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Narek Margaryan, Ninel Kokanyan, Edvard Kokanyan. Low- Temperature Synthesis and Characteristics of Fractal Graphene Layers. Journal of Saudi Chemical Society, In press, 85, pp.30502. 10.1016/j.jscs.2018.03.004 . hal-01763912

HAL Id: hal-01763912

<https://hal.science/hal-01763912>

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Accepted Manuscript

Original article

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PII: S1319-6103(18)30034-6

DOI: <https://doi.org/10.1016/j.jscs.2018.03.004>

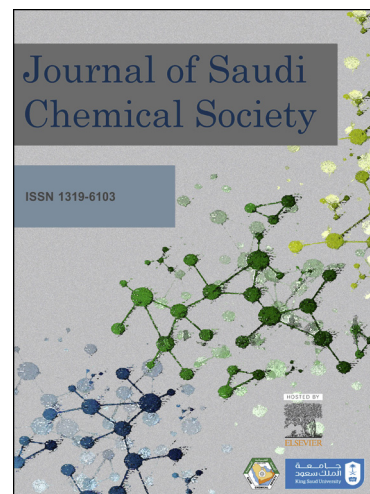
Reference: JSCS 953

To appear in: *Journal of Saudi Chemical Society*

Received Date: 3 March 2018

Revised Date: 27 March 2018

Accepted Date: 29 March 2018



Please cite this article as: N. Margaryan, N. Kokanyan, E. Kokanyan, Low- Temperature Synthesis and Characteristics of Fractal Graphene Layers, *Journal of Saudi Chemical Society* (2018), doi: <https://doi.org/10.1016/j.jscs.2018.03.004>

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Low- Temperature Synthesis and Characteristics of Fractal Graphene Layers

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Abstract Large scale fractal graphene layers are obtained by complex method of liquid phase exfoliation and self- organization. Atomic force microscopy (AFM) is used to study the surface properties of formed layers and to assess their thickness. Surface potential of graphene and potential transition between the graphene and substrate is measured by Kelvin probe method. The influence of the effect of dielectric confinement on the optical properties of graphene is discussed in this work. Raman scattering spectra were used for structural analysis and assessment of the level of defects. Current-voltage characteristics of graphene ribbons were measured and discussed for different number of layers.

Keywords: Graphene, AFM, Absorption, Raman spectroscopy, Current-Voltage characteristic.

1. Introduction

Carbon nanostructures and especially graphene are under general attention of international science society due to their unique physical properties and huge application potential [1-5]. Production of such nanostructures by the most optimal methods is the goal of many studies [6-9]. At present, intensive research is being carried out to develop simple low-temperature methods for the synthesis of graphene and related materials [10, 14]. The methods based on exfoliation deserve special attention, among other methods. [12-14]. The formation of graphene using this method basically does not require the creation of chemical strong σ -bonds in the graphene plane. That's why there is no need for high energy while obtaining graphene. There is only needed to break the fragile π chemical bonds between the graphene sheets, which are forming highly oriented pyrolytic graphite (HOPG). Consequently, the use of such methods for the production of graphene is optimal and easy to implement. The only problem in this context is the small surface area of single-layer graphene and the high level of defects. On the other hand the majority of graphene production processes, including the method, based on joining of already exfoliated graphene flakes, is accompanied

by the process of self organization at the nano and micro levels. Such self-organized films have fractal structure [15]. Fractal character of graphene and graphene based quantum dots and some physical phenomena in these structures such as quantum Hall effect are discussed in various articles [16, 17]. Furthermore, not only the quantum Hall effect, but also other physical phenomena associated with the electron transport in graphene and related structures have been intensively studied in the last decade. From this point of view, special consideration is given to the analysis of the current-voltage (I-V) characteristic of graphene. Studying of I-V characteristic and other optoelectronic properties of graphene indicate a huge application potential of this nanofilm [18-20]. The next very important optoelectronic characteristic of graphene, which is specific for graphene and its internal structure, is the optical absorption spectrum. An analysis of the absorption spectrum in accordance the energy band structure of graphene indicates a significant exciton absorption component. As a rule, such spectra are characterized by an absorption peak in the energy range of ultraviolet (UV) waves [21-23]. In addition to all of mentioned researches, there are many researches, which are devoted to the influence of surrounding barrier area on optical properties of nanostructures [24, 25]. Such phenomenon, caused by the so-called dielectric confinement effect, can significantly affect the optical properties of the films, containing one or more atomic layers. Therefore, it is also important to evaluate this effect for the case of the optical absorption spectrum of graphene.

The main task of this research is to obtain and investigate single and multilayer graphene with a relatively large surface, which possess all the physical properties of graphene, by the method that does not require high energy and vacuum technology.

2. Experimental procedure

The process of production of graphene layers consists mainly of two stages. At first, there is liquid phase exfoliation (Fig. 1 a). Then already exfoliated graphene flakes are grouped and joined (Fig. 2 b). Powdery highly oriented graphite (HOPG) is used in solvent of water and acetone as source of the necessary clusters for exfoliation. The HOPG particles dispersed in a solvent form a colloidal system. As is known, HOPG consists of atomic layers, which are connected with each other by fragile π chemical bonds. In turn, the carbon atoms forming in these layers are connected by strong σ bonds. So, deformation forces arising in this system can easily separate the graphene layers from graphite, while the bonds between the atoms in these layers remain stable. To cause rotation deformation between graphite layers, ultrasonic waves, having 55 Wt power and 20 kHz frequency of vibration, are applied. In this way, ultrasonic waves lead to exfoliation. These waves lead not only to the exfoliation of graphite powder, but

also to the grouping of exfoliated graphene flakes. The grouping of graphene flakes is also promoted by their hydrophobic character. Joining together, these flakes form holistic, transparent layers of single and few layer graphene.

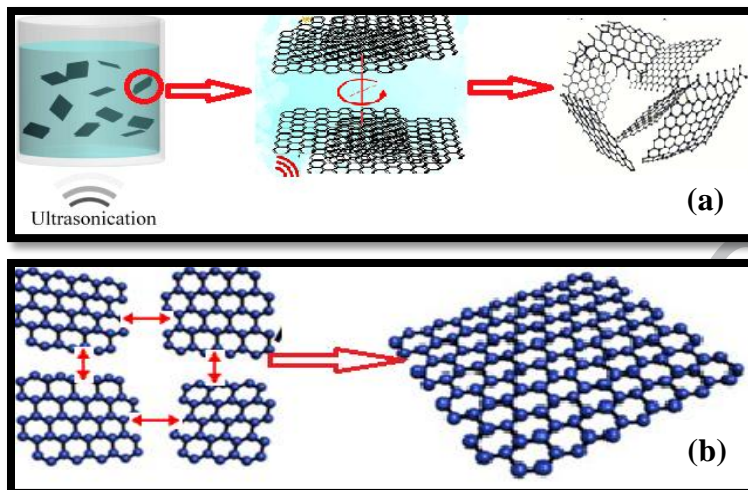


Fig. 1 a) Liquid phase exfoliation, b) joining of graphene flakes.

Thus, we can obtain graphene layers, keeping the power of ultrasonic vibration, the temperature of the colloidal solution and other physical parameters of the systems unchanged. By the other hand, the formation process of films by such method, when one or many physical parameters are not changing, is accompanied by the self-organization at the nano and micro levels. Such films have one or more fractal regularities. As it follows from [15] these fractal regularities cause some changes in several surface and optoelectronic parameters of the film.

Obtained layers keep their continuity and do not torn, when removed from the water and placed on a substrate due to their mechanical strength and elasticity. Silicon (silicon/ silica), amorphous sapphire crystal, monocrystalline salt (NaCl) and special plastic material are used as substrate material.

But often a certain amount of graphite powder remains on the surface of the resulting films. Mechanical treatment of the surface of the obtained graphene layers is carried out to get rid of these residues.

3. Investigation and analysis

3.1. Surface properties

The resulting layers are transparent, and they are difficult to detect for investigation by AFM because of their atomic thickness. To solve this problem, we have illuminated the surface of the liquid on which the film is formed, by special lighting. When the film is on the surface of the substrate, it is illuminated under a microscope attached to an

atomic force microscope. Only due to the reflection of light from their surface, graphene layers are noticeable (in both cases), because light reflection from the graphene surface strongly differs that in case of substrate (or liquid) surface (Fig. 2).

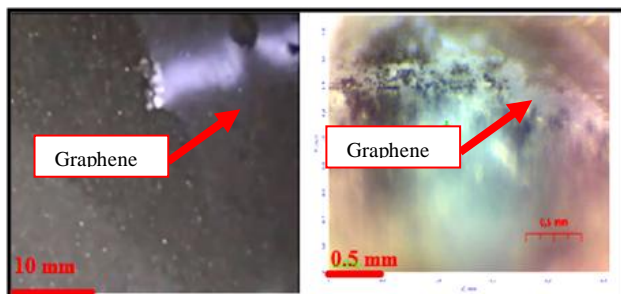


Fig. 2 Real size image of formed graphene layer on water surface (left panel) and USB microscope image (Right panel).

In this way, the graphene layers do not only differ from the substrate, but also can be easily discerned from remains of the graphite powder.

AFM studies of the area, freed from remains, show that produced layers have relatively smooth surface, though there is some waviness, because of substrate roughness (Fig. 3). In turn, AFM images for the graphene layers make it possible to provide analysis of film surface and to estimate their thicknesses.

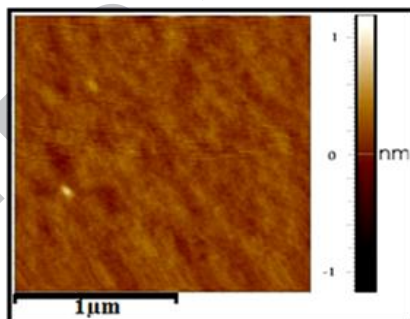


Fig.3 AFM image of graphene surface.

The provided cross sectional line scan analysis by green line direction in Fig. 3a shows that obtained films thickness at the borderline with substrate is above 0.35 nm, which is typical for epitaxial graphene layers Fig. 4. As can be seen in Fig. 4, not only complete layers are formed, but also chaotically dispersed self-organized quantum dots based on graphene.

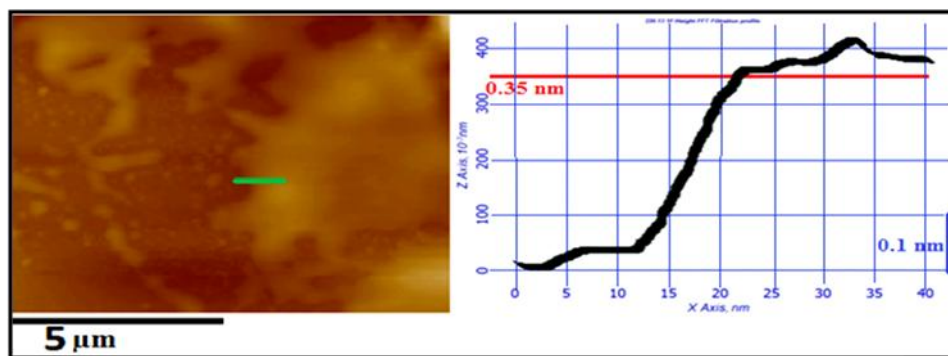


Fig.4. AFM image of graphene (left panel) and estimation of the thickness of the layer by the method of linear scanning (right panel).

In addition to other AFM studies, surface potential measurements were applied by so called Kelvin probe method. This method is based on work function, which is the minimum thermodynamic work needed to remove an electron from the film surface to a point in the vacuum immediately outside the solid surface. The potential transition between graphene and silica substrate at the borderline of layer is presented on Fig. 5.

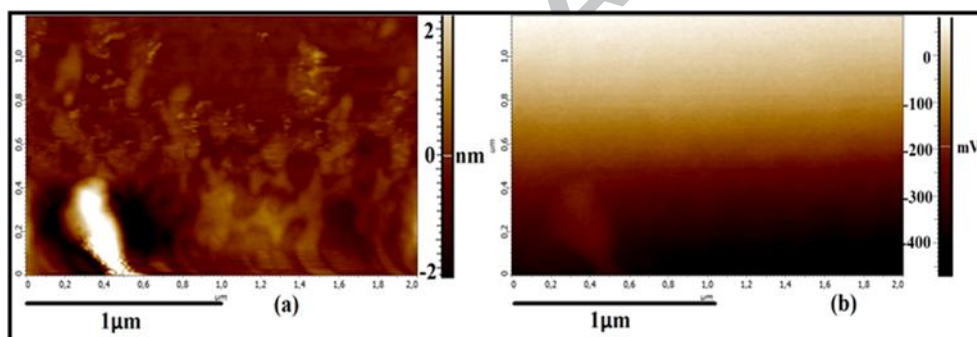


Fig. 5 a Fractal shape of the boundary lines of the layer. b Potential transition at the layer borderline.

Despite the fractal shape of the film boundary, it is obvious that the formed graphene layer is a potential well with respect to the substrate.

As follows the surface potential for obtained layers reaches to the value (-400 mV), which is typical for graphene [26, 27]. Such measurements also make it possible to distinguish the formed atomic thin layers from the upper layers of the substrate surface (due to the difference of surface potential).

3.2. Optical absorption spectra

Measurements of the absorption spectrum were carried out for the synthesized graphene layers in cases of two different substrates- sapphire glass substrate and salt crystal (monocrystalline NaCl) substrate (Fig. 6a,b). The choice of the above-mentioned substrates is due to the fact that these materials do not absorb the electromagnetic waves of

the visible and ultraviolet range (to wit from 1.6 eV to 6.2 eV). From the study of absorption spectra it follows that in both cases the spectra have a characteristic peaks in the range of the ultraviolet waves (specifically from 4.5 eV to 5.2 eV). These peaks are typical for graphene. And it seems that there is two-photon absorption enhanced by the so-called excitonic Fano resonance [22]. The comparison of the absorption spectra with the graphene bandstructure (Fig. 6c) confirms that the component of exciton absorption in the region of the point M in the Brillouin zone essentially affects these spectra.

In turn, the spectrum corresponding to the amorphous sapphire substrate case is shifted to the high energy range with respect to the salt (NaCl) substrate case (6 a,b). The reason for this phenomenon is the fact that the optical properties of thin films, such as graphene, are influenced not only by the quantum confinement effect, but also by the so-called dielectric confinement effect.

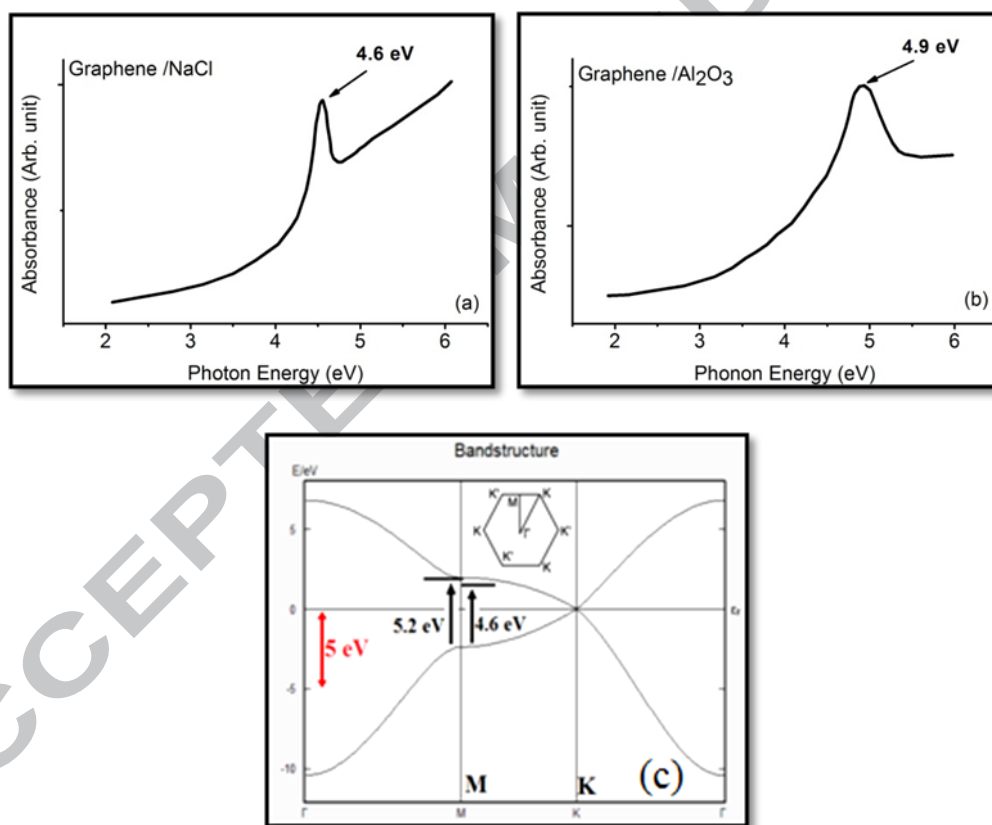


Fig. 6 Graphene absorption spectra for NaCl (a) and Al₂O₃ (b) substrates. Bandstructure of graphene, Brillouin zone and possible excitonic transitions (c).

The influence of the effect of the dielectric confinement on the excitonic component of absorption spectrum is due to the fact that the lines of the electric field between the Coulomb pair emerge from the active region and enter the

barriers area and are redistributed. The influence of the dielectric confinement effect on the exciton component of the absorption spectrum is due to the fact that the electric field lines between the Coulomb pair exit the active region and enter the barrier zone and are redistributed [28]. By this way, Coulomb interaction potential strongly depends on dielectric constant of barrier materials. So, changing barrier material, we can change the excitonic component of absorption for graphene layer.

3.3. Current-voltage characteristics

One of the most important properties of graphene is the current-voltage characteristics, because it is associated with the application of graphene in many essential areas of engineering, such as in transistor and sensor engineering.

Current-Voltage characteristics of specially prepared ribbons based on graphene for various number of graphene layers were examined (for different thicknesses). For this purpose, the voltage was applied in the range from -10 V to 10 V.

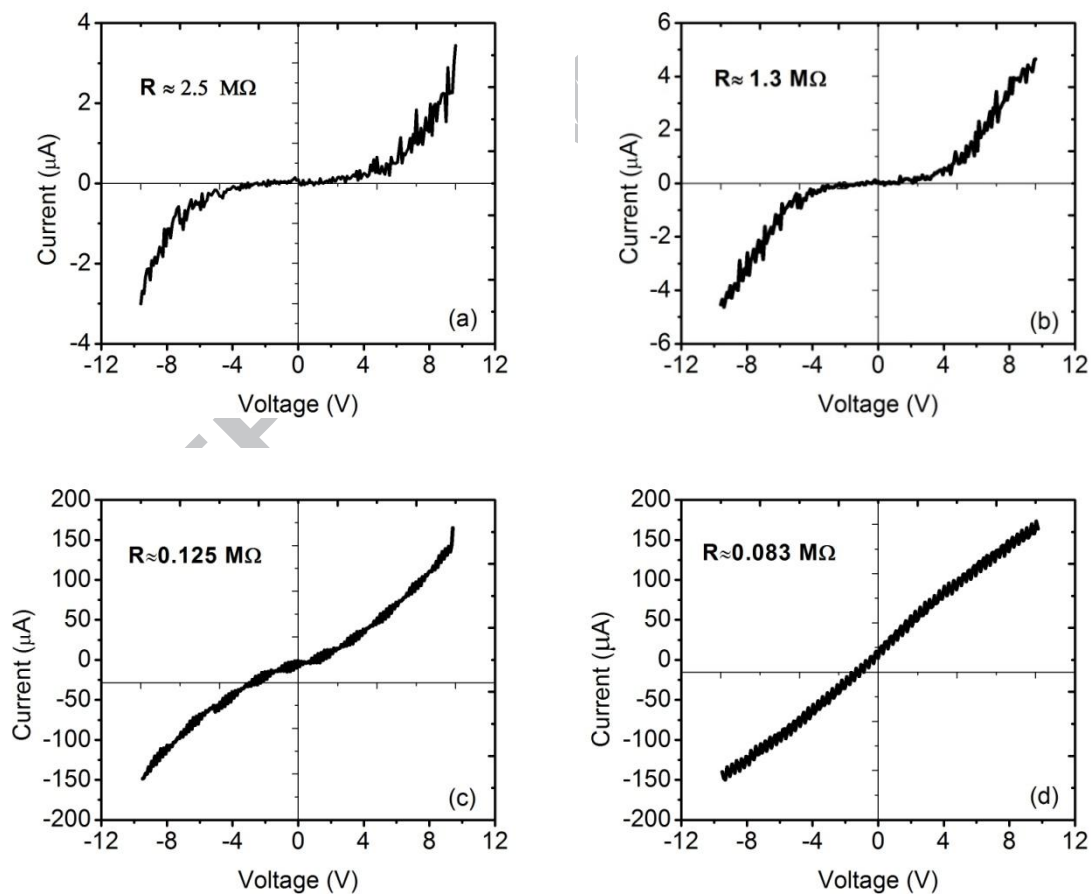


Fig. 7 Current-Voltage characteristics of four graphene ribbons having different resistance.

As it is well known, the graphene is material with 0 band gap. That is why it is easy to generate electrons in the graphene conduction zone. The applied voltage at first causes the transmission of electrons from valence zone to the conduction zone. For this reason, the Current-Voltage characteristics for both single-layer and multilayer graphene (MLG) have nonlinear forms (Fig. 7). As follows, with the increasing of numbers of the layers, the nonlinearity of curves is decreasing and the Current-Voltage characteristic is becoming ohmic (with linear form), which is, in turn, typical for graphite.

The resistance between the contacts was also measured for each sample, in addition to the current-voltage characteristics. Thus, we can estimate the boundary value of the resistance of the tape, from which the Current-Voltage characteristic reveals nonlinearity. Comparison of the resistance of the ribbons and the number of graphic layers in them makes it possible to investigate the influence of the number of layers on the resistance and, therefore, to estimate approximately the limiting number of layers, from which the Current-Voltage characteristic is nonlinear. Such measurements can serve as a method for finding the boundary between the states of multilayer graphene and graphite.

In addition to nonlinearity, the obtained curves are characterized by an almost perfect symmetrical shape.

This symmetry, along with the rest of the arguments, also suggests an isotropic crystal structure, with a low level of defects. Moreover, the results obtained by the measurements are very close to the theoretical curves, which are discussed in [18, 29].

Furthermore, the dependence of the conductivity of the ribbon on the applied voltage is studied (Fig. 8) using the sample of graphene ribbon with $2.5 \text{ M}\Omega$ resistance. After averaging and fitting, the resulting curve has a parabolic shape. So the dependence of conductivity on voltage has the form of a power function.

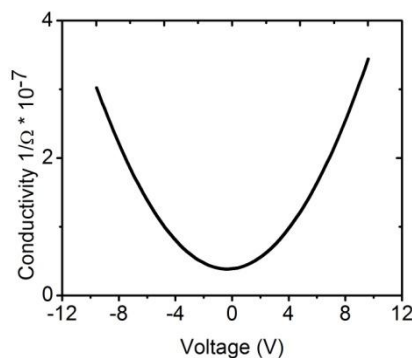


Fig. 8 The dependence of the conductivity of the ribbon on the applied voltage.

The control of the number of layers, the applied voltage, makes it possible to control the electrical properties of the resulting graphene multilayer structure.

3.4. Raman spectroscopy

In this work we present the results of detailed Raman spectroscopy investigations of multilayer graphene (MLG) deposited on sapphire substrate. Measurements of Raman scattering spectra were carried out for different number of layers (Fig. 9). In each Raman spectrum, resonance is observed, corresponding to disorders in sp²-hybridized carbon systems [30-32]. Caused by disordered structure of graphene D peak in this spectra located at 1344 cm⁻¹. The G-mode common to all sp² carbon systems, which is due to the so-called E_{2g}-mode at the Γ point of the Brillouin zone [33, 34], in our spectra is about 1585 cm⁻¹.

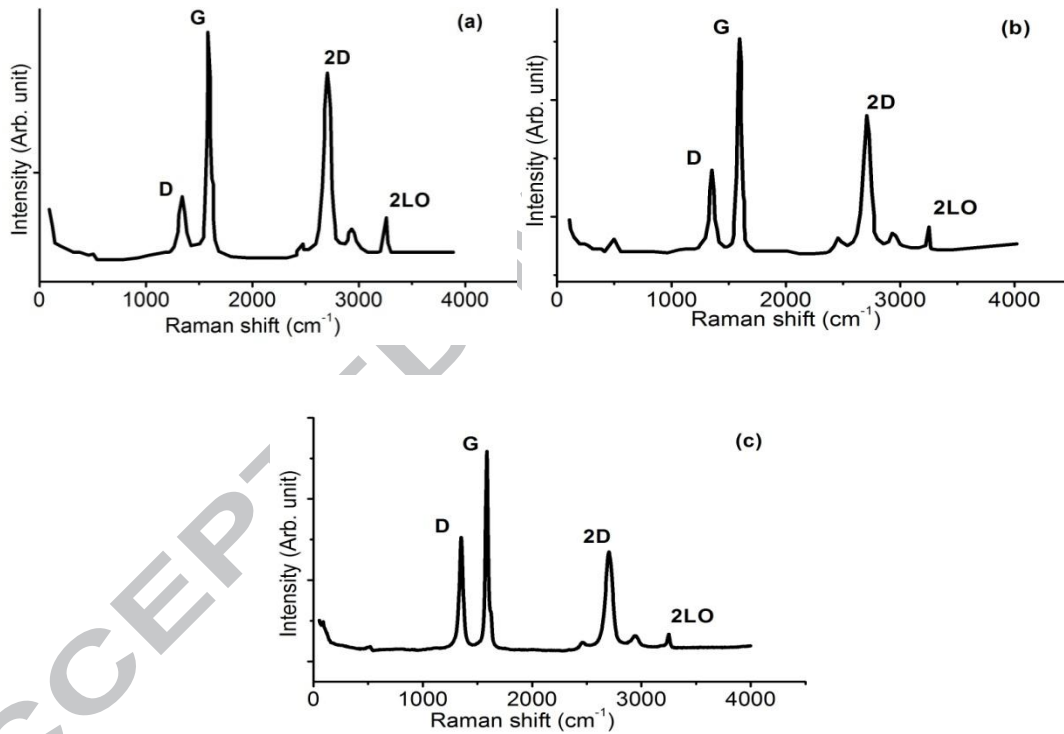


Fig. 9 Raman spectra for MLG ribbons with different number of layers.

The relations of the intensities of the D-mode (I_D) and the G-mode (I_G) for each of the presented spectra have the following values: $I_D/I_G = 0.26$ (a), $I_D/I_G = 0.38$ (b), $I_D/I_G = 0.63$ (c).

Although, the level of defects in MLG increases with the increase in the number of layers, the relation I_D/I_G is relatively small if one takes into account the synthesis method and the fractal nature of these layers.

It is well known, that Raman spectra for all type of sp² carbon materials exhibit a strong peak in the range 2600 - 2800 cm⁻¹, which is called 2D-band. And combined with the G-band, this 2D-band is a Raman signature of graphitic sp² materials. This peak changes its position from 2686 cm⁻¹ (a) to 2697 cm⁻¹ (c), depending on the number of layers for all investigated MLG samples. Being a two-phonon second-order process, this band also depends strongly on the wavelength of the exciting laser, which in this case is 532 nm. In the Raman spectra measured for all obtained films, the 2D peak has symmetric (typical for the turbostratic MLG [30, 35, 37]) form. And the comparison of the intensities of 2D and G bands gives an idea of the number of layers of graphene. In case of discussed MLG, the value of relations of mentioned intensities (I_{2D}/I_G) decreases from 0.82 (a) to 0.52 (c), which is certainly explained by the increase in the number of layers.

In turn, a weak peak is observed in range 3240-3250 cm⁻¹. Such a peak, which is designated 2LO phonons, is especially noticeable in the spectra of multilayer graphene with relative rotations between carbon layers [37]. Here the term LO means longitudinal optical. And it seems, that the stable appearance of this peak in the spectrum of Raman scattering is due to the fact that the graphene layers were exfoliated by rotational deformation.

4. Conclusion

Thus, large scale holistic (continuous) graphene layers were formed by a method based on liquid phase exfoliation and grouping processes. The main advantages of this method are simplicity of synthesis process, large surface area of graphene and possibility to control the numbers of layers. Another advantage of the suggested method is that it is possible to remove formed layers from the water surface and transfer to any substrate in a very simple way. Investigation of these layers shows that, despite the fractal nature, they have physical properties, which are typical for graphene. Raman spectra of these sheets, being typical for few layer graphene, are changing in dependence on the number of layers. These spectra show, that level of defects is lower in respect to the graphene layers synthesized by similar methods [12-15]. In Addition, the symmetric form and comparative intensity of 2D band confirm the existence of so called turbostratic few layer graphene. According to the measurements, the influence of excitonic transitions on optical absorption spectra is observed. Measurements for different substrates show, that optical properties of graphene are influenced by the dielectric confinement effect. This is evidenced by the shift in the absorption peak toward high energy, when the substrate is changed from monocrystalline salt (NaCl) to amorphous sapphire (Al₂O₃). So, by choosing a substrate, it is possible to control some optical properties of obtained graphene.

The Current-Voltage characteristics of the obtained layers have a nonlinear symmetric form, typical for single-layer graphene. Moreover, controlling of the number of layers makes it possible to control the electrical properties of the formed multilayer graphene by changing curves of current-voltage characteristics.

On behalf of all authors, the corresponding author states that there is no conflict of interest.

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Thank to dear reviewers!

1. All mistakes connected with English (misprints, inverse construction, formal grammar mistakes so on) has been corrected.
2. The novelty and key findings has been stressed in the Abstract and the conclusion.
3. Thorough work on the text has been done.
4. Experiment: Fig 1. a,b (a kind of schematics)
5. All recommended references has been added (1-9, 30-32).
6. Unfortunately, I can't include any TEM image, because there is not one corresponding microscope (TEM) in Armenia. And there is no time to do such measurements abroad.