Investigation of laser wavelength effect on optical properties of graphene oxide colloidal nanostructures prepared by pulsed laser ablation

J. S. Duque Buitrago 1*, A. M. Mesa Yandy 2, H. Riascos Landázuri 1

1 Plasma, Láser y Aplicaciones, Departamento de Física, Universidad Tecnológica de Pereira, Carrera 27 # 10 - 02, Pereira, Colombia.

2 Centro de Investigaciones Ópticas (CONICET, CIC, UNLP), Camino Centenario y 506, Manuel B. Gonnet, Buenos Aires.

*Joseduque@utp.edu.co

Abstract. In this work we prepared graphene oxide nanostructures (GONE) in a liquid environment using pulsed laser ablation technique. We used for the synthesis Nd: YAG pulsed laser operating at 1064 nm and 532 nm of wavelength, we study the effect of wavelength of the laser on the optical properties of Nanostructures (NE) synthesized. The aim was determining the optical bandgap and the characteristic peak related by bond transitions using the absorbance UV-Vis spectra. Both samples show high absorption in the ultraviolet region in the UV-Vis spectra. Using Tauc’s plot method we compute the bandgap energy for GONEs assuming indirect bandgap. In addition, we observe characteristic peak formation 1 hour after synthesized NPs at 256 nm for NPs prepared at 1064 nm and for NPs prepared at 532 nm the peak with less intensity is observed at a wavelength of 218 nm. The characteristic peak for both samples increase of intensity 24 hours after preparation.

1. Introduction

Graphene oxide (GO) has single atom layer and derived from oxidation of graphite. GO can disperse in organic and inorganic solution. GO has high potential application in optoelectronic sensor and biosensor. GO has a carboxyl group (-COO-) and hydroxyl (OH-) that they caped the nanoparticle. Graphite oxide is one of the main precursors of graphene-based materials, which are highly promising for various technological applications because of their unusual electronic properties. The graphene-related materials (graphite (Gt), graphite oxide (GtO), graphene oxide (GO) and reduced graphene oxide (rGO) exhibit unique electronic, thermal, and mechanical properties, and hold great promises in potential applications, such as nanoelectronics, conductive thin films, supercapacitors, nanosensors and nanomedicine [1- 4].

Pulsed laser ablation in a liquid is a widely recognized method of synthesizing contamination-free nanostructures especially nanoparticles [5]. In addition to the generation of NPs by laser ablation of a solid target in ambient air or a gas atmosphere, in case that the ablated target is immersed in a liquid environment the NPs are generated within the liquid that surrounds the target, resulting in the formation of a colloidal solution. The main difference between ablation in the air and in a liquid is that liquid produces stronger confinement of the expanding plasma plume, and this can greatly affect the thermodynamic and kinetic properties of the evolution of the plasma plume [5-7].
In this work, we used pulsed laser ablation (PLD) technique using a solid target of graphite plate in deionized water environment. We have studied optical and morphological characteristics of GO sensitized using UV-VIS absorbance spectroscopy and Scanning Electronic Microscopy (SEM), also the composition was done by Energy–Dispersive X–ray Spectroscopy (EDS) and infrared spectroscopy with Fourier transform (FTIR).

2. Experimental details

Graphene Oxide NPs were synthesized using a solid target of graphite plate (99.99 % of purity), in 40 ml of deionized water, using PLD technique, in Figure 1 shows laser ablation set up, two Nd: YAG laser was used, operated at its fundamental wavelength of 1064 nm and its harmonic 532 nm at 9 ns pulse duration, the repetition rate was 10 Hz and 20 Hz respectively. The energy pulse, at the moment of deposition, was 80 mJ. The samples were ablated for 45 minutes, the experimental details can be found in previous works [8].

The optical properties of the NPs were studied using UV-Vis spectrophotometer evolution 201/220 from the Thermo Scientific series of quartz cuvettes with an optical path of 1 cm. To determine vibration modes of GONE we used infrared spectroscopy by Fourier transform (FTIR), using an Agilent Carry 630 FTIR Infrared spectrometer. For the analysis of the morphology of NPs, a scanning electron microscope (SEM) was used: The X-ray energy dispersion analyzer system (EDS) (Burker, Quantax200, software: Esprit 1.9), coupled to the scanning electron microscope (MEB) TESCAN brand, model VEGA3. The drying temperature of the samples in the supports was 60 °C.

Figure 1. Laser ablation set up for nanoparticles production in a liquid environment
2.1 Band gap determination using absorption spectrum

The optical absorption was measured by a UV–vis spectrometer and the Tauc model was used to estimate optical energy band gap ($E_g$). Thus, the value of $E_g$, in electron volt, can be calculated from the parameter $\lambda_g$, where $\lambda_g$ is wavelength corresponding to the optical band gap using $E_g = 1239.83/\lambda_g$; the value of $\lambda_g$ can be extrapolating the linear of the $\left(\frac{\text{Abs}(\lambda)}{\lambda}\right)^2$ vs $1/\lambda$ curve at $\left(\frac{\text{Abs}(\lambda)}{\lambda}\right)^2 = 0$. Extrapolating the straight-line portion of the plots shown in Figure 4 (b) y 5 (b) to zero $\left(\frac{\text{Abs}(\lambda)}{\lambda}\right)^2$ gives the corresponding $E_g$ values these values are shown in table 1 and table 2 [9].

3. Results and Discussion

3.1. Morphology of Graphene Oxide NPs

Morphology of the GONE was determined from the SEM image. Regarding the shape as shown in the Figure 2 (a) nanoballs and nanowires were obtained and figure 2 (b) shows the chemical composition of GONE, the EDS pattern shows the elemental composition of GONE, where the predominant peak is carbon (C) due to the presence of graphene oxide nanostructures, and the second peak of aluminum (Al) and bromine (Br) are present due to the composition of the sample holder. The size distribution of GONEs was determined by analyzing SEM images using the Image J software from the National Institutes of Health. As shown in Figure 3 (a), the nominal size (D) of GONE (nanoballs) is given by $D = D_0 \exp(-\sigma^2) = 2.68 \mu m$, where $\sigma$ is deviation standard of size histogram as shown Figure 3 (a) and the average diameter (center of distribution) was $<D> = D_0 \exp(-\sigma^2/2) = 2.51 \mu m$ (as shown in Figure 3 (b)) and the nominal size of GO nanowire is $D = 1.89 \mu m$ y $<D> = 1.9 \mu m$, Denghu Wei et al [2013] reported that this pattern is according to previous structures mentioned [10, 11].

Figure 2 (a) GONEs SEM image ($\lambda$ =532 nm)  
Figure 2 (b) GONEs EDS
3.2. Composition of graphene oxide

To study the structural changes, the samples were analyzed by FTIR spectroscopy. In Figure 4 the spectrum obtained from the GO is shown for GONE synthesized at 532 nm. In Figure 4 the infrared spectrum of graphene oxide illustrates the presence of a wideband, with a wave number of 3414.266 cm\(^{-1}\), which corresponds to the stretching vibrations of the hydroxyl groups (O-H). The peak that appears at 1705.088 cm\(^{-1}\), corresponds to the stretching vibrations of carbonyl / carboxyl groups (C = O). The band at 1421.042 cm\(^{-1}\) can be attributed to the C-O stretch vibration of the carboxyl group. Finally, the peak located at 1222.473 cm\(^{-1}\) is assigned to the stretching vibration of the functionality (C-O) [12-14].

![Figure 3 (a) Histogram GONEs - nanoballs](image1)

![Figure 3 (b) Histogram GONEs - nanowire](image2)

![Figure 4 FTIR Spectra of GONE synthetized by laser ablation](image3)
3.3. UV-Vis results

In Figure 5 (a) and 6 (a) the absorbance UV-VIS spectra of the GONEs are observed for synthesized with the two wavelengths (1064 nm and 532 nm) and the positions of the characteristic peak for both cases are shown in tables 1 and 2. From the figures, it is observed that the intensity of the absorbance in the case of the GONEs synthesized with the wavelength of 1064 nm decreased 78 days after the synthesis, and in the case of the GONEs with \( \lambda = 532 \) nm the absorbance intensity was increasing as the time elapses since the synthesis. It is also observed that the principal peak presents red shift with respect to the other wavelength, in the first case a small displacement of 7 nm and in the second case a greater shift of 40 nm is observed, this can be due to formation of wires and clusters after the synthesis. In UV-Vis absorption results the samples show the typical peak at about 250 nm related to \( \pi-\pi^* \) transitions of the aromatic C–C bond and the peak at about 300 nm correspond to \( n-\pi^* \) of the C=O bond transition. Similar results were also obtained by Zafer et. al [2015] [15].

The \( E_g \) of GONEs, using the Tauc plot was calculated for wavelengths 1064 nm and 532 nm as shown in Figure 5 (b) and 6 (b) respectively. The \( E_g \) values obtained are shown in tables 3 and 4. In Figure 5 (b) corresponding to the GONEs synthesized with 1064 nm the \( E_g \) remained very stable, it is evidenced both in the figure and in Table 3. In Figure 6 (b) for the GONEs synthesized with 532 nm the \( E_g \) up the 96 hours were increased and after 78 days of synthesized decreased to 4.29 eV (Table 4) also there is an abrupt shift of the curve.
4. Conclusions

In this work synthesis of GONE was carried out. UV-VIS was used to study the optical properties, observing the characteristics of the absorbance over time. It was possible to calculate the energy of the bandgap based on the Tauc plot model using the absorbance response.

In the absorbance spectra was observed that at 1064 nm, the absorbance decreased as the time elapsed and the $E_g$ increased but for the case of the NE synthesized at 532 nm, the absorbance increased and the $E_g$ decreased, and did not present to shift. It is also observed that for the NPs deposited for 96 h, the $E_g$ was the same for the two wavelengths, indicating the samples stability.

EDS and FTIR results show the composition of GONE with the different characteristic bands and SEM image show that the morphological GONE are in the form of nanoballs and nanowires, the size of the nanoballs was determined to be 2.68 $\mu$m and for the nanowires 1.89 $\mu$m.

5. References

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