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Photothermal, photoconductive and nonlinear optical effects induced by nanosecond pulse irradiation in multi-wall carbon nanotubes

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ABSTRACT

The influence of the optical absorption exhibited by multi-wall carbon nanotubes on their photothermal, photoconductive and nonlinear optical properties was evaluated. The experiments were performed by using a Nd:YAG laser system at 532 nm wavelength and 1 ns pulse duration. The observations were carried out in thin film samples conformed by carbon nanotubes prepared by an aerosol pyrolysis method; Raman spectroscopy studies confirmed their multi-wall nature. Theoretical and numerical calculations based on the heat equation allow us to predict the temporal response of the induced effects associated to the optical energy transference. A two-wave mixing method was employed to explore the third order nonlinear optical response exhibited by the sample. A dominant thermal process was identified as the main physical mechanism responsible for the optical Kerr effect. Potential applications for developing a monostable multivibrator exhibiting different time-resolved characteristics were analyzed.

1. Introduction

Due to their remarkable physical properties, carbon nanotubes (CNTs) have been considered potentially useful in a wide range of attractive applications related to materials sciences [1]. There have been explored fascinating optical characteristics associated to CNTs that can be employed for controlling mechanical [2,3], thermal [4,5] electrical [6,7] and nonlinear optical functions [8]. Particularly, all-optical operations based on the powerful and ultrafast third order nonlinear optical phenomena of CNTs have been found [9]. Besides, it has been demonstrated that carbon nanotubes could be not only related to different physical mechanisms of optical nonlinearity, but also, they can show opposite nonlinear optical processes, as it is the case of two-photon absorption (TPA) and saturated absorption (SA) [10,11].

The helicity, morphology, tube diameter, intertube distance and tube length are among the most important parameters to take into account to tailor the resulting optical features exhibited by multi-wall CNTs (MWCNTs) [12]. More to the point, other forms of carbon nanostructures also exhibit unique properties [13]. CNTs have a band gap determined by circumferential quantum confinement, which depends on the tube diameter [14,15]. Then, optical and conductive properties of MWCNTs depend on their morphology; particularly on the number of their layers. On the other hand, the conductivity and the nonlinear optical properties are strongly related to the temperature; the conductance increases if the temperature rises [16], and the mass density, resulting in a change of refractive index, decreases in proportion to the increment of temperature. Particularly, large-diameter CNTs do not typically show gate effect, but structural deformations can modify enough their electronic structure to allow Field Effect Transistor (FET) behavior [17]. Generally, low-dimension structures based on CNTs present very weak optical reflectance and relatively high optical absorbance. Nevertheless, with a high volume fraction, MWCNTs arrays exhibit a large optical absorbance together to a strong optical reflectance that can be essential for optical limiting applications [18].

It is worth noting that impurities and structural defects in CNTs samples originate noticeable modifications on their thermal response [19]. Additionally, the effect of incorporating MWCNTs on nanocomposites yields an enhancement in a resulting thermal conductivity that is increased several times [20]. On the contrast, it has been indicated that in the field of nanofluids, the heat transference

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decreases by increasing the MWCNTs concentration in suspensions [21].

The CNTs have proved to be useful as an active material for field effect transistors [15], photovoltaic devices [22], supercapacitors [23], solar cells [24], and nonlinear optical systems [25]. In this direction, an important influence of thermal properties of carbon nanostructures on their molecular dynamical characteristics has been reported [26]. It has been demonstrated that different configurations of CNTs show a photoconductivity dependence on temperature; which is monotonically increased with a decrease in temperature [27]. The response time of thermo-resistive sensors based on MWCNTs is about 5 s and the curves between temperature and resistance show a deviation from linearity in the 20–50 °C range [28]. Due to the distribution of energy states exhibited by CNTs, a high thermal conductivity much better than the correspondent for Silica and Germanium semiconductors can be obtained [29]. Superlative mechanical properties have been found in CNTs and they can be employed for developing outstanding filler materials for polymeric fiber reinforcement, because they improve tensile properties [30]. Their Young's modulus has been reported between extraordinary values in the range of 100–260 GPa, their tensile strength reaches 1–3 GPa, and their toughness is about 100–900 J/g [31]. Also, they have applications in photonics, since their nonlinear optical absorption and nonlinear optical refraction can be useful for noise suppression, passive mode-locked lasing and additionally, CNTs can present a large potential into the implementation of optical switches [32].

Within this work, we selected to study a thin film form sample for future designing of thin film optical devices. Thin films based on CNTs can systematically absorb optical irradiation, and this can become another form of energy [33]. Some results confirm the proof of this principle by testing photovoltaic devices based on thin films conformed by CNTs as transparent and conducting electrodes [34]. The thermal conductivity of MWCNTs in suspensions, or as powders, depends on random particle concentration; besides mechanically, it could be difficult to manipulate the stability and the optical properties of a solution if it can change by liquid evaporation or precipitation of the tubes. Moreover, this nanofluids only enhance their conductivity with respect to the based fluid, up to 20% [21]. Regular considerations for carbon based thin films with thickness in the range of 10–1000 nm ensure outstanding thermal properties [35]. However, for a clear observation of nonlinear optical effects by a nanosecond TWM, we identified a thickness close to 10 μm for a MWCNTs thin film sample. The strong nonlinear optical parameters related to MWCNTs seem to be attractive for a variety of nonlinear optical systems [36,37]. Particularly, in this research, we want to extend the knowledge about nonlinear optical properties of MWCNTs that in combination with thermal and conductive phenomena induced by light, can be considered as potential candidates for developing monostable multivibrator functions. Then, for further investigate potential applications that can be derived from the contribution of combined physical effects, this paper presents photothermal, photoconductive and nonlinear optical properties induced by nanosecond pulse irradiation on CNTs in a thin film configuration.

2. Materials and methods

2.1. Sample synthesis

The preparation of MWCNTs was carried out by an aerosol pyrolysis method [38]. Within the process, 0.5 wt% ferrocene and 2.5 wt% ethanol were employed. The aerosol was produced ultrasonically and it was constituted by a solution of hydrocarbon and an organometallic precursor, as solvent and solute, respectively. An argon flow (2.5 l/min) allows us to manipulate the aerosol to be placed inside of a furnace system settled in a temperature of about 800 °C during 30 min. Finally, the sprayer delivering process was completed, and the Ar flow was decreased to 0.3 l/min until a room temperature was achieved. The resulting MWCNTs were deposited on different SiO_2 substrates. The selected thin film samples present a thickness close to 10 μm.

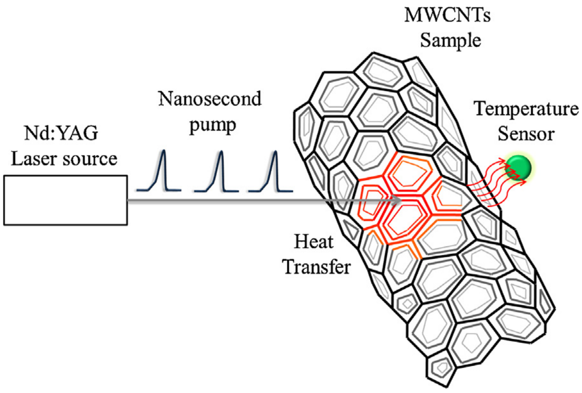

Fig. 1. Experimental scheme for inducing a phothermal effect under optical irradiation.

2.2. Morphology characterization

Transmission Electronic Microscopy observations were performed in the studied sample. The micrographs were recorded by using a JEOL Transmission Electron Microscope JEM 2100 at an acceleration voltage of 200 kV equipped with an ultrascan CCD camera Model 994 TEM *CCD*. Scanning electronic microscopy (SEM) studies were acquired by using a FEI Quanta 3D FEG Microscope system in STEM mode (scanning transmission electronic microscopy).

2.3. Raman spectroscopy evaluation

Raman spectroscopy studies were performed in order to investigate the multi-wall nature of the sample. A micro-Raman Horiba Jobin Yvon LabRam HR system with a He–Ne laser emitting at 632.8 nm wavelength allows us to analyze the samples without previous purification.

2.4. Photothermal experiments

The photothermal response exhibited by MWCNTs was induced by the second harmonic of a Nd:YAG laser source Continuum Model SL II-10 with 532 nm wavelength and 1 ns pulse duration. Fig. 1 schematizes a sketch of the experiment. The pump beam presents linear polarization, 6 mm beam diameter and 1 Hz repetition rate. Different levels of energy per pulse were employed to illustrate the representative results of the exploration avoiding optical ablation. The thermal dissipation was measured by a Wheastone bridge circuit with a thermistor as a sensor of temperature. The electronic signal was acquired by an ATmega328 8 bits microcontroller of the ATMEL family; the sampling of the signal was performed by using 0.1 s of temporal period.

2.5. Electrical evaluations

Electrical explorations were conducted with an Autolab/PGSTAT302N high power potentiostat/galvanostat. The impedance magnitudes were characterized with a 10 mV signal and an integration time of 1 s. The electrodes were separated by a distance of 5 mm in direct contact with the sample. The