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One-step and Cost-effective Conversion of Polyimide to Graphene by Utilizing a Desktop Laser

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Abstract

Herein a one-step, cost-effective, chemical-free, and versatile graphene fabrication by employing a CO_2 laser is presented. A cost-effective desktop laser, compared to expensive and bulky lasers reported in the literature, is utilized for the conversion of polyimide films to graphene. Optimization of the fabrication is enabled by the examination of laser parameters such as laser power and scanning speed. Also, various 2D pattern drawings and in-situ fabrication were realized by the Laser Draw software. Furthermore, characterization experiments such as Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD), Raman Spectroscopy, and X-Ray Photon Spectroscopy (XPS) were performed to prove the successive graphene fabrication.

Keywords: Graphene, laser scribed graphene, CO_2 laser

1. INTRODUCTION

Graphene has gained a considerable amount of attention in the last decade due to its high conductivity, super capacitive nature, enhanced mechanical properties as well as high thermal conductivity [1-3]. Hence, it has been utilized in various applications such as supercapacitors[4, 5], biosensors[6, 7], Li-ion batteries[8, 9], solar cells[10], field effect transistors [11, 12] etc. Due to the high demand for such applications, researchers investigated and developed different fabrication methods for graphene[2, 3]. The top-down approaches included mechanical exfoliation [13], chemical exfoliation[14], electrochemical exfoliation [14], and chemical synthesis [15] whereas bottom-up approaches were pyrolysis[16], epitaxial growth [17], chemical vapor deposition (CVD) [18]etc.

The first method was suggested based on the mechanical exfoliation of graphene layers from graphite by using an adhesive scotch tape [13]. The consecutive stick and pull moves on subsequent surfaces led to the deposition of a few layers of graphene which was enough to investigate the properties of the material. Even though this study was awarded by Nobel Prize in 2010, clearly a more robust, repeatable, and scalable methodology is needed for further studies. One notable strategy is the Hummers' method where graphite is chemically exfoliated to form graphene oxide in the presence of strong oxidants such as H_2SO_4, $KMnO_4$, and $NaNO_3$ and then obtained graphene oxide is treated by reducing agents such as hydrazine and

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$NaBH_4$ to form reduced graphene oxide (RGO) [14, 15].

In the case of electrochemical exfoliation, the graphite rod is connected as the working electrode (WE) and a platinum rod as the counter electrode (CE) [19]. Both electrodes are inserted into an electrolyte solution containing $(NH_4)_2SO_4$ and a direct potential of 10V is applied for 3-5 minutes yielding dispersed graphene flakes on the top of the solution [19]. Both Hummers' and electrochemical exfoliation produces graphene in powder form whereby further steps and additives are required for film fabrication.

Chemical Vapour Deposition (CVD) allows the production of either single or a few layers of graphene films. Either nickel (Ni) or copper (Cu) films are used as substrate [18]. The CVD chamber is purged with CH_4/H_2 mixture and at high temperatures CH_4 decomposes leading C atoms to dissolve in the Ni or Cu substrate [18]. When the camber is cooled, the C atoms diffuse out and join on the substrate surface to form hexagonal graphene structures [18]. Studies indicate that, in the case of Ni substrate, multiple layers of graphene are obtained whereas a single layer of graphene can be grown on Cu substrate. Despite yielding graphene films with high quality, high conductivity, and controllable thickness, CVD method requires expensive instrumentation and extensive labor which diminishes its applications in the short term.

Addressing the need of scalable and less labor-driven fabrication, Laser Scribed Graphene (LSG) or Laser Induced Graphene (LIG) was introduced whereby various organic materials can be utilized to produce graphene films via different types of lasers [20-23]. As the lasers are computer controlled, the films can be obtained in any shape, design, or pattern as desired. Hence, device fabrication can be proceeded in situ with the graphene film production. The laser reduction mechanism is based on 1) absorption of the laser light by the material and 2) breaking down of functional groups due to the high and localized energy leaving carbon atoms behind, and 3) re-coordination of C atoms to form hexagonal graphene sheets [23].

First example of LSG was presented by El-Kady and Kaner whereby the graphene oxide (GO) solution was spin coated on PET substrates and consecutively reduced by a DVD writer laser with a wavelength of 405nm [20]. The laser absorption is crucial as the necessary energy for the graphene conversion is dependent on this step. One should note that each material might absorb laser at a distinctive wavelength range of value. Hence, lasers with different wavelengths have been utilized for various materials. For instance, the graphene conversion from polyimide (PI) films were realized with the CO_2 laser which has 10.6 μm wavelength [21]. The resulting film consisted of graphene flakes packed in a highly porous film with around 30 μm thickness and was applied in supercapacitor applications. CO_2 laser was also utilized for treating lignin films to produce graphene films which were used as electrochemical biosensors for the detection of glucose, lactate, and alcohol [24]. Despite the ease of fabrication, the major drawback for LIG production is the cost of the laser which usually starts from 20.000 USD. However, there are more cost-effective versions of this laser that can be bought from Asia.

Herein, the represented study employs a desktop K40 CO_2 laser that is worth only 500 USD. To the best of our knowledge, this is the first study utilizing K40 laser for the fabrication of LIG. The fabrication parameters were investigated and as well as detailed characterization such as Scanning Electron Microscopy (SEM), X-Ray Photon Spectroscopy (XPS), X-Ray Diffraction (XRD) and Fourier-transform infrared spectroscopy (FTIR) were performed.

2. MATERIALS AND METHODS

The desktop K40 CO_2 laser engraver was purchased from Peixu Tool Store in the Aliexpress e-commerce platform. Following the acquisition, the 40W default laser was changed with a 50W CO_2 laser tube to expand its potential to cut and engrave a wider range of materials. However, one should note that the default 40W laser is also sufficient for the graphene fabrication and the instrument can be used as acquired. Adhesive free Polyimide (PI) films with 100 µm thickness was obtained from Yatiz Electrics (Istanbul/Turkey) and they were used as acquired with no additional cleaning process. The characterization experiments were performed by using; Rigaku D-max RINT 220 for XRD measurements, Phillips XL 30 SFEG for SEM measurements, SPECS XRC 1000 for XPS measurements, Renishaw inVia Reflex Raman Microscope and Spectrometer for RAMAN measurements.

3. RESULTS AND DISCUSSIONS

3.1.Graphene Fabrication

The K40 Laser engraver/cutter utilized in this study can be seen in figure 1A. The system consists of a 50W CO_2 laser, optics to transfer and focus the laser beam on the substrate, a sample stage, a laptop computer, and a software (Figure 1a-1b). These types of lasers work in two distinctive modes namely cut or engrave. For the graphene fabrication the engrave mode is utilized. The Laser DRW 3 software was utilized for the laser control and pattern design. The main parameters effecting the graphene are laser power and scan speed which can be adjusted through the software. A range of power between 10-25 % of 50W was tested and found that power with %18 (±2) was best for repeatable graphene fabrication. The laser speed was adjusted to 375 mm/s with 1000 dpi setting.

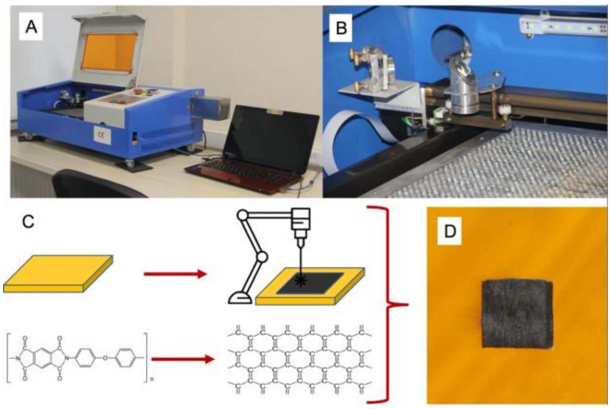

Figure 1 a) The K40 CO_2 laser system, b) Close up to optics, laser head, and sample stage c) Schematic representation of the working mechanism, d) Graphene film directly written on the PI surface.

The working mechanism of LIG is based on the absorbance of the laser light and the molecular conversions such as bond breakage due to the absorbed energy as well as the removal of certain molecules as gaseous side products and then re-arrangement of the remaining atoms [20,21]. When the laser beam reaches the surface, the energy is absorbed by the PI film and the bonds of functional groups are broken. Then, the remaining carbons come together in graphene form (Figure 1c). Indeed, the natural color of the PI is amber, whereas areas engraved with laser turn to black (Figure 1d). It is usually not possible to remove all the groups, hence a negligible amount of oxygen and hydrogen may remain as defects.

3.2.Characterization Results

Following the fabrication, obtained films were first characterized by SEM for visual inspection. Figure 2a represents the morphological difference between PI and graphene. Indeed, the PI film has a very smooth and flat surface, whereas graphene films are in foam form, extremely porous and consist of flakes with a few nanometers thickness (Figure 2c and figure 2d). These nanoflakes are packed in a foam type film which has a thickness of 30 µm (± 2µm) as it can be seen in Figure 2b. The nature of the graphene foam obtained by LIG method is proven itself to be a porous film consist of connected nanoflakes similar to the observed in the literature [21].

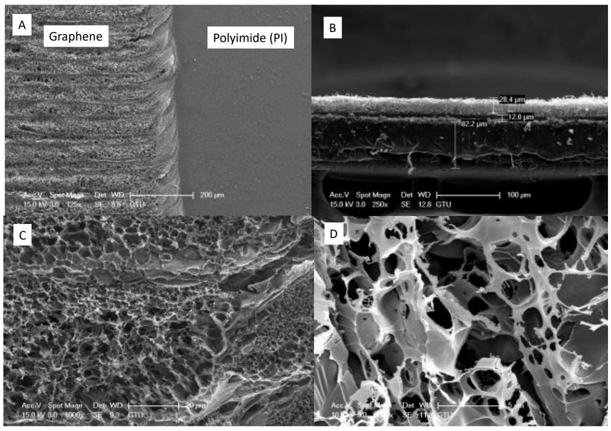

Figure 2 SEM micrographs of graphene films with magnifications of a) 125x, b) 1000x and c) 5000x, c) the cross-sectional image revealing the thickness of the graphene film

The crystallinity of the LIG was investigated by XRD (Figure3) and also elemental analysis experiments were carried out through XRD and RAMAN studies (Figure 4 and Figure 5). The XRD pattern exhibits an intense peak centered at 26.10 (2θ) indicating a high degree of graphenization with multiple layers and a small peak at 43.1 (2θ) corresponds to in-plane structure (Figure 3) [21]. The spacing between planes of the graphene was calculated to be 3.42 Å.

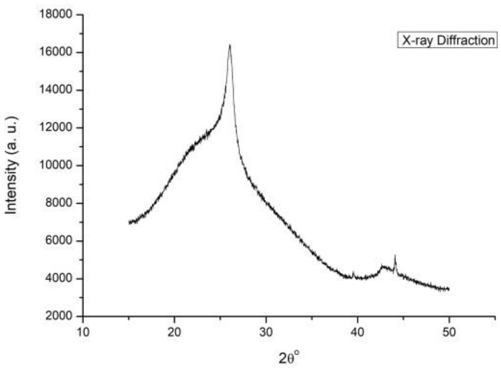

Figure 3 XRD analysis of Laser Scribed Graphene.

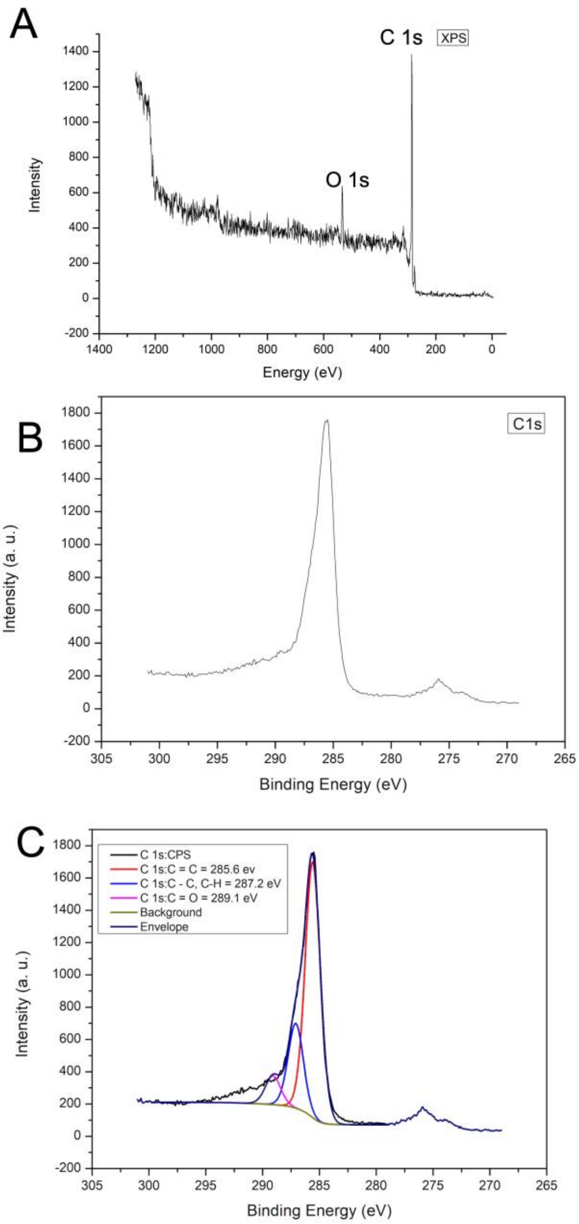

Figure 4 a) XPS Survey, b) XPS detailed C1s and c) fitted C1s analysis of the laser scribed graphene samples.

XPS survey spectrum reveals that obtained film contains mainly carbon presented at 286 eV and corresponds to sp2 carbons (C1s) and a few amounts of oxygen presented at 534 eV and corresponds to O1s (Figure 4a) in agreement with the literature values [21]. There was no peak corresponding to Nitrogen which indicates the breakage of the N-C bonds and removal of the nitrogen as a gaseous side product. The further detailed analysis on the C1s (Figure 4b and 4c) revealed that a C=C bond at 285.6 eV, C-C and C-H bonds at 287.2 eV and C=O bonds at 289 eV corresponds the existence of graphene with defects [25]. These defects make graphene more hydrophilic and hence they are desirable in the case of applications such as biosensors, liquid phase supercapacitors that performed in aqueous media [26]. The oxygen amount was found to be %17.14 and the carbon amount was %82.86 by calculating the area under each peak.

Raman spectrum of the LIG predominantly consists of three peaks which are referred to as D, G, and 2D bands (Figure5). The presence of the D band at the absence of D' band corresponds to the edges with high density due to the foamy nature of the LIG. D band is also a representation of the defects within the graphene structure which is in agreement with the XPS survey results that represents a few amount of oxygen in the LIG. The G band represents the stretching vibration of the sp2 carbon lattice. The 2D band is the secondary D band which arises from the stacking of graphene sheets. The I_D/I_G ratio has been calculated as 0.52 which also represents the high-density edges of the foamy structure.

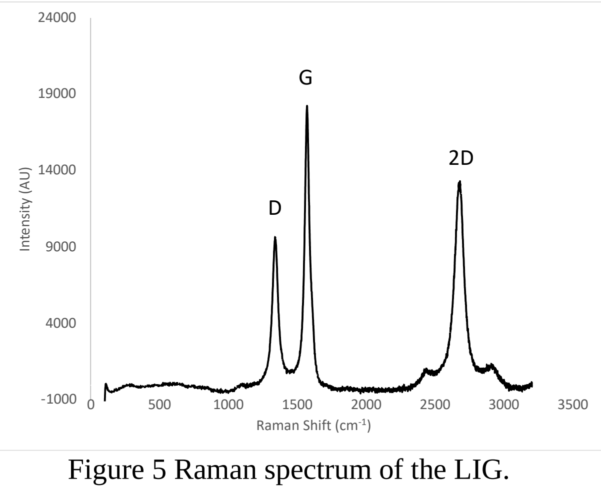

Figure 5 Raman spectrum of the LIG.

4. CONCLUSIONS

Graphene films consisting of nanoflakes were fabricated utilizing a cost-effective desktop laser. The main parameters for the successive fabrication are the applied laser power and scanning speed. Obtained films are mainly dominated by the sp2 Carbons with a few amount of oxygen corresponding to the defects on the planar structure. The proposed CO_2 laser, despite costing only 500 USD, fabricated high-quality graphene from polymer films. The proposed system can be utilized to fabricate electronic devices such as supercapacitors, biosensors, solar cells, batteries etc.

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The Declaration of Conflict of Interest/ Common Interest

No conflict of interest or common interest has been declared by the authors.

The Declaration of Ethics Committee Approval

This study does not require ethics committee permission or any special permission.

The Declaration of Research and Publication Ethics

The authors of the paper declare that they comply with the scientific, ethical and quotation rules of SAUJS in all processes of the paper and that they do not make any falsification on the data collected. In addition, they declare that Sakarya University Journal of Science and its editorial board have no responsibility for any ethical violations that may be encountered, and that this study has not been evaluated in any academic publication environment other than Sakarya University Journal of Science.

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