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DETERMINING GRAPHENE LAYERS NUMBER AND N-LAYER REGION COVERAGE BY XRD DATA DISTRIBUTION MODEL

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Abstract
A model consisting of an equation which includes graphene thickness distribution is used to calculate theoretical 002 XRD peak intensities. An analysis was performed upon graphene samples produced by two different electrochemical procedures: electrolysis in aqueous electrolyte and electrolysis in molten salts, both using reverse change of the applied potential. The model applied to the corresponding 2θ interval enables obtaining theoretical curves that exhibit fitting with a sufficient accuracy to the XRD intensities curves of the studied graphene samples. The employed equation parameters make it possible to calculate the n-layer graphene regions coverage of the graphene samples, and the average value for number of graphene layers. Results of the analysis are in agreement with the calculated number of graphene layers from Raman spectra C-peak position values, and indicate that graphene samples are few-layered.

Key words: Graphene, electrochemical production, XRD analysis, layers.

1. Introduction

Graphene is 2D building unit of all wide-variety carbon allotropes, having unique and exotic properties largely due to its structure. Graphene can be produced by many ways such as mechanical exfoliation of graphite, chemical vapor deposition (CVD) of carbon bearing gases on the surface of copper films [3], cutting open nanotubes [4]. Electrochemical approach is a proven low-cost method for a high-yield production of graphene.
Depending on the production procedure, graphene can be produced as a mixture of monolayers, bi-layers and multilayers (3–10 monolayers) in form of flakes or flat sheets [5].

Herein, an XRD pattern around a graphene 002 peak was used for layer number non-uniform distribution determination for graphene samples obtained by two different electrochemical procedures: electrolysis in aqueous electrolyte and electrolysis in molten salts, both using reverse potential.

2. Model that provides calculation of graphene thickness distribution by XRD data

The XRD pattern was analyzed by using the following Equation 1 that uses Laue functions which includes graphene thickness distribution and certain parameters, hence XRD intensities of the curves were calculated thereof: [6]

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

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, λ is a wavelength of X-ray, and β_j is an occupancy of 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 n-layer graphene regions coverage of the graphene samples produced by the two electrochemical procedures.

2.1. Graphene produced by electrolysis in molten salts and model (1)

Two graphene samples produced by electrolysis in molten salts are considered and discussed herein: graphene sample 2G and graphene sample x.

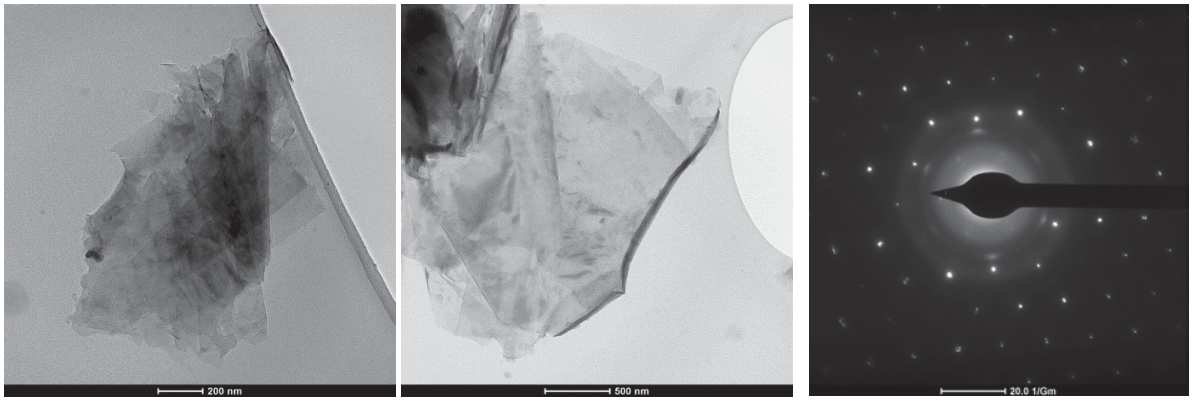

Figure 1. a) TEM images of 2G graphene sheets; b) Diffraction pattern of image

Using Eq. (1), XRD intensities of the curves in Fig. 2 are calculated as further discussed. The three red lines are calculated curves from the Eq. 1 for $\beta_j \neq 1$, which suggests that the number of graphene layers has a distribution.

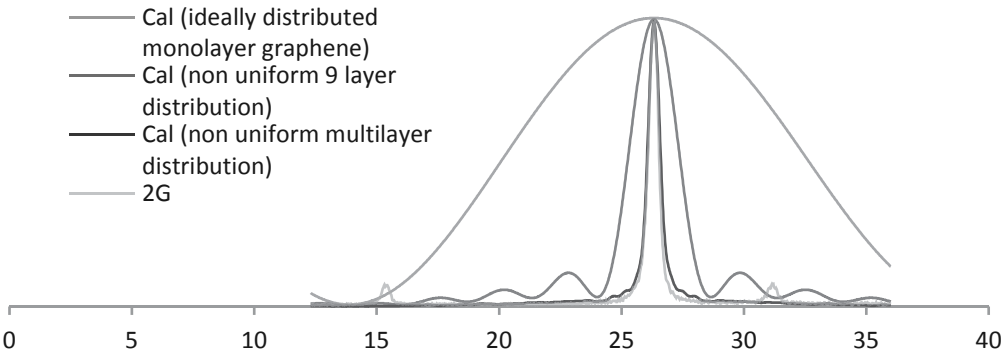

Figure 2. Non uniform multilayer distribution curve for Sample 2G calculated from Eq.(1)

The broadest red dotted line in Fig. 2 is calculated curve for ideally distributed monolayer graphene, the light red line which is narrower than the monolayer graphene line, but broader than the green experimental curve, is calculated curve for a non uniform distribution of graphene layers number for a 9-layered graphene. The dark red line is calculated curve for a non uniform distribution of graphene layers number for a multi-layered graphene, which exhibits a good fitting to the experimental curve, as it is symmetrical and the correlation coefficient is $\rho = 0.986$. According to its β_j parameters, the coverages of n-layer graphene regions are calculated as in Table 1 a).

Apparently, the dominant structure is few-layered, and the average value for number of graphene 2G layers is calculated as N_{GL}=2.87 for the dominant structure and N_{GL}=5.16 for the overall structure.

In Fig.3 a), there are calculated theoretical curves from Eq. 1 presented in red, for graphene sample x, and the experimental curve x in green. In Fig 3 b), there is part of the Raman spectrum for sample x, showing off its C-peak. Its position $\mathrm{Pos}(C)_N$ is directly connected to the graphene layers number N, and it varies with N as in the formula: [7]

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

where $\alpha = 12.8\times10^{18}\,\mathrm{Nm}^{-3}$ is the interlayer coupling, and $\mu = 7.6\times10^{-27}\,\mathrm{kg\,\mathring{A}}^{-2}$ is the graphene mass per unit area.

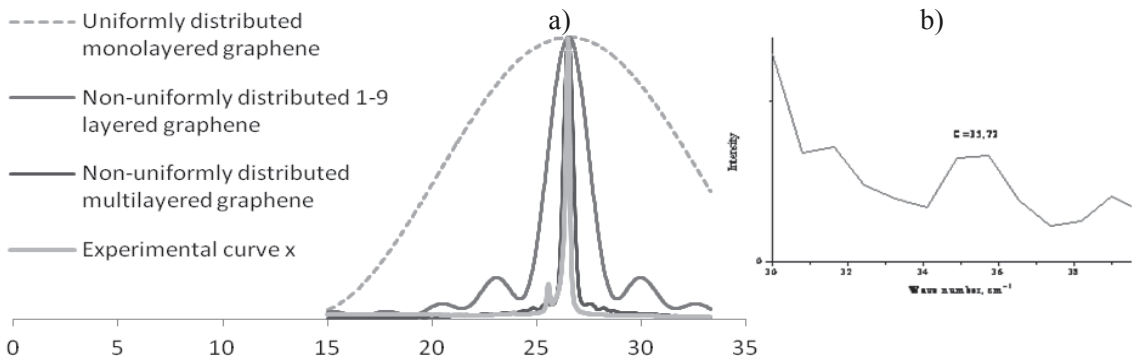

Figure 3. a) Non uniform multilayer distribution curve for Sample x calculated from Eq.1; b) C-peak position in Raman spectrum for graphene sample x

According to the analysis of the XRD 002 peak, the n layer region coverages are as in Table 1 b).

Table 1. a) Coverages of n-layer 2G graphene regions
b) Coverages of n-layer x graphene regions

a)		b)	
Monolayer region coverage	~ 35%	Monolayer region coverage	~ 18.75%
2-3 layers region coverage	~ 5-10%	2 layers region coverage	~ 21.25%
5-6 layers region coverage	~ 5%	3 layers region coverage	~ 3.75%
7-8 layers region coverage	~ 5%	4-6 layers region coverage	~ 2.5%
9-10 layers region coverage	~ 5%	7-8 layers region coverage	~ 2.5%
> 10 layers region coverage	< 20%	9-10 layers region coverage	~ 1.25%
		> 10 layers region coverage	< 25%

The average value for number of graphene x layers is calculated as N_{GL}=2.4 for the dominant structure and N_{GL}=7.43 for the overall structure.

According to the C-peak position, the number of graphene x layers for sample x is N=2.54.

2.2. Graphene produced by electrolysis in aqueous electrolyte and model (1)

Graphene samples 4 and 10 produced by electrolysis in aqueous solution, using reverse potential, are considered herein and analyzed.

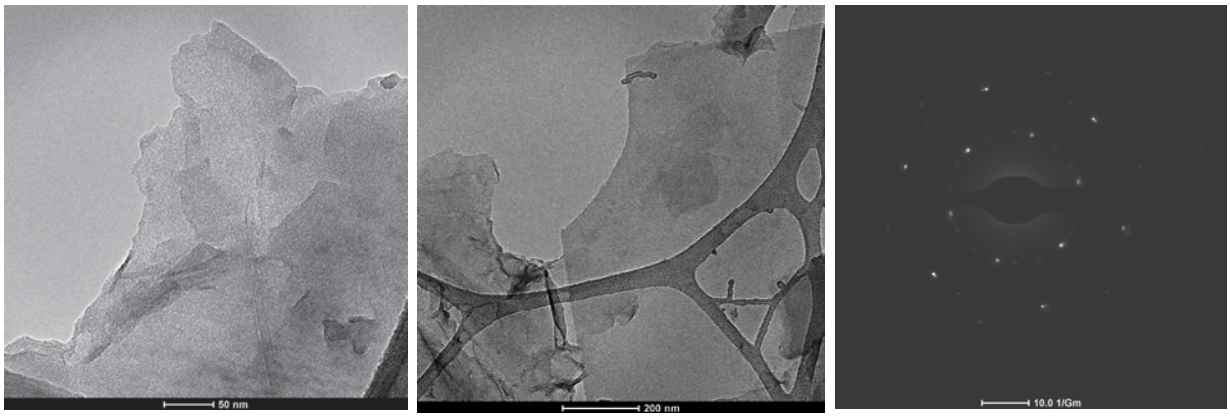

Figure 4. a) TEM images of Sample 4 graphene sheets; b) Diffraction pattern of image

The three blue lines in Fig. 5 are calculated curves from the Eq. 1 for $\beta_j \neq 1$, which suggests that the number of graphene layers has a distribution.

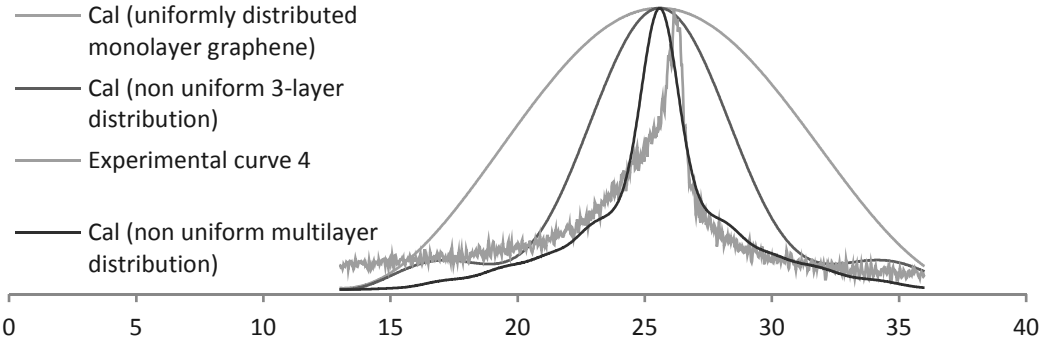

Figure 5. Non uniform multilayer distribution curve for Sample 4 calculated from Eq.1

The broadest blue dotted line in Fig. 5 is calculated curve for uniformly distributed monolayer graphene, the light blue line which is narrower than the monolayer graphene line, but broader than the green experimental curve 4, is calculated curve for a non uniform distribution of graphene layers number for a 3-layered graphene. The dark blue line is calculated curve for a non uniform distribution of graphene layers number for a multi-layered graphene. There is a noticeable discrepancy with the experimental curve due to its asymmetry. However, as the correlation coefficient is $\rho = 0.92$, it provides an additional insight into n-layer graphene regions share, and the results are in agreement with the results obtained by other methods. According to its β_j parameters, the coverages of n-layer graphene regions are calculated as in Table 2 a).

According to these calculations, the dominant structure is few-layered, and the average value for number of sample 4 graphene layers is calculated as N_{GL}=2.57 for the dominant graphene structure and N_{GL}=4.25 for the overall graphene structure.

In Fig. 6 the three blue lines are calculated curves from the Eq. 1 for $\beta_j \neq 1$, which again suggests that the number of graphene layers has a distribution.

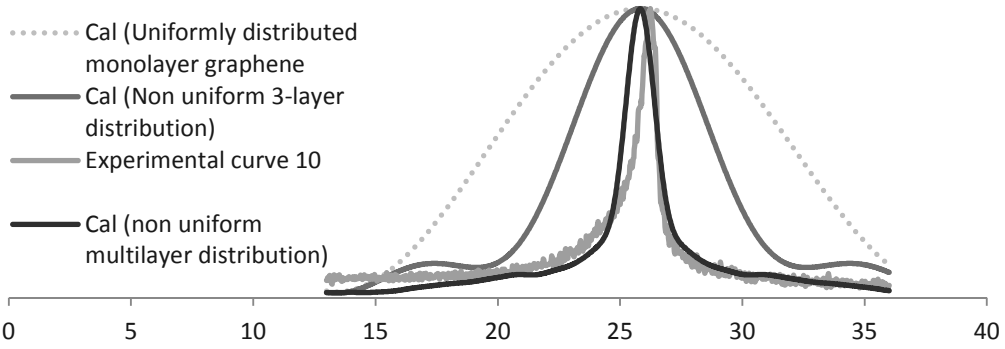

Figure 6. Non uniform multilayer distribution curve for Sample 4 calculated from Eq.1

The broadest blue dotted line is calculated curve for uniformly distributed monolayer graphene, the light blue line which is narrower than the monolayer graphene line, but broader than the green experimental curve 10, is calculated curve for a non uniform distribution of graphene layers number for a 3-layered graphene. The dark blue line is calculated curve for a non uniform distribution of graphene layers number for a multi-layered graphene with a correlation coefficient $\rho = 0.93$, and according to its β_j parameters, the coverages of n-layer graphene regions are calculated as in Table 2 b).

Table 2. a) Coverages of n-layer graphene sample 4 regions
b) Coverages of n-layer graphene sample 10 regions

a)		b)	
Monolayer region coverage	~ 40%	Monolayer region coverage	~ 30-35%
2 layers region coverage	~ 10%	3-4 layers region coverage	~ 5-10%
3-6 layers region coverage	~ 15%	5-6 layers region coverage	~ 5-10%
7-10 layers region coverage	~ 5%	7-10 layers region coverage	~ 5-10%
> 10 layers region coverage	< 10%	> 10 layers region coverage	< 10%

The dominant structure is few-layered, and the average value for number of sample 10 graphene layers is calculated as N_{GL}=3.53 for the dominant graphene structure and N_{GL}=5.6 for the overall graphene structure.

3. Conclusions

There are several clear conclusions to be drawn from the preceding analysis. The model that is used provides an additional insight into graphene samples n-layer occupancies and therefore coverages with a sufficient accuracy. However, a limitation to this model that should not be disregarded is the fact that in general case graphene sheets which are subject of research may have layer structure that varies across the studied sample and hence an asymmetrical 002 XRD peak. Experimental 002 XRD peaks which are highly asymmetrical are inconvenient to be analyzed by this model, and therefore adequate alterations to the model should be considered and researched. The results relevant to graphene samples produced by electrolysis in aqueous electrolyte and by electrolysis in molten salts, both using reverse change of the applied potential, which were studied and analyzed herein using this model, are in accordance with other methods results, and have shown that these graphene samples are few-layered.

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