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EMPHASIZING PHYSICAL ASPECTS AND APPLICATIONS OF GRAPHENES

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ABSTRACT

Graphenes have attracted much attention due to their properties and possible applications. This approach is dedicated to shortly describe the problems related to this promising element. Some aspects concerning physical description and material characteristics are discussed. The paper presents methods for graphenes obtaining and major means of morphological investigation and structural characterization. Also, mechanical, thermal and tribological properties are reviewed. Finally, concluding remarks are drown.

KEYWORDS: graphene, synthesis methods, structure, properties

1. Introduction

Carbon has four allotropic forms: diamond, graphite, fullerene and graphene. Graphenes are formed by one-layer of carbon atoms placed in a honeycomb structure. It is the main material for all allotropic carbon forms: fullerene (0D), nanotubes (1D), or graphite (3D) as it can be seen in Figure 1. They are very light, 1 m^2 weighting only 0.77mg [1]. In their natural state, graphenes are arranged as bulks with maximum 10 layers with monoatomic thickness, through π-π interactions. In order to mix them with other materials these interactions must be weakened.
The major difficulty in synthesis and processing of graphenes is their tendency of aggregation. As the value of graphene characteristics is given by its structure in separate layers, it is essential to avoid their aggregation caused by Van der Vaals forces.

2. Methods of obtaining graphemes

In practice, there are used various methods of obtaining graphenes.

2.1. Mechanical exfoliation

An empirical method is mechanical exfoliation in solution. The method was used by 2010 Nobel laureats for physics, Geim and Novoselov [1].

The strength energy of Van der Vaals interaction is of approximately 2eV/nm^2, and the necessary force for breaking this interaction is of approximately 300nN. This small force can be easily obtained by means of a scotch tape [1]. Another method is the intercalation of small molecules by mechanical exfoliation. Graphite stocking can be substantially reduced by molecule insertion between graphene layers or by non-covalently attaching of polymer molecules between graphene layers, generating graphite intercalation compounds. The graphite layers remain unaltered with guest molecules located in the interlayer galleries [6].

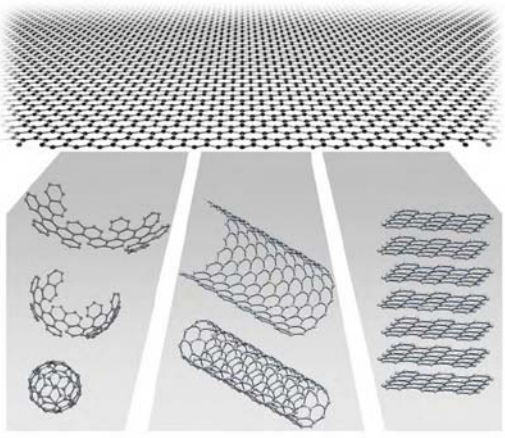

Fig. 1. *Graphene is a building material for carbon materials. It can be wrapped up into 0D buckyballs, rolled into 1D nanotubes or stacked into 3D graphite [1]*

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2.2. Chemical vapor deposition (CVD)

Thermal CVD is recommended for obtaining graphene layers on a wide scale at a temperature of approximately 1000^{0}C [20]. A foil of Ni is placed in CVD chamber at a temperature of approximately 1,000^0 C with a diluted hydrocarbon gas. The process starts by inserting carbon atoms into the superficial layer of the Ni substrate, similar to the carburization process. Oversaturation of carbon atoms of the superficial layer is followed by out-diffusing carbon atoms on the surface which forms graphene structures [2, 19]. Plasma enhanced CVD has an advantage compared to the previous method given by the temperature (650^{0}C) and smaller deposition time. It is used a gas mixture of 5-1000% CH_4 in H_2 at a pressure of 12Pa [22].

Another method is thermal decomposition on SiC, where SiC is introduced into a UHV chamber which is heated at 1200^{0}C for a few minutes, sublimation of Si into gas atoms from the superficial layer, allowing carbon atoms to form graphenes [27, 28].

2.3. Chemical reaction

In order to obtain oxidated graphenes, graphite is oxidated with: sulfuric acid, nitric acid and potassium permanganate, potassium dichromate, hydrogen peroxide, using *Hummers* method [2, 4, 3, 10, 12, 24]. Schema of this method can be seen in Figure 2.

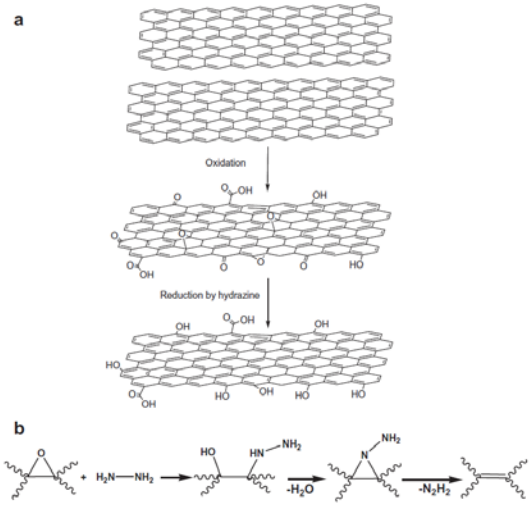

***Fig. 2**. General scheme for a) oxidation of graphite and obtaining graphenes oxide; b) epoxy reduction by hydrazine [3].*

Another method used is *Staudenmaier*, and consists of an oxidation reaction followed by pyrolysis in an oven heated at 1000 ^{0}C [29].

3. Structure characterization

Study of graphene may be done by using optical microscope, SEM, TEM and AFM. Using optical microscope, graphenes could be studied on substrate of SiO and SiN. It was used a silicon layer with an overlayer of 300nm of SiO. The number of layers was identified according to contrast colour as it can be seen in Figure 3 [13].

Using AFM it can be revealed a topographic contrast where no distinction can be made between graphene oxide (GO) and graphene reduce (GR). It was observed a thickness of 1nm for GO and of 0.6nm for GR. The difference in thickness is given by functional oxigen groups which are removed during chemical reductions (Figure 4) [14]. TEM gives the best results when studying the materials at atomic layer.

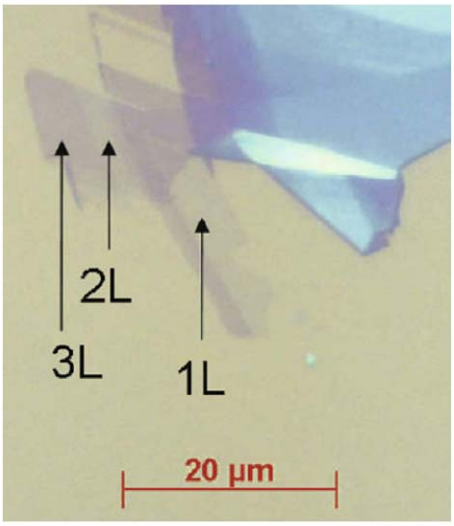

***Fig 3**. Image obtained by means of optical microspy of graphene layers. (1L, 2L, 3L are the number of graphene layers) [13]*

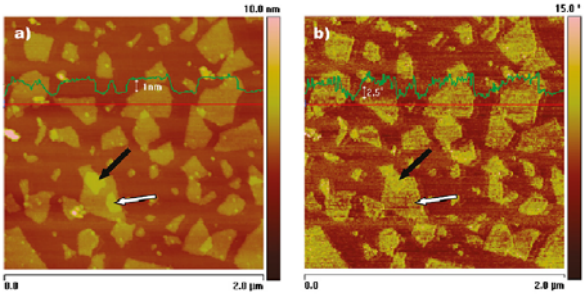

***Fig. 4**. AFM images of graphenes. In a) and b) are GO. a) surface image and; b) cross section image [14]*

The results in studying graphene layers is limited by their resolution at a lower voltage, as a higher voltage may destroy graphene layers. The latest TEM allows for a resolution of 1Å at a 80kV voltage. The images are seen in Figure 5[15]. STEM show us both structure defects and contamination with other atoms. The images are seen in Figure 6 [16].

4. Graphene characteristics

4.1 Mechanical characteristics of graphenes

Besides CNT, graphenes are considered to have the highest Young's modulus, E=1TPa, several times bigger than that of steel (E=0.21 TPa). Taking into consideration the fact that this material has only two dimensions, the value of the modulus was calculated as follows: E^{2D} = 3.41TPa(E^{2D} – Young's modulus in two dimensions). The tensile strength is σ =130GPa and strain is ε = 0.25 measured by AFM [17]. For shear modulus it was measured the value of G= 0.408 TPa [5].

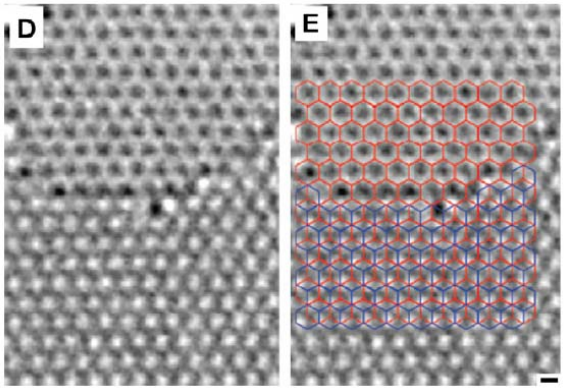

Fig. 5. *D-the upper part represents a single graphene layer and the bottom part represents two- layer graphene. In E, we have two layers of graphene [15]*

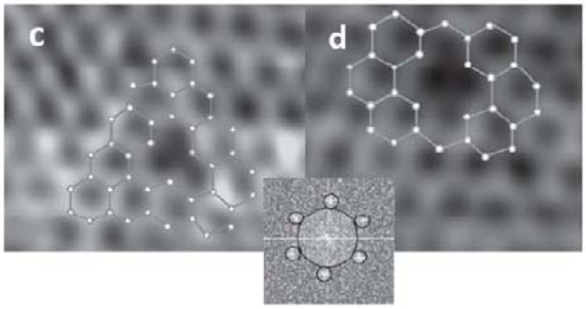

Fig. 6. *Graphene layer with structure defects which can be c) one atom or d) two atoms. The raw image is in the middle [16]*

Young's modulus of graphenes obtained by chemical reduction was 0.25TPa, close to the pristine graphene. The difference in value is due to structure defects, because of the lack of carbon atoms from graphene structure [26]. Other scientists found out that the value of Young's modulus varies according to the thickness of graphenes and Poisson's coefficient remains constant, no matter the variation in graphene thickness. These curves are shown in Figure 7 [8].

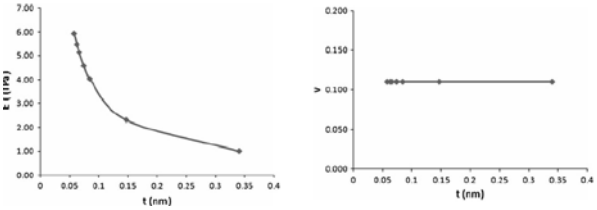

Fig. 7*. a) Young's modulus of graphene sheet (L = 7.137 nm,W = 6.252nm) with various thicknesses; b) Poisson's ratio of graphene sheet (L = 7.137 nm, W = 6.252nm) with various thicknesses [8].*

Starting from the hypothesis that graphenes are ortotropic materials there were established different values of "zigzag" or "armchair" Young's modulus as well as different values of tensile strength and stress for longitudinal and transversal loads [9]. Compressive and tensile behaviour of graphenes have been studied at both longitudinal and transversal loads, bigger differences being noticed during compressive loads between the two methods of applying load, Figure 8 [23].

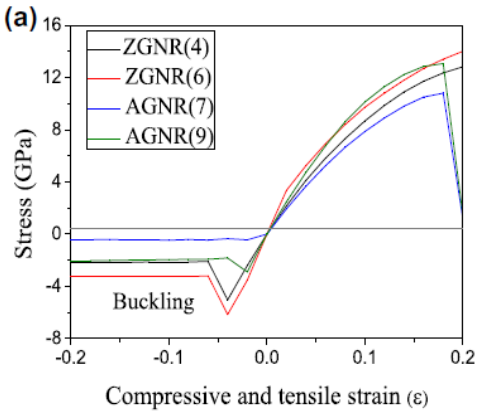

Fig. 8*. Compressive and tensile behaviour of graphenes at both longitudinal (ZGNR4 si ZGNR6) and transversal loads (AGNR7si AGNR9) [23]*

After measurements it has been noticed that the variation of elastic properties of graphenes is non-linear, and can be expressed under a uniaxial load as folows:

$$\sigma = E\varepsilon + D\varepsilon^2 \quad (1)$$

where σ represents the strength, E – Young's modulus, σ is the symmetric second Piola-Kirchhoff stress, ε – uniaxial Lagrangian strain, D – third-order elastic constant [21].

***Tab. 1**. Properties of graphenes [7]*

Measured values	*Armchair*	*Zigzag*
Young's modulus	710GPa	737GPa
Tensile failure strain	0.269	0.198
Tensile failure stress	120GPa	95GPa
Failure rigidity	241GPa/nm	250GPa/nm

Graphene adhesion to other materials is described as (2):

$$\eta = Et^3h^2 / \Gamma\lambda^4 \quad (2)$$

where E –Young's modulus, Γ – adhesion energy between graphene and substrate, h- asperities height, λ – spacing between asperities, t – asperities thickness, η – the competition between Γ and the elastic energy of the deforming to conform a rough surface.

For h<<1nm the graphene conform to the rough surface while for h>1 it can only partially conform [25].

4.2. Thermal properties

In order to determine the value of thermal conductivity of graphenes, it has been suspended a layer of graphene in a substrate of silicon oxide/silicon and a focused laser light was pointed towards this. Thermal conductivity of graphenes, measured with micro-Raman spectroscopy is very high, reaching 5000W/mK compared to copper (400W/mK), carbon steel (43W/mK) or diamond (0.2W/mK) and it is higher than CNT (single wall CNT ≈3500W/mK and multi wall CNT≈3000W/mK) [18]. Graphene can be used in electronic devices where an important problem is dissipation of thermal energy accumulated during functioning, these properties thus giving the possibility of replacing silicon as material for electronic microdevices.

4.3. Tribological properties of graphenes

For studying the wear behaviour of graphene there have been used values of loads smaller than 250nN, without causing graphenes breakage. Wear behavior of graphene can be affected by the number of graphene layers, thus a small number of layers (1-4) have a different friction behavior than a bigger number (13-16). Thus graphenes with more than 5 layers have a similar friction behaviour as graphite. Graphenes used for determining wear behaviour have been deposited on a silicon substrate by mechanical exfoliation. Using AFM it has been studied the graphene friction behaviour using loads with values between 30 and 5nN [11]. Initially AFM height of the tip came in contact with the cantilever and friction force has been measured on a 20μm distance for 2 cycles. The cantilever was retracted slightly to lower the applied load and the friction force was measured again. This process was repeated until the tip got detached from the specimen surface due to excessive negative load (Figure 9) [11].

***Fig. 9**. Schematic of AFM tip/specimen contact under negative and positive applied loads [11]*

Graphenes used were 6nm thick. Figures 10 and 11 show the image obtained by AFM of graphenes used in the experiment [11].

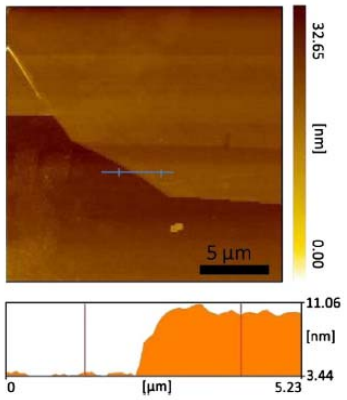

***Fig. 10.** AFM image of the graphene specimen, 2D profiles [11]*

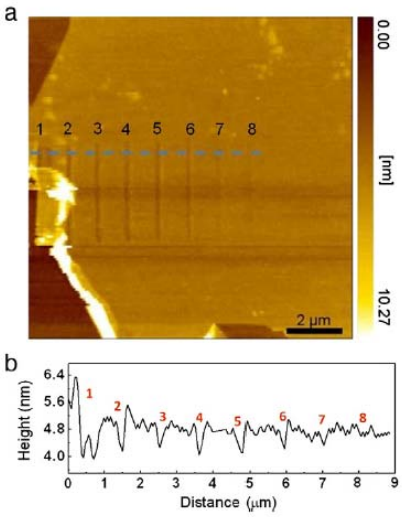

***Fig. 11.** (a) AFM image of wear tracks and (b) the cross-sections of wear tracks [11]*

5. Conclusions

Due to its unique properties (mechanical, electrical, thermal, optical) graphenes applications are diverse:

- electronic devices with integrated circuits, touchscreens, LCDs, LEDs, organic photovoltaic cells, transistors, frequency multipliers;

- water desalination, ethanol distillation, thermal management materials, optical modulators, additives in coolants, ultracapacitors, engineered piezoelectricity, biodevices, single-molecule gas detection.

Meanwhile, the main problem remains graphenes mass production and a price as small as possible. Preparation methods must solve the transfer, the number of layers or graphenes folding from the substrate they have been chemically deposited.

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