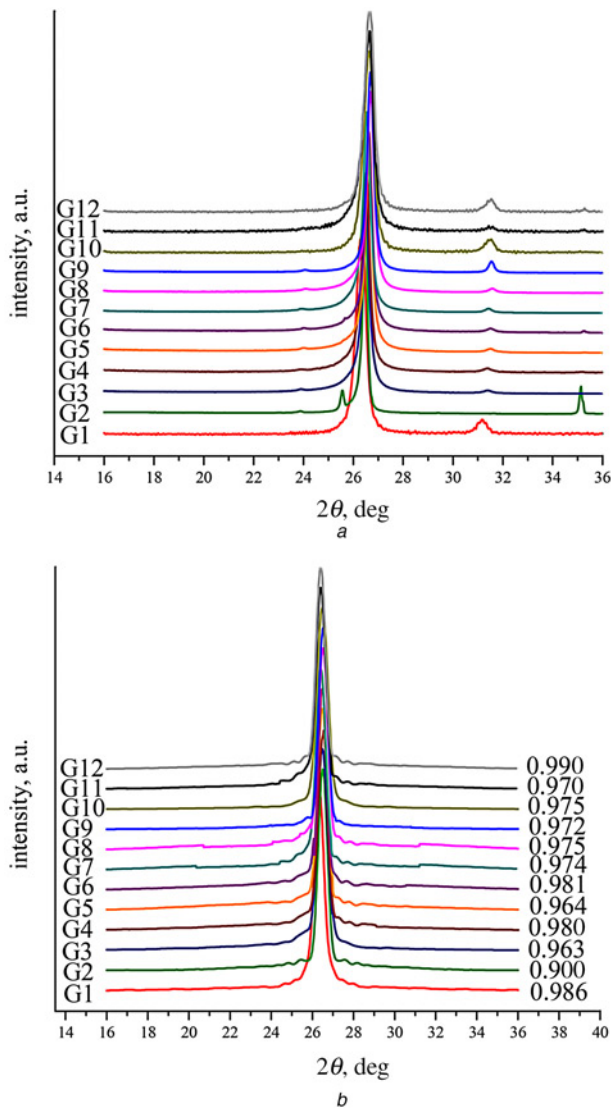
Fig. 1 *Calculation of theoretical XRD curves and experimental XRD curves of graphene*
a Experimental XRD curves of graphene with characteristic peak for 002 crystal plane positioned at $2\theta = 26.4°$
b Calculated theoretical curves fitting of XRD spectra around the same peak
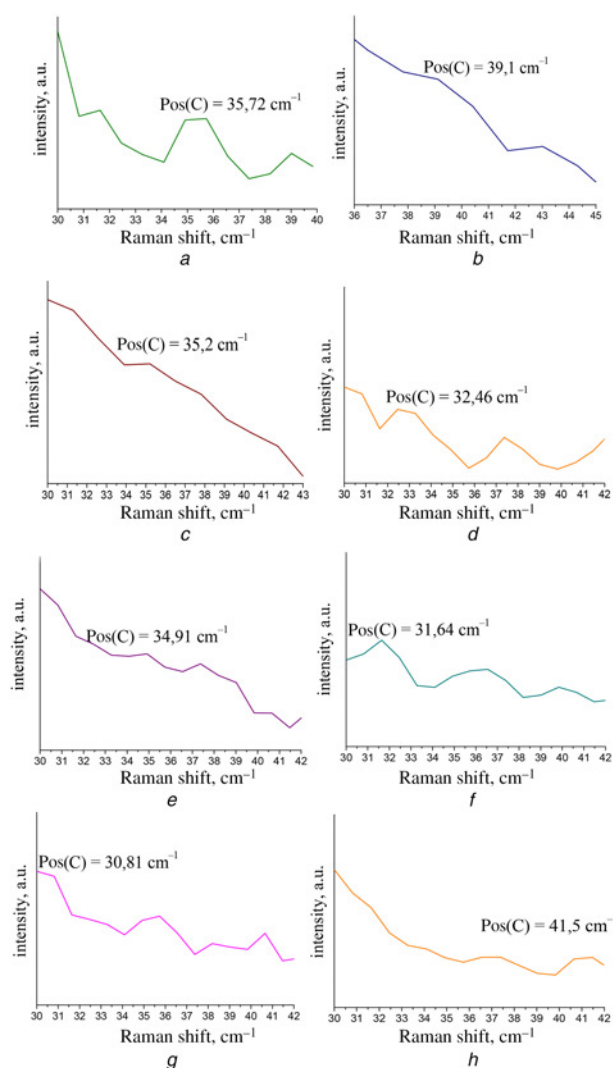
Fig. 2 *C-peaks in Raman spectra for graphene samples*
a G2
b G3
c G4
d G5
e G6
f G7
g G8
h G9

and the fact that Scherrer equation uses just the value of the full width at half maximum regarding the 002 XRD peak, and not the whole line shape [9].

5. Conclusion: This work offers an approach for calculating graphene's samples stacking height L_C which is different from Scherrer equation method. This is important because obtained graphene samples by electrolysis in molten salts have non-uniform thickness distribution. Using a model that enables acceptable approximation of the average number of graphene layers, with a fair accuracy regardless of whether the sample thickness is or is not uniformly distributed, provides a calculation of the stacking height L_C^{XRD} for each sample. There is a control method included, the Raman spectra C-peak position values, which enables direct calculation of the number of graphene layers. Having obtained the stacking height L_C^{RS} for the studied samples from the latest calculations, shows an excellent accordance when the two methods are compared. The results show that the stacking height L_C is within the range of 3.23–15.4 Å for the studied graphenes.

7 References

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