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Investigation of Nanoscale Structure by Means of X-ray Small Angle Scattering

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The structure of carbon nanotubes and porous graphite has been studied by means of X-ray small angle scattering method. Analysis of scattered intensity curves was carried out according to Guinier approximation and parameters of porous structure were calculated. Obtained experimental results were used for estimation of fractal dimension.

Key words: carbon nanotubes, graphite porous, X-ray small angle scattering, fractal dimension.

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Introduction

Nanostructured materials reveal unique physical-chemical properties and on that reason attract the interest of researchers. In order to understand these properties and predict their behavior the structure studies are carrying out commonly [1-4]. But is should be not that estimation of some structure parameters (nanocrystal size, distances between nanocrystallites) is behind the limits of common X-ray diffraction method. The same problem exists also in studying of porous materials. Therefore for studies of nanoscale structure a small angle scattering method may be considered as the most effective one. In this work we used the small angle X-ray diffraction for investigation of structure of carbon nanotubes and porous graphite.

I. Experimental procedure

The investigation of porous structure of grafite and carbon nanotubes was carried out with using of DRON-3 X-ray diffractometer CuKα-radiation (λ=1.5418 Å), monochromatized by reflecting from (111) planes of Ge single crystal has been passed through the specimen. In order to avoid the "parasite" scattering, the slit system was installed before standart one. Another slit system was installed before detector for reducing of atmospheric scattering. Using the perfect single crystall and collimating of initial and diffracted beam with high accuracy permitted us to obtain the small angle scattering spectra down to 0.01-0.02 $Å^{-1}$ value of wave vector. The 0.1 mm slit was installed before detector that allowed us to have the high experimental angular resolution $\Delta(2\theta)_d$= 0.03°. Scattered intensities were recordered by scanning within 0.25-4.00° angle region with 0.05° step and 100 s exposition.

II. Results and discussion

The small angle scattering curve for carbon nanotubes is presented in Fig.1 (1). Curve (2) describes

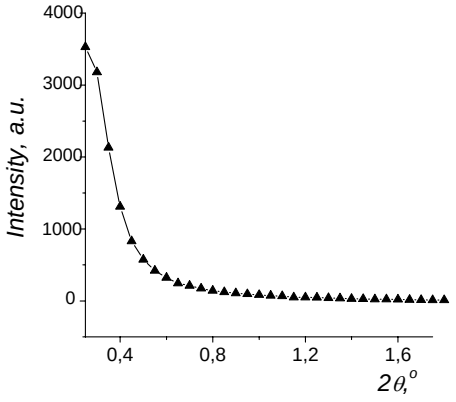

Fig. 1. Small-angle scattering for carbon nanotubes.

the intensity distribition in initial beam. Hence the correction should be taken into account and it can be done in such way:

$$I(2\theta) = I_{exp.}(2\theta) - KI_o(\theta)/cos(2\theta) \qquad (1)$$

were $I_{exp.}(2\theta)$ – experimental intensity; $I_0(2\theta)$ – initial beam intensity; K –absoption coefficient.

In order to estimate the absorption coefficient value

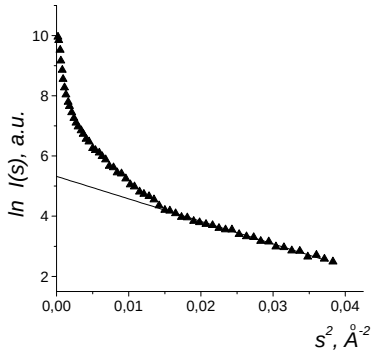

Fig. 2. Intensity of small-angle scattering in Guinier coordinates.

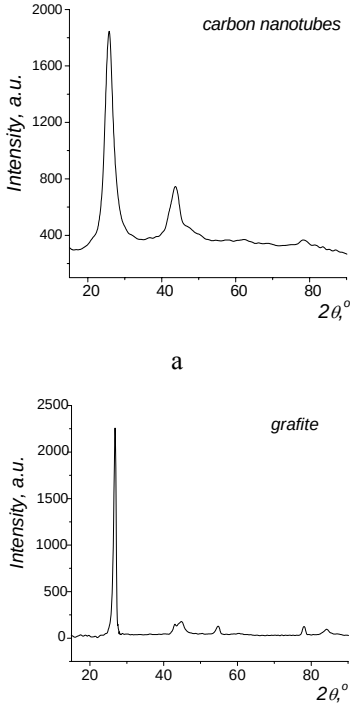

Fig. 3. X-ray diffraction patterns for a) nanotubes and b) graphite.

the measuring of initial beam intensity at $2\theta = 0^o$ with sample and without it was carried out. This allowed us to write the absorption coefficient in form:

$$K = I(0)/I_o(0) \qquad (2)$$

The analysis of obtained data on diffraction was carried out with use of Guinier approach. It is known, that within small angle region the angular dependence of intensity can be written:

$$I(s) = I(0) \cdot exp(-1/3\, s^2\, Rg^2) \qquad (3)$$

where R_g – electron inert radius, which describes the electron density fluctuation scale, I(0) – scattered intensity at s = 0.

Using the logarithmic coordinate system permits to rewrite:

$$ln\, I(s) = ln\, I(0) - 1/3\, s^2\, Rg^2 \qquad (4)$$

For system of monodispersed particles (poroes) this dependence shows the linear behavior in log(I(s); s^2 coordinates (Fig. 2). In this figure the similar dependence is shown also for carbon nanotubes. As it can be seen the studied material is a polidispersed systems with various values of poroes size. For more detail analysis of experimental data the tangent method [5] was used. As follows from equation (3) the poroes of small size mainly contribute to total intensity at large s-values. The slope of curve allowed us to determine the size of smaller fraction poroes (Rg_1 = 15 Å), which in case of carbon nanotubes can be considered as minimum radius. The ordinate of point, corresponding to crossing of tangent with log(I(s)) axis yields $I_1(0)$ value. Using the obtained data and equation (3) one can calculate $I_1(s)$ for poroes ofsmaller fraction. The rapid increase of curve at low values of scattering angles is supposed to be caused by existence of larger size poroes. The similar calculation allowed also to determine both Rg_k and $I_k(0)$ values for poroes of each fraction. The main results of are listed in table 1. The obtained data were used also in order to estimate the parameters of porous structure. For instance, for each fraction of nanoporoes its volume part can be calculated as follows:

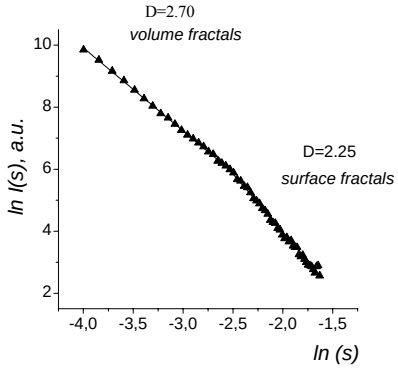

Fig. 4. Fractal dimension of carbon nanotubes.

$$m_k = (I_k / Rg_k^3) / \sum (I_k / Rg_k^3) \qquad (5)$$

We have also studied the carbon nanotubes by X-ray diffraction method withim wide range of scattering angles (20-100°). The diffraction pattern is shown in Fig. 3. where it is compared to one for pure graphite. The significant differences between two kind structures are observed. Main structure parameters were estimated from experimental intensity curves. It was found that nanotubes, studied in this work, have a few layers and distance between them equals to corresponding interlayer distance in graphite. It was found also that size of structural units in nanotubes is about 35 Å.

Beside these results we have estimated the fractal dimension of nanotube structure (Fig. 4). Obtained

Table 1

Parameters of poroes structure carbon nanotube

№	Rg_k, A	$I_k(0)$	m_k
1	15.0	205	0.286
2	26.0	1570	0.431
3	74.0	24200	0.282

№ – fraction number, Rg_k- electron radius of giration, $I_k(0)$ – intensity of scattering at s=0, m_k- volume part of poroes.

results reveal the existense of two kind fractals. For first of them the fractal dimension D was founded to be 2.70 and for last- 2.25. These values correspond to volume and surface fractals respectively.

Conclusion

The X-ray small angle scattering method is effective in studying of nanoscale structure. The use of this method allowed us to determine the fractal dimension for carbon nanotubes which was founded to be 2.7 (volume fractals) and 2.25 (surface fractals). The parameters of porous structure in carbon nanotubes and graphite were also determined.

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С.І. Мудрий, Ю.О. Кулик

Дослідження наноструктур за допомогою малокутового Х-променевого розсіювання

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Структура вуглецевих нанотрубок і пористого графіту досліджувалась методом малокутової дифракції рентгенівських променів. Аналіз кривих інтенсивності розсіяння проводився згідно апроксимації Гіньє, що дозволило отримати значення параметрів пористої структури. Експериментальні дані використані для оцінки величини параметра фрактальної розмірності.