

# Influence of the per pulse laser fluence on the optical properties of carbon nanoparticles synthesized by laser ablation of solids in liquids

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## ABSTRACT

In this work we present experimental results on the optical characterization of carbon-nanoparticles (CNPs) synthesized by the laser ablation of solids in liquids technique (LASL). A pulsed Nd-YAG laser, a graphite disk and acetone were used in the laser ablation experiments. The per pulse laser fluence was varied, while all the other irradiation parameters (irradiation time, repetition rate, etc.) were kept constant. Both the graphite target and the obtained CNPs were characterized by Raman micro-spectroscopy. The colloidal solutions were characterized by UV-vis and photoluminescence (PL) spectroscopies. Additionally, the CNPs were also characterized by TEM and HRTEM. Our results show that spherical nanoparticles in the range of 4–20 nm in diameter were obtained. UV-vis and PL results for the obtained CNPs colloidal solutions showed that the optical absorption and PL intensity are dependent on the per pulse laser fluence. We also found that the PL spectral emission of the CNPs can be tuned from blue to yellow by varying the excitation wavelength.

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## 1. Introduction

Carbon-based nanomaterials with different structural and physical properties for diverse applications have been fruitfully synthesized through many different techniques [1,2]. For instance, carbon nanotubes have been produced using arc-evaporation [3] and through the confined combustion of aromatic compounds [1,4]. In the case of graphene it has been synthesized through chemical vapor deposition or epitaxial growth, and alternatively by micromechanical exfoliation of graphite and some other methods [1,5]. Novel carbon nanoparticles called carbon dots due

to the fact that its optical properties depend on size, in an analogous way to quantum dots, have been synthesized by arc discharge soot or electrochemical shocking [6,7]. A new route for the synthesis of nanostructured materials in solution known as laser ablation of solids in liquids (LASL) technique has been recently reported as a novel, easy and green method to produce nanomaterials of different precursor materials [8,9]. The LASL technique consists basically the synthesis of nanomaterials during the interaction of laser pulses with solid targets immersed in liquid environments. This technique is suitable for controlling many different parameters such as the solvent and solid target features and laser irradiation parameters (irradiation time, repetition rate, pulse duration, wavelength among others). The growth mechanism of the nanomaterials obtained by this technique still remains not very well-understood, demanding the continuous work on this research topic from both, theoretical and experimental points of view in order to have a better control of the final optical and structural properties of the nanomaterials produced through this route of synthesis [8–11].

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The LASL technique has been used to produce for instance, metallic nanoparticles (Au, Ag and copper [12,13]), semi-conductors (ZnO, CdTe [14,15]), and others. There does not exist many reports in the literature about the synthesis of carbon nanostructures by using LASL. Some of those include the production of amorphous carbon nanoparticles [16,17], nanodiamonds [17,18] and photoluminescent (PL) graphene oxide [19], all of them in aqueous solution and under similar laser irradiation parameters. The synthesis of multi-wall carbon nanoparticles and onion like carbons in deionized water has also recently been reported [20], with the particularity that the synthesis was carried out by using picosecond pulses at high repetition rate (kHz), while in other cases nanosecond pulses at low repetition rate (Hz) were used. Some other structures like carbon nitride nanocrystals in liquid ammonia [21] and onion-like carbon-encapsulated cobalt carbide core/shell nanoparticles in acetone [22] have also been obtained using nanosecond laser pulses. The LASL technique has been likewise reported to be an efficient technique to produce graphene in liquid nitrogen [23] or for the obtaining of dispersed in ethanol carbon nanoparticles with blue-green PL emission [24] or dimethylformamide [25]. Carbon dot-like nanoparticles suspended in deionized water have been also obtained through this technique using an UV laser for its production. These carbon dots have attracted special attention no matter that no PL emission is observed after its synthesis. However, an activation/functionalization process enables light emission in these carbon dots on a broad band centered at 430 nm [26] or 490 nm [27].

In this work we report the synthesis of carbon nanoparticles (CNPs) dispersed in acetone through the LASL technique. We study the dependence of the optical properties of these CNP colloidal solutions on the per pulse laser fluence. For the synthesis of these CNPs, all the irradiation parameters were kept constant except the per pulse laser fluence, which was varied in the range of 0.17–1.0 J/cm<sup>2</sup>. UV–vis and photoluminescence (PL) spectroscopies were used to optically characterize the colloidal solutions. In addition, Raman spectroscopy and transmission electron microscopy (TEM) were used to characterize both the structure and morphology of the CNPs. Results showed that the LASL technique is an efficient route of synthesis to obtain CNPs with good PL response tunable upon the excitation wavelength.

## 2. Experimental

### 2.1. Synthesis of the CNPs colloidal solutions

The colloidal solutions of CNPs were synthesized by using a graphite target and acetone as liquid medium (Sigma-Aldrich, Co.). The experimental setup used in the laser ablation experiments is shown in Fig. 1. Nanosecond (ns) laser pulses ( $7 \pm 2$  ns pulse duration) from a Nd:YAG laser (Minilite II, Continuum) were used to ablate the graphite target (a disk of 2.54 cm  $\times$  0.375 cm, 99.999% pure, Kurt J. Lesker Co.). The laser was operated in its fundamental emission wavelength (1064 nm) at 15 Hz repetition rate. The per pulse laser fluence ( $F$ ) was varied by adjusting the per pulse energy ( $E$ ), and keeping the laser beam cross section on target ( $A=0.03$  cm<sup>2</sup>) constant. Five CNPs colloidal solutions were prepared at the following per pulse laser fluences: 0.17, 0.42, 0.70, 0.90 and 1.0 J/cm<sup>2</sup>. The on target irradiation time was set to 180 s for all the prepared CNP solutions.

### 2.2. Sample characterization

Both the graphite target and the CNPs were characterized by Raman microspectroscopy. A microRaman (LabRama HR-800 of Jobin-Yvon-Horiba) system equipped with a He–Ne ( $\lambda=632.8$  nm)

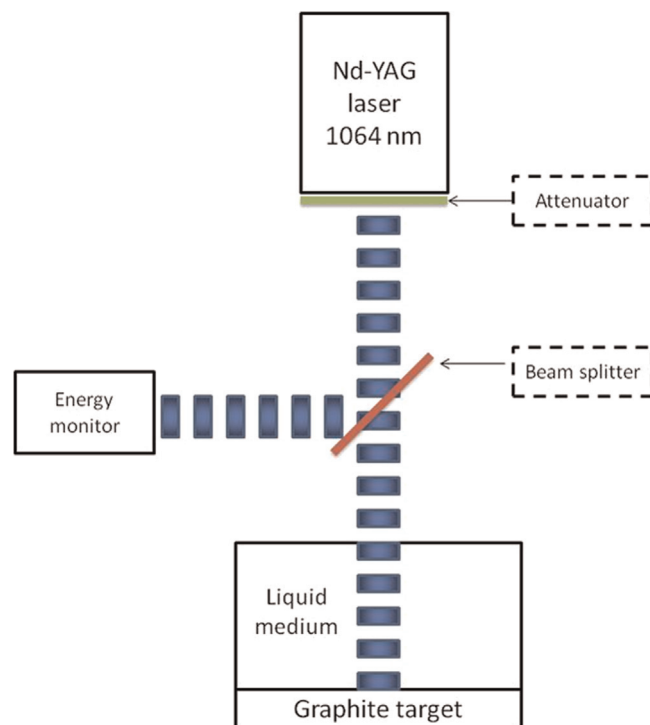


Fig. 1. Experimental setup for the laser ablation of solids in liquids technique.

laser and an optical microscope (Olympus, BX-41) was used. An objective lens of 50 $\times$  was used to focus down the laser beam, with 0.5 mW laser power on the sample. The CNPs sample was prepared by drying at room temperature some drops of the colloidal solution on a silicon wafer. The Raman spectra are captured over 10 acquisitions of 60 s each.

The optical absorption spectra of the colloidal solutions were taken using a double beam spectrometer (Lambda7 Perkin-Elmer) from 330 to 900 nm. A quartz cuvette with an optical path length of 10 mm was used for the optical characterization. For reference purposes, the acetone absorption spectrum was recorded. The photoluminescence characterization was carried out using a spectrophotometer (Jobin-Yvon-Horiba, Fluoromax-p), exciting the samples at various wavelengths. The PL spectrum of the quartz cell filled with acetone was also recorded for the sake of reference. The excitation and emission spectra of all samples were then collected. All the experiments were performed at environmental (25 °C and 1 atm pressure) conditions without any special monitoring or control.

The samples for transmission electron microscopy (TEM) characterization were prepared on Cu grids coated with carbon. Evaporation of a drop of the colloidal solution placed on the grid leaves behind the CNPs. The TEM and HRTEM measurements were both carried out using a JEOL 2010 transmission electron microscope, at an accelerating voltage of 200 kV.

## 3. Results and discussion

On the structural characterization side both the carbon target and the CNPs were analyzed by microRaman spectroscopy. As it can be seen from Fig. 2(a and b), the Raman spectrum (Fig. 2a) for graphite presents Raman peaks in the 1000–3500 cm<sup>-1</sup> range. It is well known that within this range the graphite is characterized by the D, G and D' peaks located at 1335, 1583 and 2667 cm<sup>-1</sup>, respectively. For the case of the CNPs, the Raman spectrum shows the presence of the D and G bands (see Fig. 2b). This spectrum was

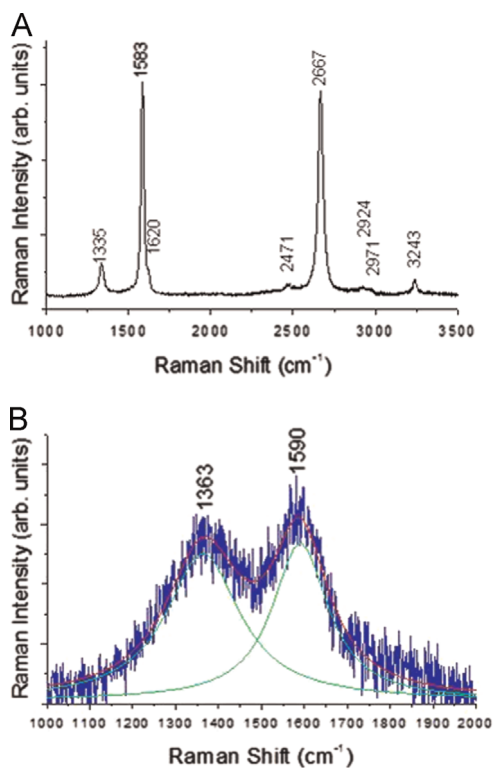


Fig. 2. Raman spectra (a) graphite target, (b) CNPs.

Table 1

Parameters for graphite and CNPs obtained from the fitting applied to Raman spectra.

Bands	Raman frequency ( $\text{cm}^{-1}$ )	FWHM	Intensity	$I_D/I_G$
Graphite target				
D	1335	32	2.1	0.15
G	1583	21	14	
CNPs				
D	1363	209	12.7	0.87
G	1590	157	14.5	

fitted using two Lorentzian curves; the D and G bands appear at 1363 and 1590  $\text{cm}^{-1}$ . Some useful parameters extracted from fitted Raman spectra (not showed in here) of Graphite and the CNPs (Fig. 2b) are listed in Table 1. It must be noted that the D and G peaks for the CNPs shifted towards higher Raman frequencies as compared to the peaks location of graphite. This is in good agreement with Raman studies reported by Ferrari et al. for graphite and NC-graphite [28]. The FWHM of the D and G bands is significantly wider for the CNPs than those for the graphite peaks. This effect is attributed to defects and disorder in the CNPs due to a low crystallinity in comparison to the crystalline graphite target [28]. Al-Hamaoy et al. have reported that the  $I_D/I_G$  ratio falls between 0.90 and 0.99 for CNPs obtained by the laser ablation of solids in liquids technique [20]. Our results produce a  $I_D/I_G$  ratio of 0.87 for the CNPs and 0.15 for the graphite target, therefore it is in good agreement with what Al-Hamaoy et al. reported.

Fig. 3 shows the optical absorption spectra for the CNPs colloidal solutions obtained at the selected per pulse laser fluences. The black line spectrum corresponds to the acetone reference. One can easily see that within the UV–vis–NIR range acetone presents weak absorption at 665 nm and 890 nm. For the colloidal solutions the absorbance increases over a wider wavelength range with

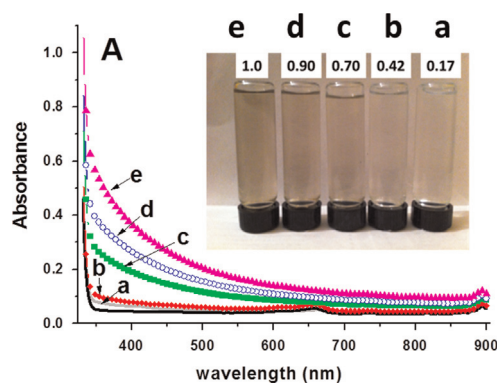


Fig. 3. Absorbance spectra of the CNPs colloidal solutions at different per pulse laser fluence. In the inset, a photograph of the CNPs colloidal solutions is showed.

increasing per pulse laser fluence. These results indicate that the per pulse laser fluence leads to modify the size and concentration of CNPs in the colloidal solution. Increasing the incident laser per pulse fluence gives place by laser induced fragmentation to an increasing density of smaller nanoparticles. Then, for colloids obtained at the higher per pulse fluences we see that its absorbance increases through a larger wavelength range. As it can be seen in the inset of Fig. 3, homogenous colloidal solutions were obtained. The CNPs solutions have shown very good stability for over a year since the CNPs were first synthesized, within this period of time no agglomeration was at all observed.

Fig. 4 summarizes the results of the photoluminescence (PL) characterization of the CNPs colloidal solutions. Fig. 4A shows the PL emission of the CNPs solutions excited at 369 nm and Fig. 4B corresponds to the Gaussian fit of the PL spectrum of the sample obtained with 1.0  $\text{J}/\text{cm}^2$  per pulse fluence. All the spectra were taken within the 375–700 nm range. The reference PL spectrum

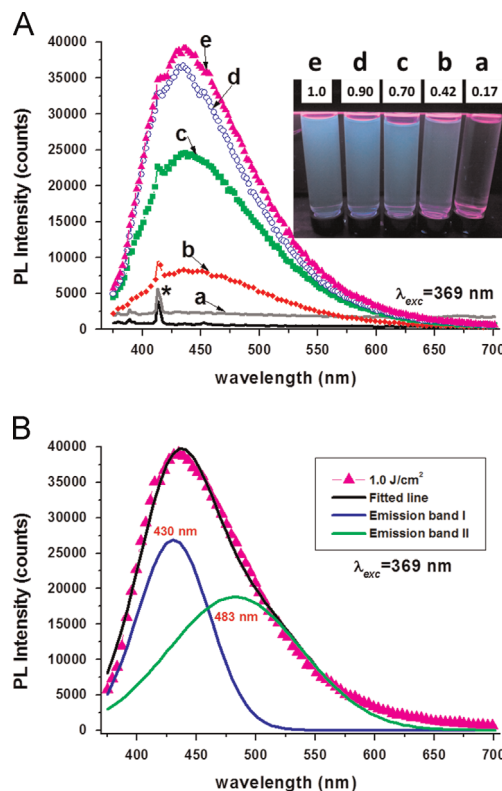


Fig. 4. (A) PL spectra of the CNP colloidal solutions obtained at different per pulse laser fluences (inset, photograph of CNPs solutions under UV illumination). (B) Gaussian fitting of the PL spectrum for the sample obtained at 1.0  $\text{J}/\text{cm}^2$ .

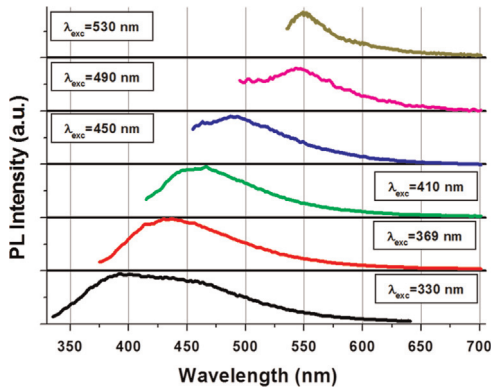


Fig. 5. PL spectra of CNPs colloidal solutions by exciting at various wavelengths.

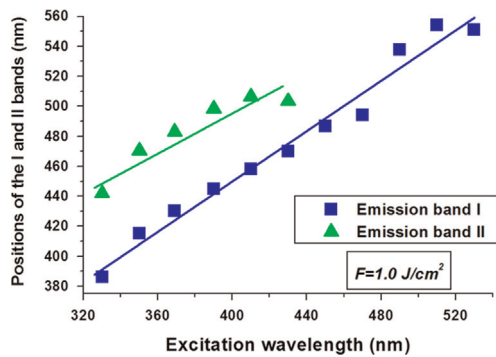


Fig. 6. Spectral position of the PL emission bands (I and II) as a function of excitation wavelength.

for the pure acetone is included in this figure (solid black line). As one can see from Fig. 4A, PL spectra of the CNPs colloidal solutions are constituted by a broad band emission ranging from

approximately 390 to 600 nm and centered at 440 nm. It is clear from the results that CNPs produced at the lower per pulse laser fluence ( $0.17 \text{ J/cm}^2$ ), either have no PL emission at all or its PL emission is very weak such that it is not detectable by the spectrometer detector. The PL measurements produce very similar spectra for the lower per pulse laser fluence CNPs colloidal solution and the acetone one. It must be noted that the peak appearing at around 413 nm (identified with an asterisk in the spectra) corresponds to the peak emission of the spectrophotometer lamp; therefore it does not belong to the PL contribution of the CNPs solution. The inset in Fig. 4A shows a photograph of the CNPs solutions under UV (369 nm) illumination. A blue-green emission is observed whose intensity increases for colloidal solutions obtained at increasing per pulse laser fluence. This is a good indication that the per pulse laser fluence can be used during the CNPs production by LASL to control the CNPs concentration in the colloidal solution and hence the PL response. From Fig. 4B it can be seen that the PL spectrum is composed mainly by two emission bands centered at 430 nm (band I) and 483 nm (band II). The emission band is tied to the optical resonance (absorption) which for nanoparticles is closely related to its size and geometry. Although we have single geometry spherical nanoparticles, it is clear from our results (see Fig. 7) that we have a size distribution dominated by the 10–12 nm diameter carbon nanoparticles, but we also have particles as small as 4 nm and as large as 20 nm. Therefore, it might be expected to see more than one emission band contributing to the photoluminescent signal. One of the bands will be narrower than the other one since the size distribution peaks are around 10–12 nm in diameter size.

Fig. 5 shows the PL spectra for the CNPs colloidal solutions synthesized at  $1.0 \text{ J/cm}^2$ . This colloidal solution was excited at the following wavelengths: 330, 369, 410, 450, 490 and 530 nm. It is clear how the emission band is shifted towards the red side as the excitation wavelength goes from short to longer ones. In Fig. 6 the center wavelengths of the two emission bands (I and II) are plotted as a function of the excitation wavelength. From these results, it is

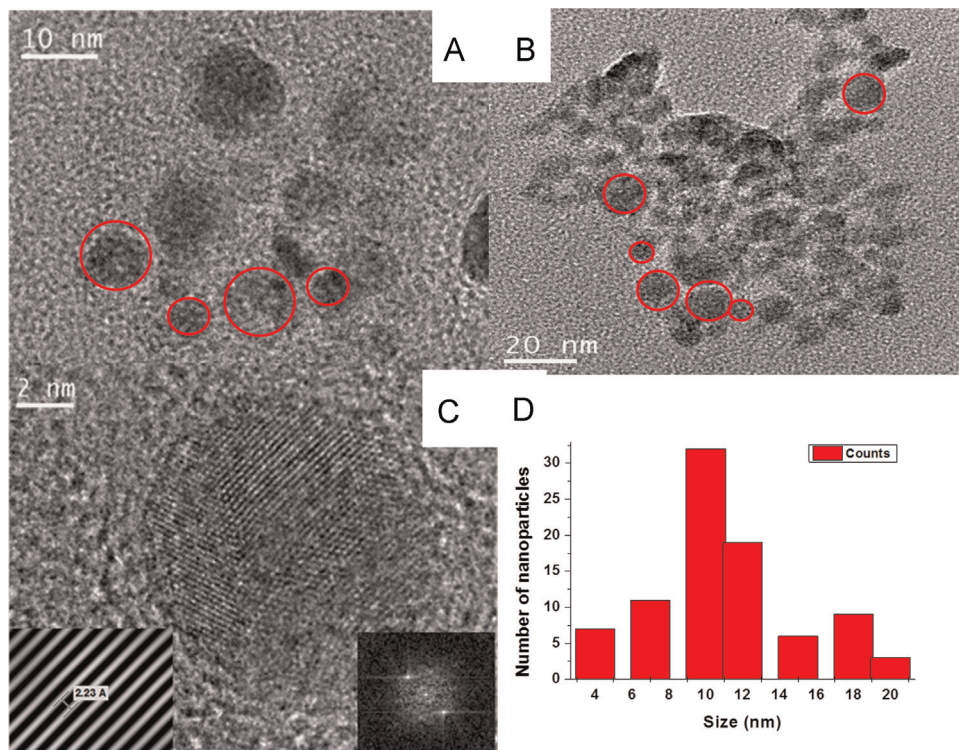


Fig. 7. (A,B) TEM micrographs of the CNPs obtained at  $1.0 \text{ J/cm}^2$  per pulse laser fluence. (C) HR-TEM of a Carbon nanoparticle. (D) Histogram shows the CNPs size distribution.

clear that the PL emission can be tuned from blue to yellow color. This effect has been previously reported for CNPs obtained using the same technique by Thongpool et al. and Li et al. [24,25,29]. Tunability of color emission of carbon nanostructures is not a new result; it has been also reported in those carbon-based nanomaterials produced through chemical methods [30]. However, as it can be explained here that the goal of the present work is to show that the CNPs can be produced in a very simple and fast way as compared to those chemical routes, where it is necessary to use many different chemical reactants, besides a long time of reaction and purification (several hours); the LASL technique can be considered as an efficient technique to produce CNPs in colloidal solutions with tunable PL properties.

Fig. 7 shows TEM (A, B) and HRTEM (C) micrographs of the CNPs obtained at  $1.0 \text{ J/cm}^2$ , as well as (D) a histogram of the CNPs size distribution. The carbon nanostructures are quasi-spherical as shown in micrographs Fig. 7(A–C), the CNPs sizes range from 4 to 20 nm, and the size distribution peaks at the 10–12 nm diameters. In the HRTEM micrograph Fig. 7(C), a spherical CNP with size of around 10 nm is observed. The insets in micrographs Fig. 7 (C) were obtained by using the Fast Fourier Transform (FFT) technique. This allows us to determine the interplanar distance which is  $2.23 \text{ \AA}$  corresponding to the cell parameter of the CNP.

#### 4. Conclusions

We have successfully reported synthesis by LASL close to spherical CNPs. Our results show that using ns laser pulses at  $1064 \text{ nm}$ , at varying per pulse laser fluence and low repetition rate ( $15 \text{ Hz}$ ) is suitable for producing CNPs with PL features. Raman, UV–vis and PL spectroscopies revealed the structural, optical and emission properties of the LASL obtained CNPs. TEM and HRTEM allowed determining both the size distribution and shape of the CNPs, and to gain insight into the characteristic atomic planes for carbon based NPs. Our study shows very clearly that the PL emission intensity i.e., the concentration of CNPs in the colloidal solutions, depends on the per pulse laser fluence used during the synthesis. Another finding shows that the PL emission wavelength can be tuned across the blue–yellow region by varying the excitation wavelength. This result agrees well with a previous report in the literature. The work presented and discussed here confirms LASL as an easy, “green”, fast and efficient technique for the synthesis of photoluminescent CNPs, being another route of synthesis to produce carbon-based nanomaterials with tunable photoluminescent properties. These CNPs in colloidal solutions have wide potential application in biomedicine, for marking purposes thanks to its good PL properties.

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