Photochemical reduction of carbonyl group of polyimide by 450 nm diode laser

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Abstract. In this article, we report directly patterned graphene nanoribbons by laser irradiation. The transformation of polymer into graphene nanostructure by breaking oxygen bonding and followed by graphitization of carbon atoms has been employed by using the photochemical technique. The scalable and fast growth of graphene nanoribbon was carried out by irradiating 450 nm diode laser directly onto polyimide polymer. Patterned graphene was characterized by Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR) and Field emission scanning electron microscopy (FESEM). The ability of polyimide to absorb laser light in the near-ultraviolet region contribute to the tailoring of graphene nanoribbon which reduces oxygen bonding as well as paves way for the development of optoelectronics applications.

1. Introduction
Graphene is an emerging two-dimensional carbon allotrope that has attracted tremendous research interest. The unprecedented feature of graphene including being lightweight and highly flexible with high charge carrier mobility of 200000 cm² V⁻¹ s⁻¹ [1] and Young’s modulus of ~1.0 TPa [2] has lead to various potential future applications in photonics [3], optoelectronics [4] microelectronics [5], biosensors [6] and energy [7, 8]. Graphene has been produced in many different ways including mechanically exfoliation [9] chemical and thermal reduction [10], and chemical vapour deposition [11]. Laser-induced synthesis of graphene is being carried out using CO₂ laser [12], Nd:Yag laser [13], and KrF laser [14] but the synthesis using diode laser has not been reported yet to the best of our knowledge. Laser irradiation technique applied in the fabrication of integrated graphene microstructures has attracted increasing attention due to its advantages of single-step capability, rapid material processing speed, and large scan area. In some cases, the processing of graphene can be easily achieved in free-space intense laser heating. Numerous laser-assisted methods including pulsed and continuous lasers have been developed to produce graphene. These methods involve laser-induced unzipping of carbon nanotube [15], pulsed laser deposition [16], laser-induced chemical vapor deposition [17] and laser-
induced epitaxial growth [18]. Until now, various integrated, flexible and wearable graphene-based architectures have been developed through direct growth and patterning, with laser irradiation technique for wide applications. In this study, we are investigating the fast synthesis of graphene by the photochemical reaction of polymer chain induced by laser diode irradiation highly potential for sensors, energy conversion, and optoelectronics applications.

2. Methodology
Polyimide was characterized by repeating the imide structure as a linear or heterocyclic unit. Polyimide is considered a strong synthetic polymer with astounding heat and chemical resistant. Local heating caused by laser irradiation brought local chemical/physical reactional changes in the polyimide structures. Laser irradiations broke oxygen-containing bonds of polyimide and new chemical bonds with the molecules/compounds around the local ambient environment are formed.

The transformation from polyimide to graphene via laser irradiation strategy usually follows two basic processes (i) first one is light absorption and photochemical removal of oxygen from the polyimide and (ii) structural reorganization of the newly formed, reduced carbon lattice into the planar, hexagonal, sp²-conjugated graphene structure. The experimental setup for direct patterning graphene nanoribbon is shown in figure 1. Power supply connected with diode laser was used to control the output power of the laser. The laser head was equipped with an adjustable laser focus. The focus of the laser was set at 8 cm. The polyimide tape was attached on a glass substrate. Intense laser power up to 2500 mW was applied through polyimide tape. The polyimide tape absorbed the laser light and broke the oxygen bond. The remains C atoms then rearranged themselves to form graphene nanoribbon replacing polyimide.

![Figure 1](image_url)

Figure 1. (a) Schematic diagram for laser irradiation and (b) Experimental setup for direct patterning of graphene by 450 nm diode laser.

3. Result and Discussion
Patterned graphene nanoribbon as grown by laser irradiation left a black mark on the glass substrate and are easily distinguishable by naked eyesight (figure 2). Intense laser heating left graphene with C-C bonding discernible with polyimide tape. As the polyimide tape was peeled off from substrate mechanically, the graphene remained on top of the substrate.
3.1. Electron microscopy

![FESEM images of carbon layer with different magnifications](image)

(a) ×3000 (b) ×1000

**Figure 3.** FESEM images of carbon layer with different magnifications (a) ×3000 (b) ×1000

The details of the carbon atom that formed after laser irradiation has been captured by field emission scanning electron microscope (FESEM). The image of carbon atom under FESEM as shown in figure 3.

3.2. Raman spectroscopy

Raman spectroscopy used a laser to excite molecular atom of carbon. The scattering effect by lattice vibration gives the Raman signal. It’s prior to emitting signal at 1580 cm\(^{-1}\) that indicate G band and signal at 1350 cm\(^{-1}\) of D band released by lattice vibration of carbon. The result of Raman spectroscopy for the carbon upon laser irradiation on polyimide are shown in figure 4.
3.3. Fourier Transform Infrared Spectroscopy (FTIR)
The Fourier Transform Infrared (FTIR) spectroscopy results are shown in figure 5. C=O bond lies at wavenumber between 1720 cm$^{-1}$ – 1708 cm$^{-1}$ [19]. For the C=O bond at 1775.20 cm$^{-1}$, the peak intensity after the laser irradiation was also slightly reduced. The intensity of the peak corresponding to the C=O bond reduced after the laser irradiation on polyimide polymer as shown in figure 5. For C-O bond lies around wavenumber 1225.84 cm$^{-1}$ as shown in figure 5(a), this peak totally disappeared after laser irradiation on polyimide polymer as depicted in figure 5(b). This means that the laser irradiation on polyimide broke the C-O bond on the polyimide polymer.

Figure 4. Raman spectrum of the irradiation area.
Figure 5. FTIR spectra of polyimide tape (a) before irradiation and (b) after laser irradiation.

4. Conclusion
Graphene nanoribbons have been successfully directed patterned on a substrate by using 450 nm diode laser with a power of 2500 mW. This method can be considered a fast and economical way to produce graphene. We have also studied the breaking of the chain of carbon atoms in the polymer by laser irradiation to produce graphene verified by FTIR spectroscopy results. Images of carbon atom layer by FESEM spectroscopy test support the formation of layered carbon and Raman spectra confirm the presence of sp² orbital of honeycomb carbon formation upon laser irradiation.

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