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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.

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]), semiconductors (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-encapsuled 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 dimethyformamide [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^2. UV–vis and photoluminiscence (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 ± 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 repletion 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^2) 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^2. 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 (λ=632.8 nm) 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.

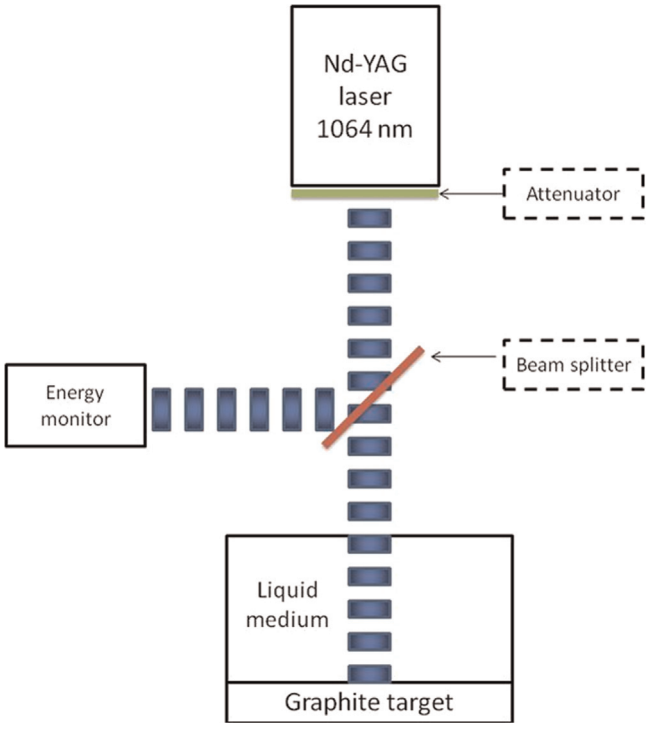

Fig. 1. Experimental setup for the laser ablation of solids in liquids technique.

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^{-1} 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^{-1}, 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