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Measurement of optical nonlinear refractive index response of graphene nanoparticles dispersed in an aqueous solution by Z scan technique

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A B S T R A C T

In this paper, colloidal suspension of graphene oxide nanoparticles (GONPs) were synthesized using the novel microwave assisted hydrothermal method. Different concentrations in distiller water is reported. Nonlinear optical properties of the samples were measured by the z-scan technique. For the experimental, a diode laser was used as an excitation source, the excitation beam was focused to a small spot by using a lens. Then, the sample was moved across the focal region along the z-axis. It was shown that the concentration of GONPs can greatly improve the nonlinear optical properties of the sample. The morphology and structure of GONPs, were evaluated by transmission electron microscopy (TEM), UV–Vis spectroscopy and Fourier Transform infrared spectroscopy (FTIR), respectively. From the experimental results, the optical nonlinear refractive indices of GONPs were obtained, ranging from $-2.53 \times 10^{-9}\,cm^2/W$ to $-2.57 \times 10^{-9}\,cm^2/W$. This suggests that GONPs aqueous solution, could be a very promising nonlinear medium, establishing the bases of nonlinear photonics.

1. Introduction

Carbon allotropes, fullerenes, carbon nanotubes and graphene has been widely studied in terms of their optical, and mechanical properties. Also, carbon nanotubes have non-linear (NLO) properties of third order and are being used in several photon applications, due to their thermal and optical properties. In non-linear optical applications, the radiation-matter interaction, the intense radiation can modify the polarization of the materials, thus producing non-linear effects such as the generation of a second harmonic Kerr effect and saturable non-linearity. The changes of the non-linear refractive index are due to the dependence of the laser intensity or even the thermal effect [1,2]. Fullerenes have found potential use in the electric field and due to its outstanding nonlinear optical properties [3,4]. Also, carbon nanotubes nonlinear optical applications range from fiber lasers to photonics [5]. On the other hand, graphene, is highly flexible, more resistant than steel and possess high thermal and electric conductivity [6,7]. Graphene oxide can be synthesized in a cheaper way using graphite as a raw material with a high yield and with the ability to form stable aqueous solutions [8–13] with general applications in medicine, optoelectronic devices, solar cells, lithography, gas sensing, biomedical and composite materials [14–17]. Recently, graphene oxide (GO), which belongs to the graphene family, have become an outstanding carbon compound due to its exceptional physical and chemical properties. These properties comes from sp2-and sp3-carbon atoms hybridization. On the other hand, the oxygen containing groups of GO, allows a diversity in optical and electrical characteristics by manipulating their content and location in GO structure by chemical or physical reduction. Moreover, these oxygen containing groups makes GO hydrophilic and water soluble, facilitating its processing [18]. Furthermore, graphene can form multilayered structures, being its increase in absorption a linear function of the number of layers and, when the incident light intensity is strong enough, a broad band saturable absorption (SA) is observed due to the Pauli blocking effect. Therefore, graphene have different applications

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such as in ultrafast lasers, optical modulators, photo detectors, in plasmonics for optoelectronics materials and devices. Also, graphene has shown significant nonlinear optical (NLO) responses in the telecommunication wave range, for frequencies ranging from microwave to terahertz up to optical [19]. Nowadays, nanocomposites of gold nanoparticles with graphene oxide are being used to measure their nonlinear properties of the refractive index of these composites by increasing the concentrations of GO and AuNPs. Nanoparticles such as gold nanoparticles are recently useful in applications in photodynamic therapy and medical diagnostics for the treatment of cancer [20].

Different techniques have been used to measure the NLO properties of materials. Among them, the z-scan technique introduced by Sheik-Bahae et al. [21,22] is considered one of the simplest methods for measuring the nonlinear refractive index of materials. This technique consist to focus a high power laser on a sample. The intensity of the laser beam is a function of the focus position, and the variations of intensity should be registered. In this work, the nanoparticles GO in water were used with different concentrations and a certain nanoparticle size, using the z-scan technique. The samples were characterized using complementary techniques as; transmission electron microscopy (TEM), UV–Vis and FTIR spectroscopy.

2. Materials and methods

2.1. Samples preparation

Graphene oxide was prepared from natural graphite powder trough a novel modified Hummers method [23], as shown in Fig. 1. For the procedure, 1 g of graphite was added into 23 mL of 98% H_2SO_4. The solution was stirred at room temperature for 24 h. Subsequently, 100 mg of $NaNO_3$ was added to the mixture and stirred for 30 min. Then, it was kept below 5 °C in an ice bath and 3 g of $KMnO_4$ was slowly added. After being heated to 35–40 °C, the mixture was stirred for another 30 min. Then, 46 mL of water was added and the mixture was stirred for 25 min. Finally, 140 mL of water and 10 mL of 30% H_2O_2 were added to stop the reaction. The unreacted graphite was removed by centrifugation, the synthesized GONPs were dispersed in distilled water at a concentration of 0.5 mg/mL using an ultrasonic bath. Stable aqueous dispersion of reduced graphene oxide (rGO) was prepared by chemical reduction of GO with the use of benzylamine as a reducing and stabilizing agent as follows: 2 mL of GO aqueous dispersion was added into 4 mL of H_2O, followed by addition of 200 mL of benzylamine. After stirring for 30 min at room temperature, the mixture was heated to 90 °C for 90 min. Finally, a black rGO dispersion was obtained. The sample was centrifuged twice to remove excess of benzylamine and the resulting precipitate was redispersed in water for further characterization.

2.2. Samples characterization

Absorption UV- visible spectrum was measured by a Shimadzu UV-3101 P C double beam spectrophotometer with slit wavelength of 2 nm and light path length of 1 cm to record the absorption spectra of the nanofluids. The morphology and particle size were evaluated by transmission electron microscopy (TEM). The measurements were made with a JEOL JEM200 electron microscope with an accelerating voltage of 200 kV. The nanofluids for TEM characterization was prepared by placing a drop of colloidal solution on carbon-coated copper grid and drying at room temperature. Functional groups composition was determined using Fourier Transform infrared spectroscopy (FTIR), with a Perkin Elmer spectrometer, from 4000 to 500 cm-1, and finally, nonlinear refractive indices of GONPs with different concentrations were measured using z-scan technique.

3. Experimental

For the study of the nonlinear optical properties of the graphene oxide nanoparticles contained in water, the z-scan technique was used, with a laser diode of continuous wave at a wavelength of 534 nm, as an excitation laser. The effective non-linear coefficient, n_2, of the GONPs was determined by the z exploration technique of the closed and open aperture. The closed aperture was fixed at a distance of 120 cm from the focal plane. The experimental z-scan arrangement for nonlinear laser spectroscopy is shown in Fig. 2. Samples with a thickness of 1 mm were moved along the z axis through the focal plane of a 10 cm focal length lens. The closed and open aperture signals were proportional to the real and imaginary parts of n_2, respectively. The closed and open signals were recorded by means of a photodiode, respectively, and the signal was sent to a National Instruments data card. In the movement of the z-scan, the sample moved forward or backward along the direction of the laser beam around the focus (z = 0). By properly controlling the change in transmittance through a small aperture placed in the far field position (and a closed aperture), the amplitude of the phase shift was determined.

Experimental results of z-scan data with a closed aperture is divided by an open aperture (not shown here) to obtain normalized transmittance and to get the value of the nonlinear refraction. The peak followed by a valley normalized transmittance obtained from the closed aperture curves indicates that the sign of nonlinear refractive indices is negative, i.e. self-defocusing.

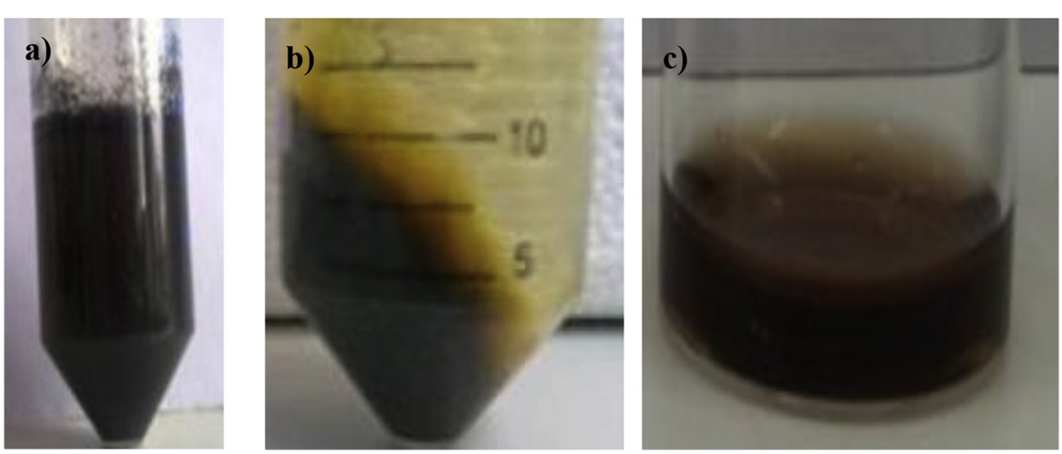

Fig. 1. Preparation of Graphene Oxide a) Oxidation (Hummers Method): H_2S $KMnO_4$, 98 °C, 30 min, H_2O_2 b) Centrifugation at 1200 rpm, 1 h. Color: Yellow c) Drying at 50 °C for 24 h removal of humidity (desiccator), hydration and sonication. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)