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Optical Kerr effect exhibited by carbon nanotubes and carbon/metal nanohybrid materials

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HIGHLIGHTS

- Structural modification of carbon nanotubes is reported.
- Noticeable enhancement of Optical Kerr effect in nanohybrids was obtained.
- Optomechanical action of carbon nanotubes was estimated.
- Contrast in the two-photon absorption of carbon-based materials was observed.

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ABSTRACT

Structural modification of carbon nanotubes in combination with metallic nanoparticles is reported. An enhancement in the nonlinear optical refraction of multi-wall carbon nanotubes by the incorporation of platinum nanoparticles was observed. Comparative results were analyzed taking into account the participation of single-wall carbon nanotubes that originate a decrease in the nonlinear optical response of the multi-wall carbon nanotubes integrating a thin film. A Nd:YAG laser system featuring 532 nm wavelength with 4 ns pulse duration in a two-wave mixing experiment was employed for exploring the studied optical nonlinearities of the samples. The contribution of optical processes to mechanical characteristics dependent on high optical irradiance in carbon nanotubes was described. A variation in the mass density associated to the optically irradiated tubes allowed us to calculate the change in Young's modulus in a thin film configuration. The estimation of an opto-mechanical phenomenon was based on the evaluation of the nonlinearity of index responsible for the optical Kerr effect. According to Raman and optical evaluations, the inclusion of metallic nanoparticles in carbon structures results in a modification of surface that also gives origin to noticeable optical Kerr nonlinearities. Potential applications for developing laser-induced controlled opto-mechanical nanohybrid systems can be contemplated.

1. Introduction

One of the most remarkable breakthroughs that distinguish nanomaterials from bulk materials is the exceptional dependence of powerful physical properties on sizes and shapes. Carbon nanotubes (CNTs) are accompanied by superlative mechanical characteristics and electronic features that can be tailored by modification on tube's diameter and chirality [1,2]. Several optical devices developed by thin films conformed by CNTs have been proposed [3]. Multiple strategies about nanofabrication have enabled fascinating applications including modulators of mechanical, electrical or optical signals [4–7]. Besides, the design of periodic films has been proposed to practical utilization in nonlinear optical effects that strictly require phase matching; like second-harmonic

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generation, parametric oscillation, and frequency conversion [8]. On the other hand, it has been demonstrated that the alignment of the tubes can originate advantages for the enhancement of the collective optical response of the whole sample [9], while other interesting approaches are based on purifying or doping CNTs for improving particular physical properties [10,11]. Outstanding functions have been also pointed out for metallic decoration of CNTs [12]. Furthermore, it has been claimed that engineering the geometrical configuration of carbon nanostructured distributions can strongly modify their physical effects [13,14]. Concerning to nanostructured thin films, a simple way that could be considered for the addition of optical resonant interactions in a sample is the contribution of different materials assembling nanocomposites [15]. An evident advantage of the participation of metallic nanoparticles with CNTs is an automatic increment in the area/volume relation when they are arranged as a thin film sample. Different electrical properties like photoconduction can be improved, and eventually, mechanical and optical effects should be also modified through nanoparticle decoration of CNTs. The physical behavior of nanostructured thin solid films makes easier to envision the development of nanophotonic devices in comparison to samples based on liquid solutions or powders. Considerably, noble metal nanoparticles supported on carbon-based structures in thin film form have attracted the attention of scientists, because of synergistic positive phenomena that result when these materials are combined. In particular, metallic incorporation in CNTs seems to increase the sensibility of the nanostructures for different wavelengths; regarding a modification in nonlinear optical resonances [16]. It is noteworthy that gold and silver nanoparticles are by far the most commonly explored materials for nanophotonic applications [17]. However, resonances in short-wavelength optical regions for high-energy photonic effects are difficult to reach by just tailoring the size and shape of these metallic nanomaterials. Nevertheless, Platinum (Pt) seems to be an interesting alternative since this noble metal in nanometric size shows resonances typically close to the UV spectrum [18]. Additionally, it has been demonstrated that photoconductivity and plasmonic characteristics are strongly influenced by Pt deposition on carbon nanostructures [19,20]. Moreover, it can be contemplated that an additional advantage of using Pt for decorating CNTs is their remarkable potential for photocatalytic functions that can be good candidates to control chemical reactions by high optical irradiances. With this motivation, in this work, samples manufactured in a thin film fashion based on CNTs and Pt were prepared. Experiments for determining the nanosecond nonlinear optical properties at 532 nm wavelength were conducted. The mechanical and optical features of the films were analyzed.

2. Theory

We consider the Lorentz–Lorenz relation [21],

$$\frac{n^2-1}{n^2+2}=\frac{4\pi}{3}N\gamma, \tag{1}$$

where n represents the refractive index, N is the average number of molecules per unit volume and γ is the mean molecular polarizability. In terms of the mass density, ρ_m, Eq. (1) can be expressed as follows:

$$\frac{n^2-1}{n^2+2}=\frac{4\pi}{3}\frac{N_A\rho_m}{M}\gamma, \tag{2}$$

with N_A is the Avogadro's number and M is the molecular weight of the chemical element. For high optical irradiances, the refractive index dependent on irradiance can be written as the well-known optical Kerr effect,

$$n=n_0+n_2I, \tag{3}$$

here n_0 represents the index of refraction at low irradiance, n_2 is the nonlinear refractive index with a negative sign when it is related to thermal physical mechanisms, and I is the optical irradiance. By substituting Eq. (3) in Eq. (2), and clearing for ρ_m, we can get,

$$\rho_m=\left(\frac{(n_0+n_2I)^2-1}{(n_0+n_2I)^2+2}\right)\left(\frac{3M}{4\pi N_A\gamma}\right), \tag{4}$$

Thus, the change in mass density, $\Delta\rho_m$, coming from the optical Kerr effect could be calculated by the following:

$$\Delta\rho_m=\left(2n_0n_2I+(n_2I)^2\right)\left(\frac{3M}{4\pi N_A\gamma}\right), \tag{5}$$

Moreover, an approximation for Young's modulus, Y, can be obtained by following the mathematical expression [22],

$$Y=\upsilon_a^2\rho_m, \tag{6}$$

where υ_a represents the acoustic speed through the media and ρ_m symbolizes the density of mass. So, if we consider that the optical Kerr effect can generate a change in the mass density expressed by Eq. (5), also this modification should be able to cause a change in Young's modulus as ΔY with dependence on optical irradiance:

$$\Delta Y=\upsilon_a^2\left(2n_0n_2I+(n_2I)^2\right)\left(\frac{3M}{4\pi N_A\gamma}\right), \tag{7}$$

3. Experiment

3.1. Sample preparation

The CNTs were obtained by separately using ferrocene/benzylamine and ferrocene/toluene in a thermal decomposition method reported elsewhere [23]. Samples containing single-wall CNTs (SWCNTs) and MWCNTs were obtained by the ferrocene/benzylamine thermal decomposition. The resulting samples were evaluated by Scanning Electronic Microscopy (SEM) observations carried out in a SEM ULTRA 55 FEG System from ZEISS with Secondary Electron and Backscattering Detector. Comparative Raman studies in the sample of SWCNTs and MWCNTs (SWCNTs/MWCNTs) were performed in air at room temperature using a Renishaw inVia Raman Microscope through a 50x lens; the excitation at 532 nm wavelength was generated by a Nd–YAG laser source.

On the other hand, Pt nanoparticles were supported on multiwall CNTs (MWCNTs) surfaces resulting from the ferrocene/toluene solution. Two sequential thermal steps were followed in a horizontal quartz tube reactor at P_{tot}=5–7 Torr. First, a mixture of Pt precursor [(CH_3–COCHCO–CH_3)$_2$Pt; Aldrich 97%] and MWCNTs was prepared by grinding with agate mortar and pestle for 10 min. The mixture was heat treated at 180 °C for 10 min and at 400 °C for additional 10 min under Ar gas flow (100 cm^3/min). Transmission Electron Micrographs (TEM) were obtained in a JEOL JSM-6701F system, in order to get information about the mean particle size and distribution of Pt particles on MWCNTs. For this analysis, a representative amount of Pt/MWCNTs material was dispersed in isopropanol for 15 min in an ultrasonic bath, then, a drop of the final suspension was deposited on a copper grid by capillarity. As a complement, in order to observe the nanomaterial structure, approximately 10 mg of MWCNTs material after and before Pt