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Letter

2D-Growth Rate Promotion of Graphene via Intensive Nd-Laser/Sonication Irradiations

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Abstract: The graphene was synthesized by two routes the 1st one application of conventional sonication in case of Tri-chloro-acetic 75% H_2SO_3 for 60hrs while 2nd is combined sonication (60 hrs) plus laser irradiations for 30hrs. The yields of two routes are collected and compared structurally to check and investigate the effect of laser on structure quality and amount of yield obtained. Results indicated that combined route gave yield higher than conventional route by ratio ∼ 39%. AFM-investigations were performed to characterize nano-structural features of produced graphene. Furthermore raman spectra were measured to confirm graphene formation.

Keywords: Nd-Laser, Synthesis, Dispersion, AFM, Graphene, Raman Spectra

1. Introduction

Graphene has shown many amazing properties and has numerous numbers of synthesizing techniques [1-11]. In the chemical exfoliation process, the insertion of reactants in the inter-layer space weakens the van der Waals cohesive force. The loosened layer stacking is disrupted when the intercalant decomposition produces a high gas pressure of CO_2 by a rapid annealing to 1050°C. As a result, the *sp2* lattice is partially degraded into *sp2-sp3* sheet that possesses less π-π stacking stability. Chemical exfoliation can be performed in a suspension known as graphite oxide. The most common method to produce graphite oxide was reported by Hummer [5], where graphite is dispersed into a mixture of concentrated sulfuric acid, sodium nitrate and potassium permanganate at 45°C for a couple of hours. In this compound, the graphite layers remain largely intact and the quest molecules or atoms are located in between. To obtain a few or even single sheet materials, the intercalated reactant is decomposed to produce large amounts of gas in the van der Waals space by chemical or thermal means [6]. Then, rapid annealing to 1050°C generates a CO_2 over pressure and splits the graphite oxide into individual sheets [7]. Graphene oxide solutions are yellow in colour or greenish-blue when non-oxidized

graphene sheets are the major constituents [8, 9]. Graphene oxide (GO) could be regarded as graphene functionalized by carboxylic acid, hydroxyl and epoxide groups. Hence, these functionalized groups make GO easily dispersed into a few select polar solvents that form an intercalated composite with polar molecules [10, 11]. The intercalation of solvent causes the graphene sheet to swell and lose its mechanical integrity [12]. Nevertheless, large quantities of structural defects introduced by the oxidation process shifts the physical properties away from pristine graphene [13].

The present studies describe synthesizing of the graphene using two different procedures. The first is conventional sonication and the second is combined sonication with laser irradiations. The investigation with two different procedures is enriched the studies. Also, the synthesized graphene samples were analyzed with Raman Spectroscopy, Atomic Force Microscopy and X-ray Diffraction. The results were sufficiently interpreted.

The major goal of the present work is to introduce application of Nd-laser irradiations as structure promoter and accelerator for growth rate of graphene.
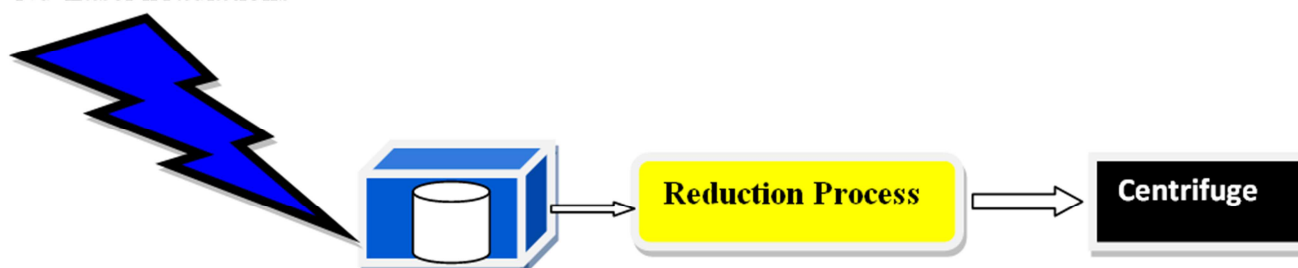
2. Experiments

2.1. Sample Preparation

Nano-graphene was prepared according to the following sequences. 2gm of sieved graphite powder with particles size $\leq$ 100 μm (Merck product) was dispersed in 50ml of Tri-chloro-acetic acid sulfonated by 75% H_2SO_3. Sonication of the dispersion process was performed via a (Wise Clean WUC-DIOH 200W, 40 kHz,) ultrasonic bath up to 60 hours with two stages of mechanical stirring 1st after 3 hrs and 2nd after 20hrs each of 1.5hrs duration. Dispersion by bath sonication provided the mechanical disruption that broke apart the graphite flakes into small pieces, which was then stabilized by the solvent system. After sonication process, the dispersion was dark grey in color and left to stand for about 10 hours to allow small aggregates to form.

To remove these aggregates and stabilize the dispersion, the top 15ml of the dispersion was taken out and consequently centrifuged for 40 minutes at $\sim$ 10,000 rpm. After this primary centrifugation, the top 20ml of the dispersion was decanted carefully by pipette, forming a homogeneous black dispersion which was retained for use.

These steps of synthesis procedures were identically repeated with only one difference each two hrs of sonication,

Nd-pulsed laser- irradiations were parallel applied for 1hr with total time = 30 hrs ($\sim$ 30 W/cm^2 for 30hrs).

No sedimentations were noticeable for the first 10 hrs that confirm graphene Oxide (GO) is relatively stable in the applied sulfonated tri-choloroacetic. Finally dimethyl hydrazine solution (60%) was added to the warmed mixture (70°C) carefully drop wise at to get graphene in highly pure state, leave solution settled for 25 hrs. Then solution has to be centrifuged in order to dispose of the thicker flakes of nano-graphene as possible.

After graphene separation yield of dried graphene 1st route$\sim$ 0.28g while 2nd route (sonication+laser irradiation) was $\sim$ 0.39 g. This result indicates that 2nd route with laser irradiationsis more efficient by 39.2%.

2.2. Nd-Laser Irradiation Source

The applied laser Nd-pulsed laser Fig. 1 has the following parameters: wavelength λ= 1.06 μm, pulsed rate η = 10^{-3} s. The graphene solution target was irradiated by dose of Nd-laser beam irradiations $\sim$ 30 W/cm^2 for 30hrs. The irradiation was carried out in air without any external heating. The energies of pulsed Nd-laser were sufficient to melthomogeneously the surface and near surface layers.

Fig. 1. *Schematic diagram shows sequences of Graphene synthesis via route 2.*

2.3. Raman Spectroscopy Measurements

The measurements of Raman spectra were carried out on the finally ground powders with Laser wavelength = 632.8 nm (He-Ne laser with power = 1mW) and laser power applied to the site of the sample = 0.4 mW with microscope objective = x 20, accumulation time = 1000 - 4000s, up to more than an hour.

2.4. Atomic Force Microscopy (AFM)

High-resolution Atomic Force microscopy (AFM) is used for testing morphological features and topological map (Veeco-di Innova Model-2009-AFM-USA). The applied mode was tapping non-contacting mode. For accurate mapping of the surface topology AFM-raw data were forwarded to the Origin-Lab version 6-USA program to visualize more accurate three dimension surface of the sample

under investigation. This process is new trend to get high resolution 3D- surface [14-16].

3. Results & Discussion

The synthesized nano-graphene flakes were investigated by both of raman spectroscopy and x-ray diffraction to prove existence of grapheme as shown in Figs. 2_a and 2_b respectively. As it clear in Fig. 2a graphene characteristic peaks (modes) appear in the zone $\sim$ 1400-1650 cm^{-1} which fully consistent with [17] while graphene oxide appears $\sim$ 1000 and $\sim$ 2600 cm^{-1}.

From Fig. 2a one can notify that original experimental raman profile is very crowded and there are many of raman modes overlapped with each other due to GO existence as clear in the refined smoothed raman profile.
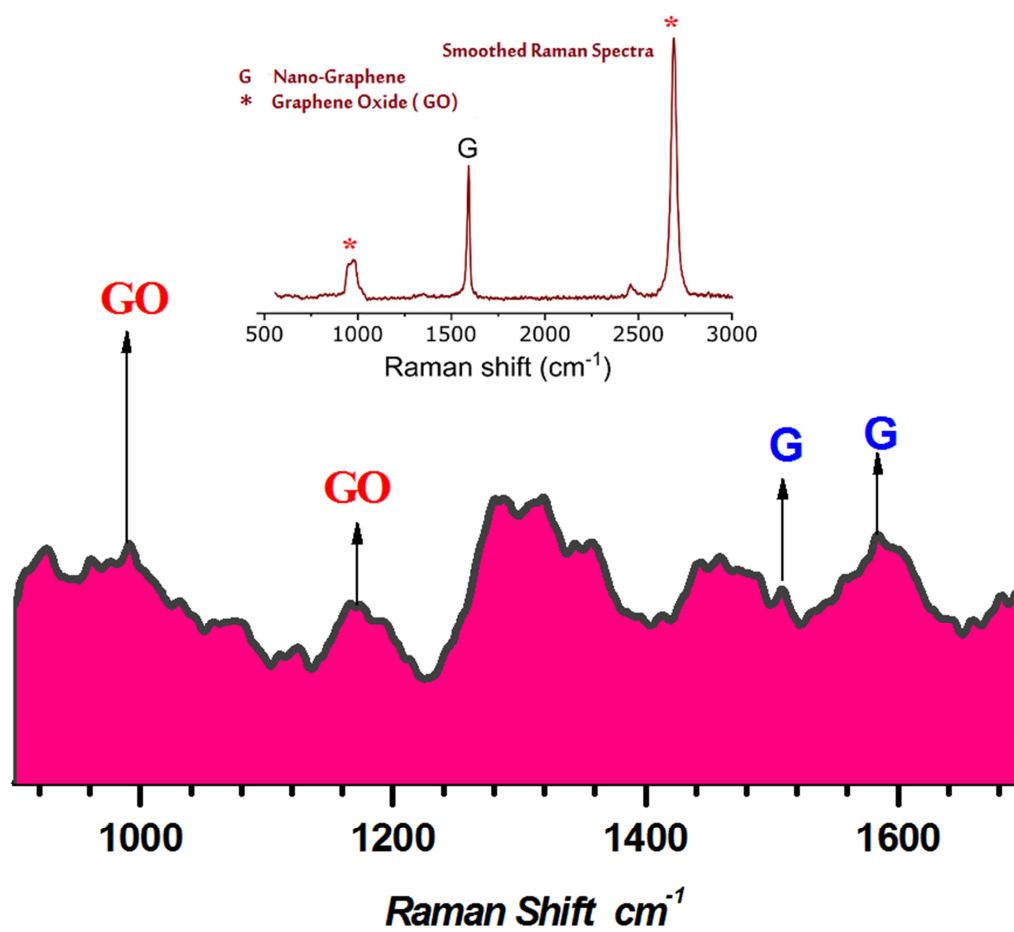
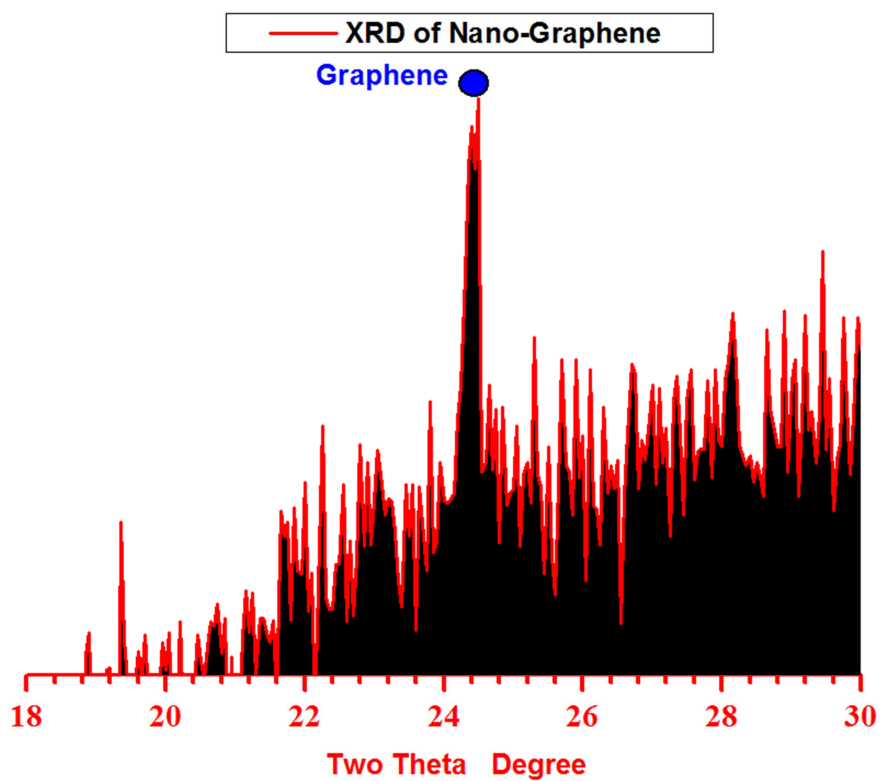**Fig. 2a.** *Raman spectra measured for ground graphene flakes.*

Fig. 2b. *X-ray diffraction pattern recorded for graphene flakes.*

Although XRD measurements is not accurate tool to identify graphene but in our case as it clear in high resolution XRD profile, it gives sharp peak at two theta ~ 24.8 which is fully consistent with literature [18]. The shift in fingerprint peak position of graphene is attributable to poly crystalline phases interference that existed together with grapheneas graphene oxide and small traces from un-reacted graphite.

To characterize nano-structural features of obtained graphene AFM measurements were made applying tapping non-contact mode as shown in Fig. 3a-c.

Fig. 3a-c shows 2D and 3D-AFM image captured for tiny scanned area (0.1x0.1 μm^2) of graphene. Fig. 3c displays honey comb structure for graphene which described in literature by author himself applying STM atomic mode [17].
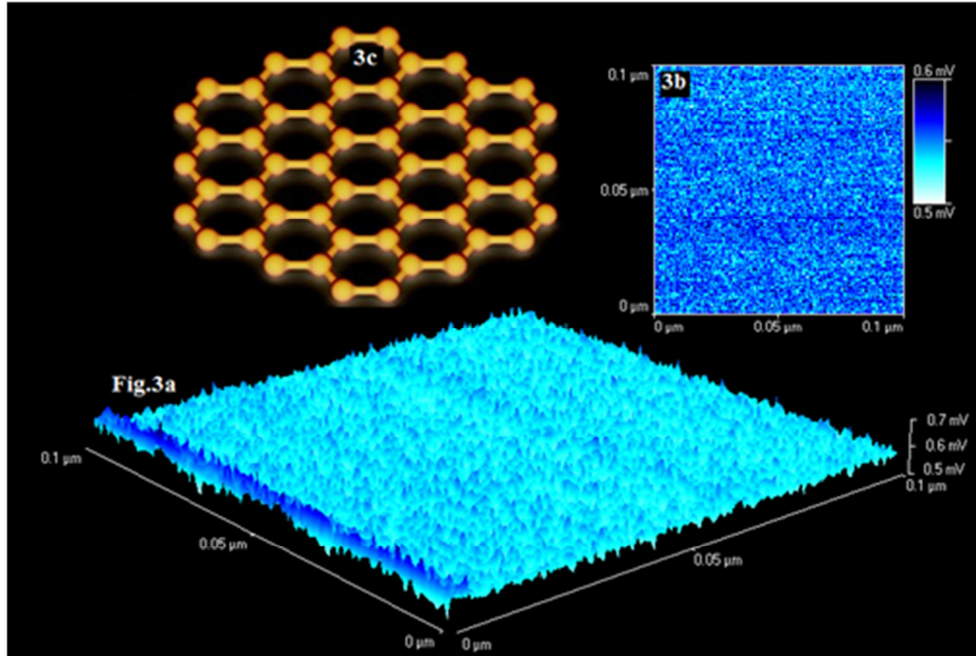

Fig. 3. *(a) 3D- image for graphene applying tapping non-contact mode. (b) 2D-AFM image for graphene applying tapping non-contact mode. (c) Honey comb structure of graphene.*
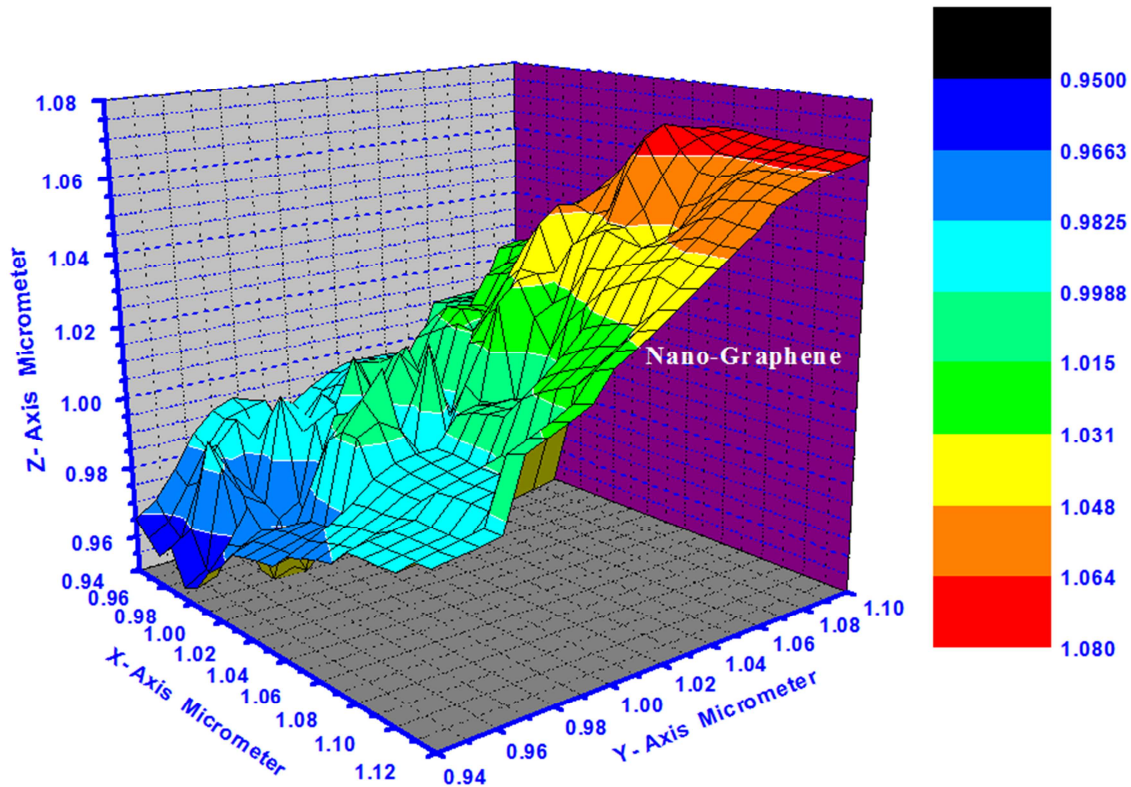

Fig. 4. *3D-AFM-visualized image for synthesized nano-graphene.*

For accurate mapping of the surface topology AFM-raw data were forwarded to the Origin-Lab version 6-USA program to visualize more accurate three dimension surface of the synthesized nano-graphene see Fig. 4. As it clear in Fig. 4 which represent very narrow 3D-scanned area with dimensional 0.16x0.16x0.16 μm. The accurate analysis of this figure one can conclude the following facts; 1[st]the maximum heights gradient ranged in between (1.065 – 1.10 μm) orange-red zones, 2nd the minimum depth gradient is ranged in between (0.96-0.995 μm) pale –dark blue zones. 3rd higher than 50% of the scanned area moderate in heights and ranged in between 0.99-1.048 μm those represented by blue-green colors. These accurate investigations interpret why graphene has huge unique exposure surface area ($\approx$2600 m^2/g) as reported in [19, 20] with different gradientson the surface topology in contrast with others carbon-based materials.

4. Conclusions

XRD analysis confirmed that, the shift occurred in fingerprint peak position at two theta ~ 24.8 of graphene is attributable to poly crystalline phases interference that existed together with grapheme as graphene oxide and small traces from un-reacted graphite. Furthermore 3D-AFM investigations answered the question why graphene has huge unique surface area and promising surface active materialin contrast with others carbon-based materials. The advanced route of application (sonication + laser irradiation) is more efficient by 39.2% than the ordinary sonication only. The energies of pulsed Nd-laser were sufficient to melthomogeneously the surface and near surface layers and as result enhance dispersed graphene to aggregate forming bigger particles.

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