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Article

Structural Defects in Few-Layer Graphene nanostructures synthesized by self-propagating high-temperature synthesis

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Abstract:

A quantitative method is proposed to determine of Stone-Wales defects for carbon nanostructures with sp2 hybridization of carbon atoms. The technique is based on the diene synthesis reaction (Diels-Alder reaction). The proposed method was used to determine Stone-Wales defects in the few-layer graphene (FLG) nanostructures synthesized by the self-propagating high-temperature synthesis (SHS) process, in reduced graphene oxide (rGO) synthesized based on the method of Hammers and in the single-walled carbon nanotubes (SWCNT) TUBAL trademark, Russia. Our research has shown that the structure of FLG is free of Stone-Wales defects, while the surface concentration of Stone-Wales defects in TUBAL carbon nanotubes is 1.1×10^{-5} mol/m^2 and 3.6×10^{-5} mol/m^2 for rGO.

Keywords: *few-layer graphene; structural defects; self-propagating high-temperature synthesis; Stone-Wales defects; graphene nanostructures, carbon nanotubes, reduced graphene oxide.*

1. Introduction

After the pioneering work of Geim and Novoselov on the preparation and study of graphene, interest in the development of production methods and the search for areas of application of two-dimensional carbon (2D) nanostructures has sharply increased [1]. The most efficient and commonly used techniques to synthesize such graphene nanostructures include liquid-phase exfoliation via sonication, chemical oxidation of graphite to its oxide, and its consequent reduction [2], as well as different CVD variations [3]. The authors of [4] synthesized few-layer graphene by passing carbon dioxide through a reactor filled with a mixture of magnesium and magnesium oxide powders used as reducers. In [5], few-layer graphene was prepared using graphene oxide and fluorinated graphite as reagents mixed with reducers (silicon, magnesium, sodium nitride, lithium nitride) to obtain a stoichiometric mixture.

The availability of various methods for synthesizing 2D carbon nanostructures makes it urgent to set up investigations on the search for common and different properties when comparing the morphometric parameters of carbon nanoparticles synthesized under different conditions and from different starting materials. In particular, an important parameter from the point of view of the practical application of 2D graphene nanostructures is the defectiveness of their planar surface. The most significant structural defects include vacancy defects that arise in the absence of a carbon atom in the hexagonal graphene lattice and Stone-Wales defects that arise when the graphene lattice is formed not exclusively by hexagons also by penta-heptagone pairs [6]. It should be noted that the general quantitative assessment of the defectiveness of graphene is an extremely difficult process and requires technically complex and expensive equipment.

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The present investigation aimed to develop a quantitative method for determining the specific (per unit surface area of a graphene sheet) concentration of defects of the Stone-Wales type.

Recently, we have proposed an original method for producing FLG based on the destruction and subsequent self-organization of natural biopolymers under the conditions of self-propagating high-temperature synthesis [7]. SHS is a chemical process analogous to combustion, which occurs in the autowave mode (combustion front) in mixtures of oxidizer and reducing agent powders. SHS is an exothermic reaction in which heat is localized in a narrow layer (synthesis zone) and is transferred from layer to layer by heat transfer. The temperature in the synthesis zone can reach 2000°C. The main advantage of SHS technology is in its principle, i.e., in the use of the released heat of chemical reactions instead of heating a substance from an external source. This allows SHS processes to successfully compete with traditional energy-intensive technologies [8].

In addition, the simplicity of the apparatus design of the SHS process makes it easy to scale the synthesis of FLG nanoplates up to the tonnage volume. It was shown that, in terms of their morphometric parameters, the obtained 2D graphene structures belong to FLG [7]. To date, it has been shown that the obtained FLG is promising in polymer materials science [9], as a basis for radionuclides sorbent [10]. The ability to obtain FLG in product volume sufficient for real application and the shown promise of their use in a wide range of practical applications determined the choice as an object of this research FLG synthesized using the SHS process.

2. Investigated materials

For the study, we used FLG synthesized from starch under the conditions of the SHS process (FLG-SHS) [7], SWCNT (TUBAL trademark, JSC "OCSiAl", Novosibirsk, Russia) [https://tuball.com/additives] and GO synthesized by modified Hammers method [11], which was treated with hydrazine to obtain reduced graphene oxide (rGO).

3. Used Methods for Analysis and Experimental Technique

The images were obtained by scanning electron microscopy on a TESCAN Mira-3M, SEM Supra55VP-3259 microscopes and transmission electron microscopy on a 50 kV FEI Tecnai G2 30 S-TWIN microscope.

In the TEM study, the powder samples were placed in ethanol, sonicated for 5 min, and mounted on a carbon grid.

The quality of synthesized samples was estimated using Raman spectra recorded on a Confotec nr500 (532 nm, SOL Instruments).

Specific surface areas of synthesized samples were determined using multilayer adsorption on an ASAP 2020 analyzer (USA). Nitrogen was used as the adsorbate. The sample preparation was performed according to the standard procedure of heating the samples in a vacuum at 300 °C for 3 h before the measurements. The measurement error did not exceed 3%.

Chromatographic studies were carried out using a Clarus 500 gas chromatograph. Research parameters: column temperature – 145 °C; detector temperature – 250 °C; evaporator temperature – 250 °C; gas rate - 30 ml/min.

4. Stone-Wales defects

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Stone-Wales defect is a crystallographic defect in carbon nanotubes, graphene, and other crystals with a hexagonal crystal lattice appear when one of the C – C bonds is rotated through an angle of 90 °, as a result of which four hexagons of carbon atoms are converted into two heptagons and two pentagons [12]. Because of this rearrangement, active dienophilic vacancies are formed in the structure of nanotubes and graphene. In the practice of organic chemistry, active dienophilic vacancies are used to obtain cyclic compounds by the reaction of the so-called "diene synthesis" - the reaction of [4+2] - cycloaddition (Diels-Alder reaction) [13]. The Diels - Alder reaction is a coordinated [4 + 2] cycloaddition occurring between a 1,3-diene and an unsaturated compound, a dienophile. Usually a diene contains an electron-donor substituent, and a dienophile an electron-withdrawing group. It is known that the walls and ends of a carbon nanotube contain defective elements (five-membered cycles) that can act as dienophiles [14]. The presence of such defects in single-walled carbon nanotubes (SWCNTs) was shown using the reaction with α-methylstyrene. The last one was selected in as a conjugated diene due to the fact that, unlike classical dienes - cyclopentadiene and styrene - it does not form homopolymer. Diene synthesis reaction scheme presented by the example of the reaction of alpha α-methylstyrene with the surface of single-walled nanotubes (Figure 1).

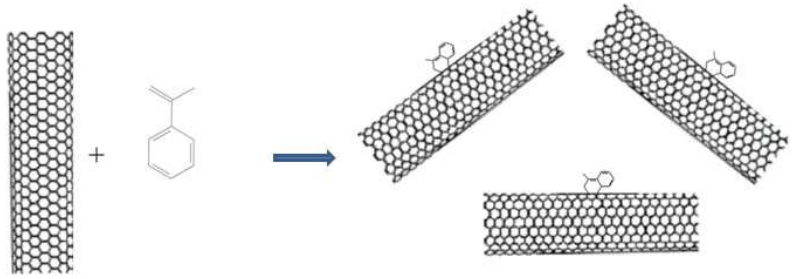

Figure 1. Scheme of joining α-methylstyrene to nanotubes.

According to the diene synthesis scheme, the formation of cyclic compounds is a thermodynamically favourable reaction; therefore, the reaction proceeds irreversibly and, accordingly, quantitatively. This nature of the reaction makes it possible to use it for the quantitative determination of possible Stone-Wells defects in carbons nanostructures, the surface of which is formed by carbon atoms with sp2 hybridization.

The progress of the reaction was monitored by the method of gas-liquid chromatography (GLC). To carry out the experiment, a mixture of α-methylstyrene (main reagent) with o-xylene (standard) was added to a suspension of SWCNTs in toluene with vigorous stirring. The resulting suspension was placed on a magnetic stirrer. Samples of the mixture taken every 4 hours were introduced into the chromatograph and the ratio of α-methylstyrene / o-xylene in the mixture was determined. From the ratio of the areas of the o-xylene / α-methylstyrene peaks for each sample, it was concluded that the reaction was progressing. The criterion for the progress of the reaction was a sequential decrease in the content of α-methylstyrene in the suspension. The calculated degree of addition of α-methylstyrene to the SWCNT surface obtained by us was 28.2 wt. %

To eliminate the systematic error of the experiment, we specially set up a blank experiment, which showed the absence of sorption of o-xylene on the surface of the selected series of nanocarbons.

5. Results and discussion

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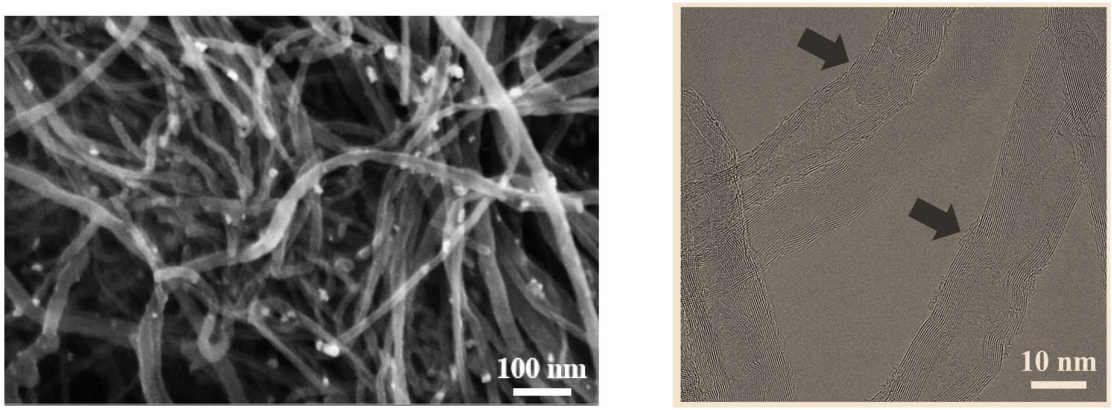
Figure 2 shows electronic images of SWCNTs obtained by SEM and TEM methods.

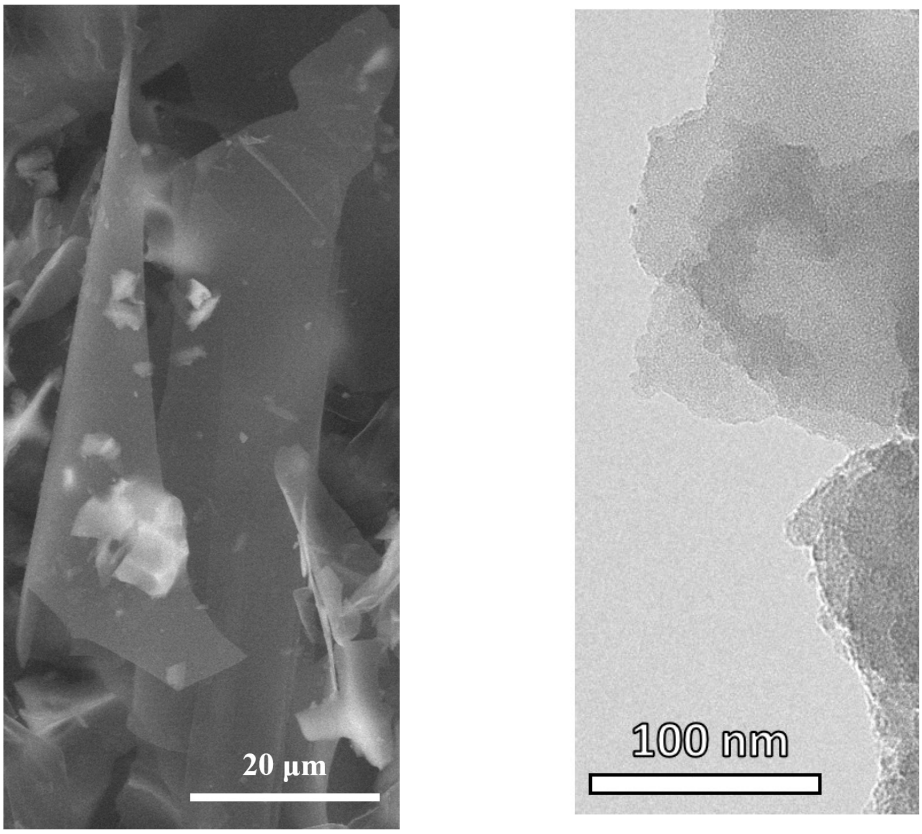


(**a**) (**b**)

Figure 2. SEM (a) and TEM (b) images of SWCNT.

As can be seen in Figure 2, SWCNTs are tangled aggregates in the form of tangles, consisting of individual CNTs. The diameter of individual SWCNTs does not exceed 20 nm. However, Figure 2b clearly shows defects in the structure of SWCNTs marked with arrows.

Figure 3 shows electron images of FLG-SHS obtained by SEM and TEM methods.



(**a**) (**b**)

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Figure 3. SEM (a) and TEM (b) images of FLG-SHS.

As shown in Figure 3a, the FLG-SHS have planar dimensions up to several tens of microns, and the number of layers does not exceed 5 (Figure 3b).

Figure 4 shows the Raman spectra of SWCNTs, FLG-SHS and rGO.

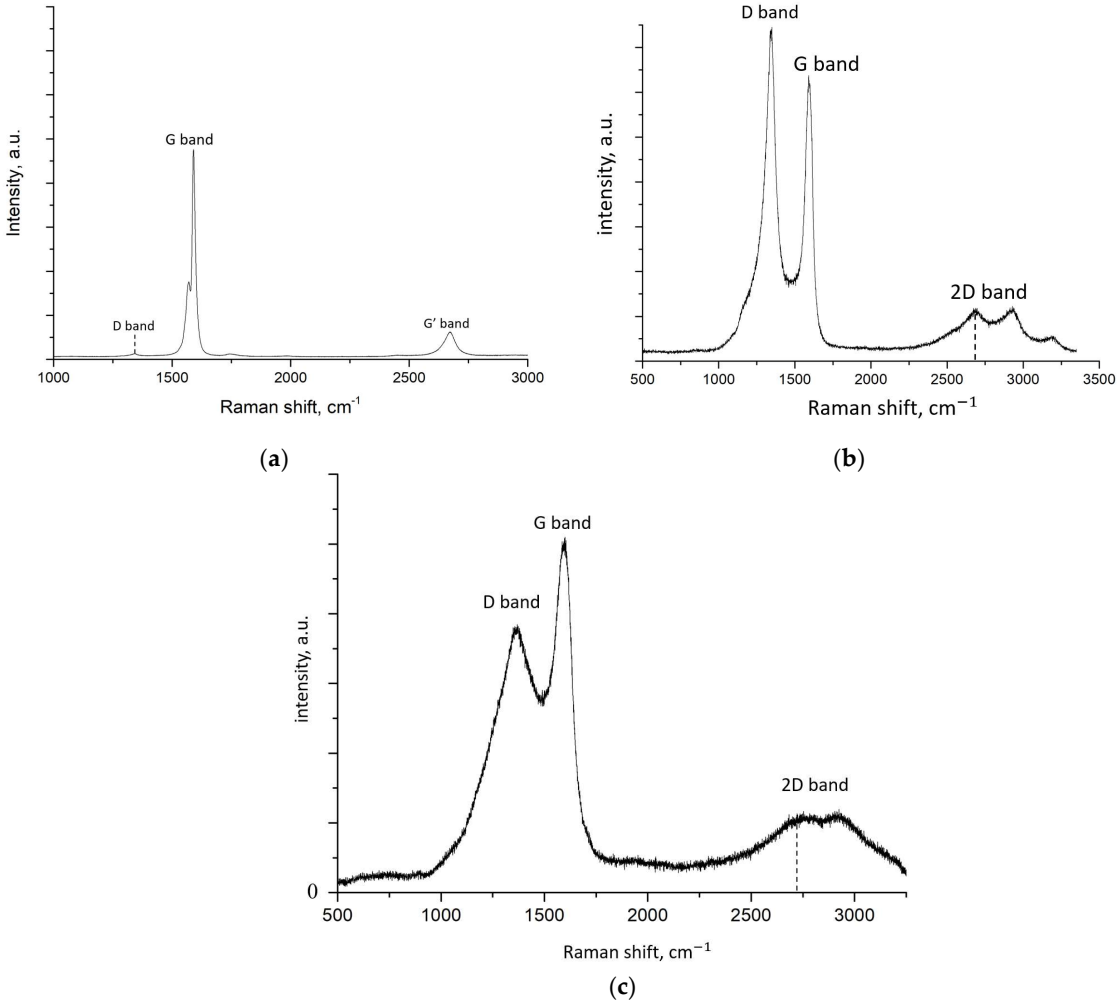

Figure 4. Raman spectra of SWCNT (a), FLG graphene nanosheets, synthesized from starch under the conditions of the SHS process (b), rGO (c).

The Raman spectrum of SWCNTs contains D peak (1345 cm^{-1}), G peak (1590 cm^{-1}), and G peak (2680 cm^{-1}) typical of CNTs. Similar spectra were observed in [15]. The intensity ratio of the D peak (I_d) and the G peak (I_g) is 0.028, which is usually attributed by researchers to the extremely low defectiveness of CNTs [16]. It should be noted that it is by the intensity of the D peak that researchers estimate the defectiveness of the sp^2 structure of such materials as CNTs and graphene nanostructures.

Sample FLG-SHS exhibits D peak (1345 cm^{-1}), G peak (1600 cm^{-1}), and 2D peak (2500 cm^{-1}) typical for graphene. Similar spectra were obtained in [17]. However, unlike CNTs, this material has a highly intense D peak, and the I_d/I_g ratio is 1.2, which, as in the case of CNTs, is usually associated with a high defectiveness of the material. The Raman spectrum of rOG is similar to that of FLG, however, the I_d/I_g ratio is 0.76, which suggests that

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this sample has less structural imperfection than FLG. Similar rOG spectra were also obtained in [18].

To check the data on the defectiveness of the structure of CNT, FLG, and rGO samples obtained by Raman spectroscopy, we experimented on the possibility of including these materials in the diene synthesis reaction. It consisted of an attempt to functionalize them with α-methylstyrene. A mixture of α-methylstyrene and o-xylene taken in equal amounts was added to a suspension of carbon nanostructures in toluene to carry out the diene synthesis reaction.

As shown by our carefully performed experiments, it can be argued that the diene synthesis reaction for FLG does not work. At a minimum, the impossibility of the diene synthesis reaction indicates the absence of defects of the Stone-Wales type or their existence at concentrations below the sensitivity of the registration method (gas-liquid chromatography).

Accordingly, the defectiveness of the structure of the FLG particles obtained by us, demonstrated by the nature of the Raman spectrum curve, can be associated exclusively with concentrated vacancy defects. It was of undoubted interest to carry out similar experiments to determine the Stone-Wales defects for SWCNT “TUBAL”.

The presence of defects in SWCNT "TUBAL" is well known, and therefore, in addition to purely practical interest, such work was necessary to verify the effectiveness of the proposed method independently. These experiments were carried out under conditions similar to the functionalization of FLG.

In contrast to FLG-SHS, the diene synthesis reaction was efficient for SWCNT and rGO. The concentration of Stone-Wells defects calculated by us for SWCNT and rGO turned out to be equal to Csw = 3.3×10^{-3} mol/g and Csw = 20.9×10^{-3} mol/g, respectively. Taking into account the specific surface area of nanomaterials (300 m^2/g for SWCNT and 580 m^2/g for rGO), the surface concentration of Stone-Wells defects is $C_{sw} = 1.1\times10^{-5}$ mol/m^2 and $C_{sw} = 3.6\times10^{-5}$ mol/m^2, respectively.

The obtained value corresponds to the number of moles of α-methylstyrene irreversibly reacted with the surface of carbon nanostructures by the reaction of diene synthesis, which quantitatively corresponds to the concentration of dienophilic vacancies - Stone-Wells defects.

Summary information with data for various carbon nanomaterials studied by us is given in Table 1. The specific surface of carbon nanomaterials needed to calculate the surface SW defects concentration was calculated from BET data.

Table 1. Parameters of studied carbon nanomaterials.

Sample	Stone-Wales defects concentration CSW (mol/m²)	I_d/I_g	Specific surface m²/g
SWCNT	$1,1\times10^{-5}$	0,028	300
rOG	$3,6\times10^{-5}$	0,76	580
FLG	0	1,2	660

The obtained value of SW defects concentration corresponds to the number of moles of α-methylstyrene irreversibly reacted with the surface of carbon nanostructures by the reaction of diene synthesis, which quantitatively corresponds to the concentration of dienophilic vacancies - Stone-Wells defects.

The difference in defects of rGO and FLG we attribute both to different mechanisms of their production (up-bottom/bottom-up) and different sources of their production. As for our best knowledge, the quantitative data on SW defects concentrations per surface unit of carbon nanostructures were available for the first time.

6. Conclusions

A quantitative method based on the diene synthesis reaction is proposed to determine Stone-Wells defects in carbon nanostructures with sp^2 hybridization of carbon atoms (graphenes, nanotubes). It is shown that from biopolymers under the conditions of the SHS process, it is possible to obtain FLG nanoplates that are free of Stone-Wells defects.

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