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Ultrafast light interaction with Graphene oxide aqueous solution

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***Abstract*-The effects of using ethanol as a diluting solution for ultrafast laser treated GO solutions were studied. It was found that adding 10 ml of ethanol to 1 ml rGO leads to production of smoother and thinner rGO flakes; however, the production of carbonyl and the signal due to the breathing mode of sp^2 were increased.**

I. INTRODUCTION

After several years of patenting and its discovery; Graphene has turned attention of advanced nanotechnology engineers for a wide range of applications in the nanometer scale due to its superior electronics, mechanical and optical properties.

Graphene, a 2-dimensional honeycomb structure, is composed of sp^2 bonded carbon atoms. Graphene oxide has excellent characteristics such as a highly accessible surface area, high electrical conductivity and transparency, properties which make it a promising candidate for various applications such as sensors, transparent electrodes and ultrafast electronic devices[1]. Synthesis and production of Graphene can be done in a diversity of ways as discussed in detail elsewhere [2]. In the case of the production of graphene from a Graphene Oxide (GO) solution, the key to a yield of high quality graphene sheets is getting rid of the oxygen functional groups within the solution, without causing any damage from reducing agents[3] or thermal treatment [4] which could be toxic and a lengthy process. Using short pulsed laser exposure [5, 6] is an alternative way of removing the oxygen component from a GO solution without causing any damage or giving rise to toxic products. Unlike nanosecond laser pulses, femtosecond laser pulses have shorter duration than the electron cooling time and give rise to minimal heat diffusion into the exposed material. Hence they have minimal thermal effects on the reduced graphene oxide (rGO) solution compared to reduction agents as discussed elsewhere[3]. In this paper, GO aqueous solutions were exposed to intense femtosecond laser radiation for different time intervals in the range of 0.5 hr to 6hrs. Raman spectroscopy was carried out to study the effects of exposure time on the GO properties. Surface morphology of rGO was studied using AFM.

II. EXPERIMENTAL

The aqueous GO solution (GO-H_2O; 500ml:1L, from Graphene supermarket) was exposed to pulses from a Ti: Sapphire ultrafast regenerative amplifier with a central wavelength of 800 nm, a 1 kHz repetition rate and pulse width of 100 fs at different time interval in the range of 0.5hr to 6 hrs. A 5cm parabolic mirror focuses the light to a bright filament inside the liquid, this limits the peak intensity to around 4×10^{13} W/cm^2[7].

Molecular vibration and surface morphology characterization were carried out using thin films from as-exposed GO solutions and diluted solutions (GO-H_2O:Ethanol;1ml:10mL). The thin films from both rGO solutions were fabricated using a silicon wafer substrate and the technique of spin coating, utilising a speed of 3000 rpm. The fabricated thin films were baked at 90^{o}C for 30 minutes and naturally cooled down to room temperature. However, the fabricated thin films from the diluted solution were dried at room temperature for 30 minutes. The Raman spectrum of samples was recorded using a Reinshaw micro-Raman spectrometer at an excitation wavelength of 488 nm. The atomic force microscope, AFM, (Dimension 3100 Scanning Probe Microscope) in tapping mode was employed to study the morphological properties of the rGO flakes.

III. RESULTS AND DISCUSSION

It was found that after 6hrs exposure the yellowish color of the GO solution changed to black as show in figure1.This was attributed to removal of oxygen components and further reduction in graphene oxide.

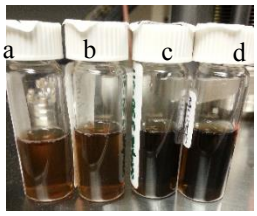

Figure 1: graphene oxide solution after exposed by ultrafast laser (λ=800nm and energy density of 4.45×10^5 mJ/cm^2) for a) 0.5hr, b) 1hr, c) 3hrs and d) 6hrs.

A. Raman Spectroscopy

Figure 2, shows the recorded Raman spectrum of as-exposed solutions (figure 2a) and diluted (figure 2b) for different exposure times ranging from 0.5 hr to 6 hr. From figure 2a, it is clear that the main Raman shift peaks of as-exposed solutions were recorded at 1348 cm^{-1} and 1593 cm^{-1} and attributed to the D and G bands. Two weaker Raman peaks were also recorded at 2688 cm^{-1} and 2931 cm^{-1} and attributed to the 2D and the D+G combination bands[8, 9]. The significant Raman peaks of the diluted GO solutions (figure 2b) were recorded at 1351 cm^{-1} and 1594cm^{-1} respectively for D and G peaks. The 2D and D+G bands were also recorded at 2680 cm^{-1} and 2924cm^{-1} [8, 9].The D peak corresponds to the breathing mode of sp^2 atoms in rings The 2D peak is the second order of D peak and the G peak is attributed to the bond stretching of all pairs of sp^2 atoms in both chains and rings[10].

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The ratio of the D and G peak intensities was calculated for both as-exposed and diluted solutions as reported in figure2. The I_D/I_G intensity ratio of as-exposed solution was increased by increasing the exposure time from 0.5hr to 6 hr, which could be attributed to production of more breathing mode of sp^2 atoms in rings and hence more defects in the reduced graphene oxide sheets. However, the I_D/I_G intensity ratio was reduced in diluted solutions. .

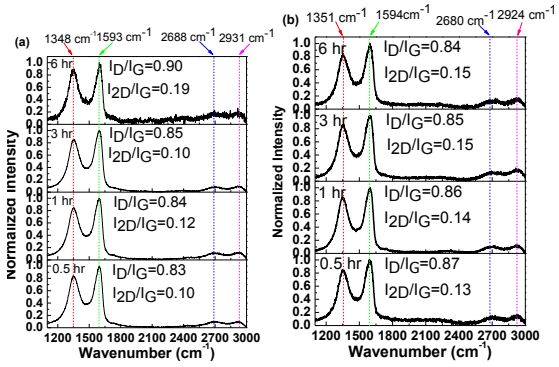

Figure 2: Recorded Raman spectrum of a) as-exposed solutions and b) diluted solutions.

B. Atomic Force Microscopy (AFM)

The surface morphology of thin films fabricated from the as-exposed and diluted solutions are shown in figure 3 and summarised in Table I. As can be seen from this table, the mean roughness and vertical height of the GO flakes of as-exposed solutions were reduced on increasing the exposure time from 0.5hr to 6 hr. The maximum and minimum average roughness was recorded as 43.9 nm and 22.8 nm respectively for exposure time of 0.5hr and 6 hrs. More reduction in the average roughness was observed on diluting the rGO solutions and the lowest roughness of 3.3 nm was measured for rGO flakes after 6hr irradiation of the GO solution. This significant reduction in average roughness and flake height is clearly shown in figure 3.

IV. Conclusion

The effects of diluting femtosecond laser treated GO solutions with ethanol were studied using Raman spectroscopy and surface morphology was investigated using AFM. It was found that although, diluting rGO with ethanol resulted in small red shift in D band, the G- and 2D-bands positions were remained fixed. It was also found that smoother and thinner GO flakes could be achieved by adding 10 ml ethanol to the exposed solution. Further investigation of the effect of ethanol addition on the optical, physical and electrical properties of the rGO solutions is currently being undertaken.

Table 1: Mean roughness and vertical height of rGO solutions at different exposure time in the range of 0.5hr to 6 hr. The exposure wavelength was 800 nm and laser energy density was 4.45×10^5mJ/cm^2.

Exposure time (hr)	Mean roughness (nm)		Vertical height (nm)	
	Undiluted sol.	Diluted sol.	Undiluted sol.	Diluted sol
0.5	41.8	6.3	200.8	8.6
1	43.9	5.2	177.4	6.6
3	29.2	4.8	83.8	5.2
6	22.8	3.3	69.4	4.4

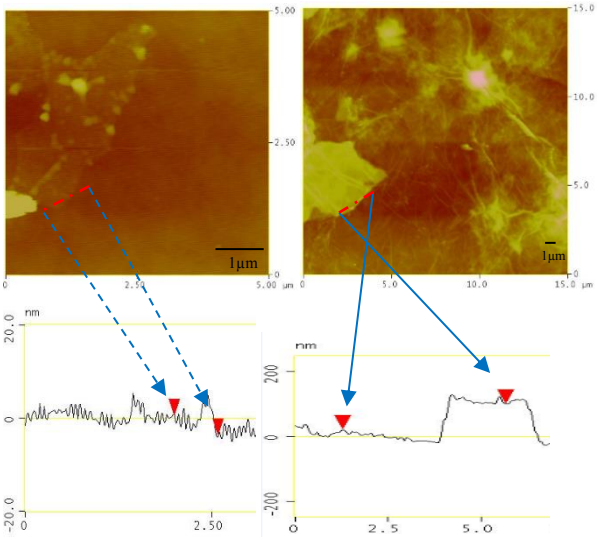

Figure 3: AFM images of diluted rGO solution (left) and as-exposed rGO solution (right). The exposure time, wavelength and laser energy density were 3 hr, 800 nm and 4.45×10^{19}W/cm^2.

V. References

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