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The atomic scale structure of nanographene platelets studied by X-ray diffraction, high-resolution transmission electron microscopy and molecular dynamics ☆

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ABSTRACT

The atomic structure of commercially available nanographene platelets has been studied by high energy X-ray diffraction, high-resolution transmission electron microscopy, X-ray photoelectron spectroscopy and molecular dynamics simulations using the reactive empirical bond order potential. Atomic models of the structure have been constructed and then relaxed using the molecular dynamics method and the model based simulations are compared with the experimental data both in reciprocal and real space. All model relaxations and the X-ray diffraction experiments have been carried out at 300 K. The proposed models consisting of about 2500 carbon atoms arranged within four graphitic layers with a diameter of 46 Å, reproduced correctly all features of the experimental data. The atomic arrangement within an individual layer can be described in terms of the paracrystalline ordering, in which lattice distortions propagate proportionally to the square root of interatomic distances. The paracrystalline structure was simulated by introducing the topological point defects such as the Stone–Thrower–Wales defects, single- and double-vacancies, randomly distributed in the network. Such defects lead to curvature of individual layers and this effect was also analyzed. The generated models are related to the observations by high-resolution transmission electron microscopy.

1. Introduction

For more than 60 years, scientists have believed that one atom thick graphene sheet could not exist in its free state based on the hypothesis that its planar structure would be thermodynamically unstable. Recently several scientific groups worldwide have obtained isolated graphene sheets [1–6]. The unique electronic, thermal, mechanical and optical properties of graphene promise a variety of applications in transparent electrodes [2], field-effect transistors [3], ultrasensitive sensors [4], and novel nanocomposites [5]. In addition to single-layer graphene, double-layer, few-layer and multi-layer graphene sheets also exhibit a number of intriguing properties. All these graphene structures are collectively referred to as nanographene platelets (NGPs) in which the platelet thickness varies from 0.34 to 100 nm [6].

The unique properties of NGPs with high perfection of the atomic lattice are outstanding, but structural defects, which may appear during growth or further processing, deteriorate the performance of graphene-based devices. Nevertheless, some kinds of deviation from perfection can be functional and may affect the local properties of graphene. Defects in nanomaterials such as NGPs may be divided into extrinsic (with the presence of foreign atoms) and intrinsic defects, in which zero- and one dimensional defects may occur as point and line defects, respectively. Amongst the point defects the simplest example is the Stone–Thrower–Wales (STW) defect [7,8], which does not involve any removed or added atoms. Four hexagons are transformed into two pentagons and two heptagons by rotating one of the C−C bonds by 90°. The STW defect has a formation energy about 5 eV [9,10], but once the defect is formed under non-equilibrium conditions, the barrier for the reverse transformation should warrant its stability at room temperature. Another defect is the missing lattice atom referred to as a single-vacancy (SV), that energy formation is higher than for the STW defects and equals about 7.5 eV [11,12]. This leads to the formation of a five-membered and a nine-membered ring. It is also possible for multiple vacancies to form, for example double vacancies (DVs) in which two pentagons and one octagon appear instead of four hexagons in a perfect graphene. Previous simulations indicate that the formation energy of a DV is of the same order as for a SV, but two atoms are missing, so the energy per atom is much lower than for a SV and DVs are more thermodynamically favoured over SVs [16,17]. It is also possible to remove more than two atoms which may lead to larger and more

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complex defect configurations, which was extensively described by Banhart et al. [13].

In this paper it is demonstrated that the atomic structure of nanographene platelets (NGPs) may be satisfactorily described using the X-ray diffraction data and the molecular dynamics (MD) simulation method for geometry optimization. We will particularly focus on the presence in the studied structure of zero-dimensional defects such as the Stone–Thrower–Wales defects, single- and double-vacancies as a dominant source of atomic disorder. These structural studies will be complemented by the high-resolution transmission electron microscopy (HRTEM) observations and the X-ray photoelectron spectroscopy (XPS) elemental analyses.

2. Experimental

Commercially available nanographene platelets (NGPs) in the form of powder are a product from Angstron Materials (N002-PDR). The sample was prepared from partially graphitized polymeric carbons, which were obtained from a polymer or pitch precursor [3,4]. The main technical data for N002-PDR according to the official producer website are gathered in Table 1. The performed XPS analyses confirmed the high elemental purity of the NGPs in the form of the powder. The content of oxygen was found to be about 2.4%. Additionally a minor contamination with sulphur and silicon was detected. Sulphur, which is present at the level of 0.09% appears in two chemical states. The dominant photoemission S 2p line can be ascribed to CS_2 whilst the lower intensity line comes from sulphates. Silicon contamination (of about 0.04%) is related to an oxidized state. The oxygen 1s line contains at least two components which can be ascribed to graphene oxide and adsorbed species like water. It is confirmed by the very low intensity of the oxide peak (GO) in the C 1s photoemission line.

The X-ray diffraction experiment was performed at room temperature using the Rigaku-Denki D/MAX RAPID II-R diffractometer (Rigaku Corporation, Tokyo, Japan) with a rotating anode Ag Kα tube ($\lambda = 0.5608$ Å), an incident beam (002) graphite monochromator and an image plate in the Debye–Scherrer geometry as a detector. The pixel size was 100 μm × 100 μm. The powdered sample was placed inside glass capillaries (1.5 mm in diameter). The measurements were performed for the sample filled and empty capillaries and then the intensity for the empty capillary was subtracted. The beam width at the sample was 0.3 mm. The two-dimensional diffraction pattern was then converted into one-dimensional intensity data using suitable software. The intensity was measured as a function of the scattering vector K ($K = 4\pi\sin\theta/\lambda$, where 2θ is the scattering angle and λ is the wavelength) up to $K_{max} = 22$ Å^{-1}. The intensity was corrected and normalized using the data processing procedure developed for high energy X-rays [15–17] and then the structure factor $S(K)$ was computed as:

$$S(K) = \frac{I(K)}{f^2(K)} \tag{1}$$

where $I(K)$ is the coherent intensity and $f(K)$ is the atomic scattering factor of carbon. For further analysis, a real space representation of the diffraction data in the form of the pair correlation function (PCF) was calculated converting the structure factor by the sine Fourier transform as follows:

$$PCF = \frac{2}{\pi}\int_0^{K_{max}} K[S(K)-1]\sin(Kr)\frac{\sin(\pi K/K_{max})}{\pi K/K_{max}}dK, \tag{2}$$

where K_{max} is the maximum value of the scattering vector available in the experiment (in the present experiment $K_{max} = 22$ Å^{-1}) and the last term denotes the Lorch modification function that reduces effects arising from the finite value of the upper K-limit.

The XPS analyses were performed with monochromatized AlKα radiation (hω = 1486.6 eV) at room temperature using a PHI 5700 Physical Electronics spectrometer. The analyzed region of raw NGP powder was a circle 0.8 mm in diameter and about 20–40 Å in depth due inelastic mean free path of photoelectrons. Atomic concentration of the detected elements was calculated with the use of Multipak programme by Physical Electronics.

For transmission electron microscopy (TEM) examination a small portion of the NGP powder was immersed in ethanol and then for 20 min placed into an ultrasonic device in order to obtain sufficient dispersion of powder. The small drop of dispersed suspension was pipetted onto 400 mesh copper grid covered by ultra thin holey amorphous carbon. The observations were performed on a Tecnai G2F20 high-resolution electron microscope at 200 kV.

Table 1
Technical data of N002-PDR [14].

Parameters	Values
Average X & Y dimensions	~10 μm
Average number of graphene layers	<3 (as estimated by BET and particle size distribution data)
Carbon content	~97.0%
Oxygen content	~2.1%
Hydrogen content	~1.0%
Ash content	~0.1%
Specific surface area	400–800 m^2/g
True density	2.20 g/cm^3

3. Computational methods

In the present work two approaches to the structure investigation were considered. In the first one, the paracrystalline model is defined by the size of the ordered region, the number of layers in the stack, the values of the graphite lattice constants a, c, the standard deviation of the interatomic distances for atoms lying in the same layer σ_{intra} and the standard deviation of the interlayer spacing σ_{inter} [18,19]. The generalized Debye–Waller factor with $\sigma_{intra} = \sigma_0 r^{1/2}$ and $\sigma_{inter} = \sigma_1(\Delta n)^{1/2}$ (where $\Delta n = n_i - n_j$, n_i and n_j numerate the layers), can be included assuming σ_0 and σ_1 as the adjustable parameters. The paracrystalline structure is based on the assumption that the distances from any atom to adjacent atoms fluctuate without statistical correlations and these fluctuations propagate proportionally to the square root of interatomic distance according to the combination law of independent probability distributions of the Gaussian type [23,24,20]. Such fluctuations result in distribution of the nearest neighbour interatomic distances instead of one distance of 1.42 Å, typical for graphite. It is essential to note that within this approach disorder was imposed on the model by the appropriate form of the generalized Debye–Waller factor.

In the second approach, the paracrystalline structure was generated assuming point defects in the form of the STW, SVs and DVs defects which are randomly distributed over the graphene network. In all models the starting positions of carbon atoms were obtained from the perfect hexagonal graphite structure.

In order to obtain stable atomic configurations for the NGPs models constructed in such a way were relaxed carrying out the MD calculations at 300 K in order to optimize the geometry of the system and to account for the thermal vibrations. Interactions between carbon atoms were described by the reactive empirical bond order (REBO) potential [21], which is the second generation of the Brenner potential [22]. It is remarkable that the REBO potential accounts very well for the features of sp, sp^2 and sp^3 bonding. Forces calculated from the REBO potential were employed to solve the Newtonian equations of motion applying the predictor-corrector method with a time-step of 0.2 fs. To keep the system at constant temperature the Berendsen