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Optical properties of carbon nanostructures produced by laser irradiation on chemically modified multi-walled carbon nanotubes

Enrique Vigueras Santiago [a], Susana Hernández López [a], Marco A. Camacho López [a], Delfino Reyes Contreras [b], Rurik Farías-Mancilla [c], Sergio G. Flores-Gallardo [d], Claudia A. Hernández-Escobar [d], E. Armando Zaragoza-Contreras [d,*]

[a] Laboratorio de Investigación y Desarrollo de Materiales Avanzados, Facultad de Química, Universidad Autónoma del Estado de México, Campus Rosedal, Km 14.5 Carretera Toluca Atlacomulco, San Cayetano de Morelos, Toluca C.P. 50925, Mexico
[b] Department of Physics and Electrical Engineering, University of North Texas, Denton, TX, USA
[c] Laboratorio de Investigación y Desarrollo de Materiales Avanzados (LIDMA), Facultad de Química, Universidad Autónoma del Estado de México, Paseo Colón esquina Paseo Tollocan, Toluca Estado de México CP50000, México
[d] Department of Chemical Engineering and Materials, Centro de Investigación en Materiales Avanzados, S.C. Chihuahua, Chih., México

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ABSTRACT

This research focused on the nanosecond (Nd: YAG-1064 nm) laser pulse effect on the optical and morphological properties of chemically modified multi-walled carbon nanotubes (MWCNT). Two suspensions of MWCNT in tetrahydrofuran (THF) were prepared, one was submitted to laser pulses for 10 min while the other (blank) was only mechanically homogenized during the same time. Following the laser irradiation, the suspension acquired a yellow-amber color, in contrast to the black translucent appearance of the blank. UV-*vis* spectroscopy confirmed this observation, showing the blank a higher absorption. Additionally, photoluminescence measurements exhibited a broad blue-green emission band both in the blank and irradiated suspension when excited at 369 nm, showing the blank a lower intensity. However, a modification in the excitation wavelength produced a violet to green tuning in the irradiated suspension, which did not occur in the blank. Lastly, the electron microscopy analysis of the treated nanotubes showed the abundant formation of amorphous carbon, nanocages, and nanotube unzipping, exhibiting the intense surface modification produced by the laser pulse. Nanotube surface modification and the coexistence with the new carbon nanostructures were considered as the conductive conditions for optical properties modification.

1. Introduction

Nanostructured materials display unexpected and unusual properties not observed in the macroscopic scale; for example, plasmon resonance [1], tunable light emission [2], or biocompatibility [3]. Generally, nanomaterials properties can be controlled by the synthesis route. Consequently, several chemical, biological, and physical methods of synthesis have been successfully implemented; however, nowadays the demand of nanomaterials for diverse applications is still an important research challenge [4]. Nanomaterials production through physical techniques, primarily those assisted by laser pulses, has gained great attention in the last decades due to its purity (no need for additives) and speed, and because nanomaterials from almost any source are produced [5–8]. One of these routes involves laser pulse incidence on solid targets confined in a liquid. Here, the pulse produce ablation, that is, material detachment (ions, clusters, etc.) from which the nanomaterials are formed [5,7]. This technique, referred as pulsed laser ablation in a liquid phase, has demonstrated its utility for long to produce a variety of nanomaterials [8–10].

An alternative way to produce nanomaterials, using laser pulses, consists of preparing a suspension of the desired source in a solvent and submit it to laser pulses; laser pulses induce reshaping, resizing or fragmentation of the suspended material. As additives are not required, this method presents several advantages as high purity nanoparticles are obtained. Under this concept, nanoparticle suspension in a liquid, as target material, presents the advantage of the coexistence of the nanomaterial produced by the laser pulses and the rests of the original, with the consequent modification of, for instance, luminescence of the entire solution [9]. Through the laser fragmentation in suspension (LFS)

* Corresponding author.
E-mail address: armando.zaragoza@cimav.edu.mx (E.A. Zaragoza-Contreras).

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technique, the size reduction of gold nanoparticles [11], fragmentation of indium tin oxide nanoparticles into smaller ones [12], the evolution of ZnO hollow nanospheres into ZnO quantum dots [13] and others, was reported. Detailed description of the evolution of ablation mechanisms of solid and particle targets confined in liquid phase are reported in literature [10, 14–16].

Concerning carbon nanomaterials (CNM), LFS methodology has been employed during the last two decades to produce a variety of carbon structures, for instance, polyynes [17–19], carbon nanoparticles [9, 20–22], carbon nanospindles [10,23], carbon nanocages [9], carbon nanodiamonds [20,24,25], or nanocubes [26]. For this purpose, diverse sources of carbon as, for instance, C_{60} [17], diamond particles [19], graphite powders [20], or carbon black [9,27], were confined either in organic solvents or in water and then laser irradiated. In these studies, the driving forces which define the nanoparticle morphology were mostly related to laser power, incidence time, solvent, and carbon source morphology. The production of CNM represents an emergent option for high-tech application as compared with quantum dots, photoluminescent CNM are more chemically stable, inert, and biocompatible [28–32]. Accordingly, research aimed at the development of new strategies to obtain new forms of CNM with active optical properties is of great interest.

For the best of our knowledge, the only report on the use of LFS technique for the modification of CNT in suspension deals with the bleaching of an SWCNT/DMF solution after its irradiation with ns laser pulse [33]. Herein, we report on the laser pulse effect using as the target chemically modified multi-walled carbon nanotubes (MWCNT) suspended in tetrahydrofuran (THF). The purpose of using modified nanotubes was to improve the dispersibility in the liquid phase, besides of providing products of certain functionalization. The possibility to produce carbon nanostructures such as polyynes, carbon nanoparticles, nanodiamonds, or carbon nanocages using LFS technique from MWCNT is discussed. The morphology and optical activity of the ablation products were characterized by electron microscopy, UV–vis and photoluminescence (PL) measurements.

2. Experimental

2.1. Materials and laser irradiation

In this work, MWCNT (Aldrich Co.) were oxidized in acid medium following the method reported previously [34]. THF (Aldrich Co.) was used as received. For laser irradiation, 5 mg of MWCNT was dispersed in 20 mL of THF; the dispersion was irradiated inside a conical vial for 30 min, using a 1064 nm laser Nd-YAG (Minilite II, Continuum), pulse duration was 7 ± 2 ns at 15 Hz of repetition frequency, pulse energy was 50 mJ/pulse. A blank suspension of MWCNT dispersed mechanically in THF was prepared for comparison purposes. Fig. 1 shows the experimental setup. During the laser irradiation, neither control of pressure or temperature was intended.

2.2. Measurements

Optical absorption spectra of the MWCNT suspensions, after and before laser irradiation, were run using a double beam spectrometer (Lambda7, Perkin-Elmer) from 200 to 900 nm. Absorbance spectra were recorded in a quartz cuvette with an optical path length of 10 mm. For reference purposes, THF absorption spectrum was recorded. All spectra were compared with the air. Photoluminescence (PL) characterization was carried out using a spectrophotometer (FluoroMax Plus, Horiba) exciting the MWCNT suspension at various wavelengths. The PL spectrum of the quartz cell filled with pure THF was also obtained. All the experiments were performed at environmental conditions without any special monitoring or control. MWCNT morphology, before and after irradiation, was analyzed using a field emission scanning electron microscope (FE-SEM, JSM-7401 F, JEOL Ltd.) and a field emission transmission electron microscope (JEM 2200FS, JEOL Ltd.). The samples were prepared by placing a droplet of dispersion on a holey-carbon-copper grid and then evaporating the solvent under laboratory conditions.

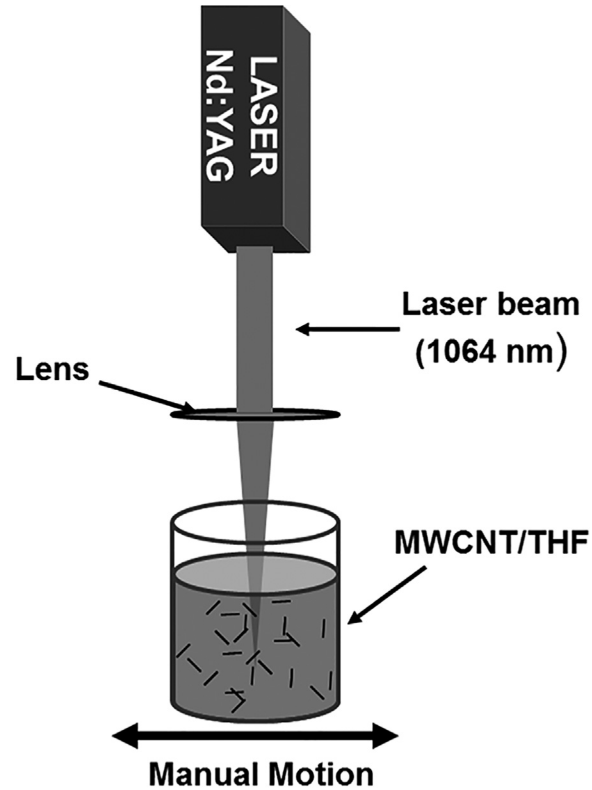

Fig. 1. Experimental setup for the laser fragmentation.

3. Results and discussion

3.1. Optical properties

During laser incidence, nanotube suspension evidenced changes in its optical properties, as the initial translucent black suspension turned progressively into a pale amber color (inset in Fig. 2). UV–vis absorbance and PL of the irradiated suspension were firstly analyzed. Fig. 2 exhibits MWCNT absorbance spectra, after and before irradiation, and pure THF. As seen, THF is nearly transparent from 340 to 850 nm; however, after MWCNT addition turned into a translucent black suspension (*), as portrayed in the inset picture. Concerning the irradiated dispersion, a great difference is seen compared to the blank. Absorbance decreased considerably from 450 to 850 nm, indicating that the dispersion evolved to a lower turbidity, as corroborated from the inset picture where the dispersion shows a pale-amber color (+). Such a change was related to the modification of MWCNT nanostructure, or to the coexistence of a new form of carbon nanostructure with the MWCNT. Absorbance modifications have been correlated to the evolution of products derived from the original nanomaterial irradiated. Mikheev et al. reported that the optical properties of MWCNT suspended in DMF change significantly after laser irradiation; the suspension was bleached and its optical density