Advanced Laser Technologies

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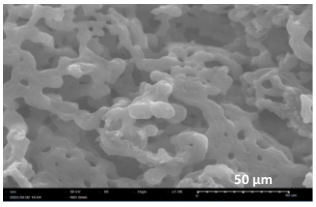
CW CO_2 Laser Induced Graphene on Biodegradable Surface

Tatsat Dwivedi[1,2], Hrithik Gupta[3], Sunita Kedia[1,2], R. C. Das[1,2] and J. Padma Nilaya* [1,2]

[1]*Laser & Plasma Technology Division, Bhabha Atomic Research Centre, (BARC), Trombay-400085, INDIA*
[2]*Homi Bhabha National Institute, Anushakti Nagar, Mumbai-400094, INDIA*
[3]*Somaiya College, Mumbai University, Mumbai-423601, INDIA*



SEM image of Coconut sample shell irradiated with CO_2 laser beam in 25 Watt and 0.9cm/sec .

ABSTRACT

Laser-induced graphenization of a surface of biodegradable substrate, viz. coconut shell, is reported. The setup involved a carbon dioxide (CO_2) laser, mechanical chopper, translation stage, and a detector for monitoring laser output power. Optimal laser fluence parameters and scan speeds were determined, which were at much variance with previous literature. Quality assessment of the graphene produced was performed using Raman spectroscopy. Scanning electron microscope images displayed varied LIG structures, including porous foam and fibrous bundles, based on the laser power employed. Additionally, XRD and sheet resistance measurements were conducted to evaluate the quality of the generated Laser-Induced Graphene (LIG).

KEYWORDS: *Laser-Induced Graphene (LIG)*

Introduction

Laser-Induced Graphene (LIG) is a versatile material used in various applications due to its exceptional properties [1,2,3,4]. It is created through a controlled, non-toxic laser irradiation process, offering advantages over the traditional chemical methods [3,4]. Any carbon precursor that can turn into amorphous carbon can be converted into graphene through laser irradiation. Amorphous carbon has a high absorption in the Infrared region and hence CO_2 laser, emitting at 10.6 µm is extensively used for this purpose. We present here the experimental results on the generation and parametric characterisation of LIG on coconut shell surface that contains high lignin content, employing an indigenous CO_2 laser system. Material properties were characterized using Raman spectroscopy, SEM, sheet resistance measurement, and XRD pattern. It is of interest to note that efficient LIG is reported here for laser parameters very different from those found in literature.

Experimental Work

The schematic diagram of the experimental set-up consisting of a in-house assembled CW-CO_2 laser operating with a gas mixture of CO_2:N_2: He :: 2:2:8 at a total pressure of ~12 mbar and capable of delivering ~80W in free running mode is shown in Fig.1. The laser was pulsed by means of a mechanical chopper at 750 Hz giving a pulse duration of 650 µsec. The fluence was increased appropriately by focusing the beam using a 10 cm f lens resulting in a spot size of ~350µm. The laser power and the scanning speed were adjusted to optimise the LIG process.

The coconut shell sample substrates, cut to the size of ~1x1 cm^2 and surface polished, were mounted on a linear translational stage and placed at the focal point of the lens. They were irradiated at different laser powers spanning 5W to 40 W at three different scan speeds (0.18cm/sec, 0.36cm/sec, 0.90cm/sec). The change in the scan speed results in a change of laser pulse overlap, that in turn is responsible for altered rise in surface temperature and efficiency of graphenisation. These irradiated samples were first characterized with Raman spectrometer for confirmation of the formation of LIG. I_D/I_G ratios (described in next section) for all the samples were compared and samples having lowest I_D/I_G value for all scanning speeds were then characterized by SEM. The laser parameters and corresponding I_D/I_G ratios are shown in Table-1. Further information about graphene formed was obtained by XRD for the best LIG sample using Cu-Kα radiation (λ = 0.154 nm) in θ-2θ geometry.

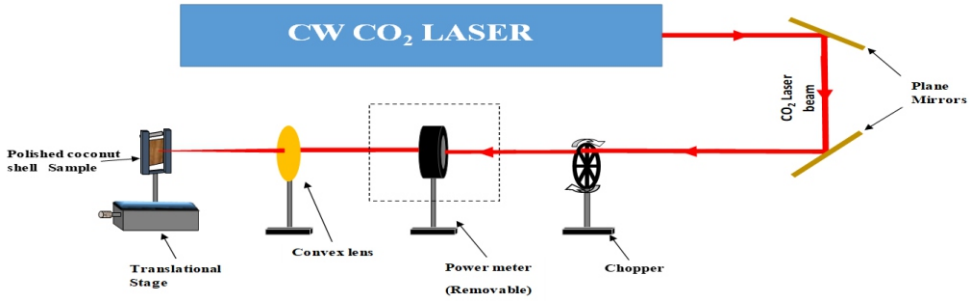


Fig.1: Schematic of Experimental set up for LIG generation using CW CO_2 laser.

*Author for Correspondence: J. Padma Nilaya
E-mail: jpnilaya@barc.gov.in

Table 1: Laser parameters and corresponding to I_D/I_G for three different scan speeds.

Scan speed	Overlapping Factor	Fluence (J/cm²)	Power	I_D/I_G
(0.9cm/s)	96.45%	7.33	5	1.07
		14.66	10	1.02
		17.59	12	0.92
		21.99	15	0.83
		26.38	18	0.69
		29.32	20	0.63
		36.65	25	0.60
		43.98	30	0.75
		51.31	35	0.89
		58.64	40	0.94
(0.36cm/s)	98.57%	7.33	5	1.09
		14.66	10	0.80
		17.59	12	0.85
		21.99	15	0.87
		26.38	18	0.91
		29.32	20	0.91
		36.65	25	0.95
		43.98	30	0.96
		51.31	35	0.98
		58.64	40	1.00
(0.18cm/s)	99.28%	7.33	5	0.87
		14.66	10	0.89
		17.59	12	0.91
		21.99	15	0.91
		26.38	18	0.92

Results & Discussion

The micro Raman spectra shown in Fig.2 revealed three conspicuous peaks: D peak (~1350 cm^{-1}) indicating defects, G peak (~1580 cm^{-1}) representing crystallinity, and 2D peak (~2700 cm^{-1}) from second-order phonons. Lower I_D/I_G indicates higher crystallinity and fewer defects. Fig.2 depicts the spectra obtained for the laser power where lowest I_D/I_G values were obtained for the 3 scan speeds, viz., 0.60 for 0.90cm/s at 25 W, 0.8 for 0.36 cm/s at 10W and 0.87 for 0.18cm/s at 5W. It is to be noted that no LIG formation is seen for the laser power below 5 Watt. Thus we find that best graphene generation occurred for sample 25 Watt at

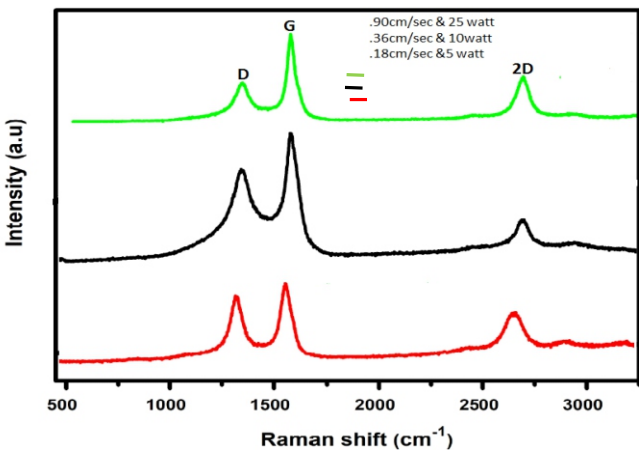


Fig.2: Raman spectra of coconut shell samples having lowest I_D/I_G for three scan speeds.

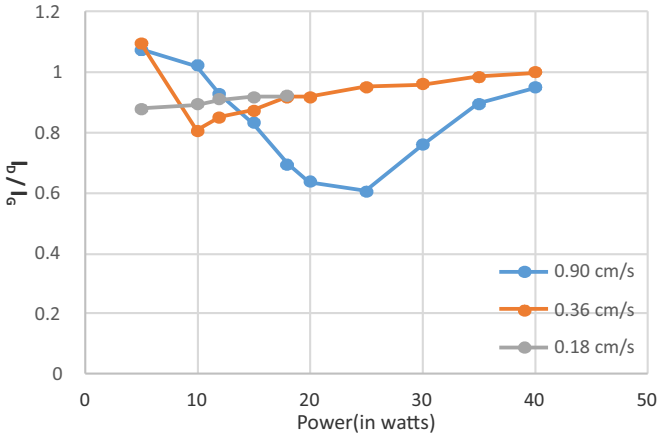


Fig.3: I_D/I_G Vs laser power.

0.90 cm/s scan speed. The ratio of I_D/I_G as a function of laser power for different scanning speeds is shown in Fig.3. It is also clear from this experiment that laser power has linear dependence on scan speed, which in accordance with the data available in literature [1]. The optimum rise in temperature required for formation of amorphous carbon that is converted into graphene by further exposure to laser pulse is governed by the laser power and duration of exposure. For a given scan speed, therefore, there exists an optimised laser power where the graphene conversion is maximum. At lower or higher incident powers these conditions are not efficiently met within the range of scan speeds employed here and hence result in poorer quality of the generated graphene. On similar lines, as the scan speed (exposure time of the substrate) increases, reduction in the exposure time of the sample surface to laser beam requires a proportionate increase in the laser power as observed experimentally. SEM images of best LIG samples for each scan speed are shown in Fig.4. For the case of low power (5Watt) the surface morphology is uniformly porous, with a structure like that of foam. This structure is known to be formed by the gas that is generated by the recombination of heteroatoms (Fig.4b). When the laser power reaches ~10Watt the fibrous clusters appear due to the overlapping domains of the adjacent scanning lines and this leads to the secondary carbonization and change of LIG structure, (Fig.4c)[5]. Most of the region remains still porous, although the size of pores are larger than those under 5Watt. When the laser power reaches to 25Watt, fiber bundles are formed and entangled with one another to form a network structure with the whole surface being covered (Fig.4d). The diameters of laser-induced fiber bundles under 25Watt are larger than those under 10Watt.

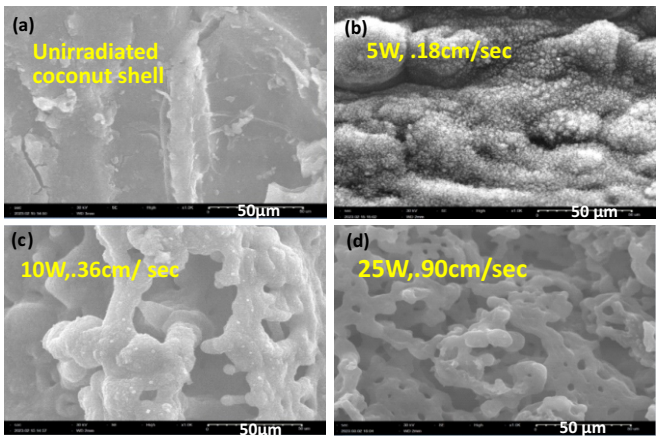


Fig.4: SEM image of Coconut sample shell irradiated with CO_2 laser beam (a) unirrdiated coconut shell (b) 5 Watt and 0.18cm/sec, (c) 10 Watt and 0.36cm/sec and (d) 25 Watt and 0.9cm/sec.

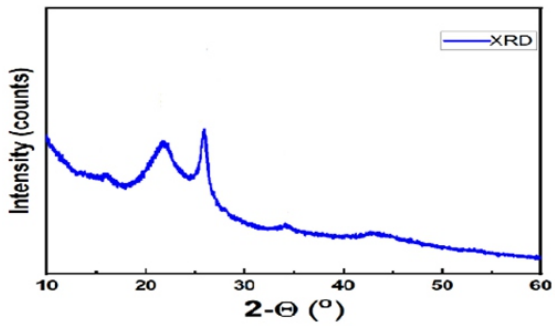


Fig.5: XRD of LIG generated from coconut shell at 25 Watt laser power & 0.90 cm/sec scan speed.

The XRD pattern of the sample irradiated with 25Watt laser power, at the scan speed of 0.9cm/s exhibited strong and sharp peaks at ~ 2θ = 26° corresponding to the (002) reflection planes of graphite (Fig.5). This indicates high degree of graphitization. It is to be noted that the peak at nearly ~2θ =22° is characteristic of coconut surface as same peak is seen on unirradiated coconut sample's XRD pattern.

The sheet resistance of the lowest I_D/I_G sample (25W, 0.9cm/sec) was also measured using four probe set-up. The sheet resistance was found to be ~ 4.6Ω/□, implying high quality of graphene formed under these experimental conditions which differ widely from that reported in literature.

Conclusion

Laser-Induced Graphene (LIG) was created on the surface of coconut shell samples using a locally assembled CO2 laser. The laser was fine tuned for fluence, pulse duration, and overlap factor. The optimal laser power for LIG formation remained fairly consistent for a given scan speed but increased linearly as the scan speed increased. The best LIG formation with I_D/I_G = 0.6 and very low sheet resistance was achieved at 650μs, 750 Hz, 25W laser pulses and a 0.90 cm/second scan speed. These laser parameters differ from those reported in previous studies. As the laser power increased, the microstructure of the LIG changed from a porous structure to fibrous bundles. This unique combination of a porous graphene surface on biodegradable substrates makes it suitable for various electronic applications including super capacitors, RFID antennae, and sensors.

Acknowledgements

The authors acknowledge the help rendered by Dr. Shovit Bhattacharya Technical Physics division BARC for XRD and sheet resistance measurement related experiments. They also acknowledge the support and encouragement extended by Head, Laser and Plasma Technology Division, BARC and Director, Beam Technology Development Group, BARC.

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