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Ultrafast optical nonlinearity and photoacoustic studies on chitosan–boron nitride nanotube composite films

Narayanan Kuthirummal [a,*], Reji Philip [b], Athira Mohan [b], Cassidy Jenks [a], Nicole Levi-Polyachenko [c]

[a] Department of Physics and Astronomy, College of Charleston, 66 George Street, Charleston, SC 29424, USA
[b] Ultrafast and Nonlinear Optics Lab, Light and Matter Physics Group, Raman Research Institute, Bangalore 560080, India
[c] Department of Plastic and Reconstructive Surgery, Wake Forest University Health Sciences, Winston-Salem, NC 27157, USA

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ABSTRACT

Ultrafast optical nonlinearity in chitosan (CS) films doped with multi-walled boron nitride nanotubes (MWBN) has been investigated using 800 nm, 100 fs laser pulses, employing the open aperture Z-scan technique. Two-photon absorption coefficients (β) of CS–MWBN films have been measured at 800 nm by Z-scan. While chitosan with 0.01% MWBN doping gives a β value of 0.28×10^{-13} m/W, 1% doping results in a higher β value of 1.43×10^{-13} m/W, showing nonlinearity enhancement by a factor of 5. These nonlinearity coefficients are comparable to those reported for silver nanoclusters in glass matrix and Pt-PVA nanocomposites, indicating potential photonic applications for MWBN doped chitosan films. Characterization of the synthesized films using Fourier transform infrared photoacoustic spectroscopy (FTIR-PAS) reveals significant interactions between the NH and CO groups of chitosan with boron nitride.

1. Introduction

Recent years have seen a tremendous growth in the development of polymer-based materials for various applications including waveguides, composites, sensors, storage, display devices, and biomedical technology [1–6]. This increased interest in such materials arises from their excellent processability, ease of use, and cost effectiveness. Their optical, mechanical, and antimicrobial properties can be easily modified by doping with inorganic dopants such as nanomaterials, and/or blending with other polymeric materials. Among the several types of polymers available, chitosan is a naturally-occurring biopolymer that exhibits several outstanding properties due to its biocompatibility, biodegradability, non-toxicity, and antimicrobial properties [7–11]. Chitosan easily blends with other polymers and materials opening up ways to synthesize an array of novel materials for various applications. More recently, there has been an interest in chitosan composites of clay, iron oxide, silver, and polynailine [12–20].

As part of our ongoing research on developing novel materials for medical and photonic applications, we have synthesized a set of chitosan films doped with multi-walled boron nitride nanotubes (MWBNs). Boron nitride nanotubes are another class of interesting materials with potential applications in developing protective shields, mechanical reinforcements for polymers, piezoelectricity, and drug delivery systems [21–24]. They are structurally similar to carbon nanotubes (CNTs) but with superior properties. For example, the asymmetric charge distribution in B-N bonds makes it partially ionic in nature resulting in a bandgap. Boron nitride nanotubes also have high structural stability and anti-oxidative ability. In the present work we have used open aperture Z-scan to measure the two-photon absorption coefficients CS–MWBN films and Fourier transform infrared (FTIR) photoacoustic spectroscopy (PAS) to understand the interaction between chitosan and MWBNs. Measured data shows that MWBN doped chitosan samples have an absorptive optical nonlinearity similar in magnitude to noble metal nanoparticles and nanocomposites which are well known nonlinear optical materials.

2. Experimental

Multi-walled boron nitride nanotubes (MWBNs) were a gift from the Center for Nanotechnology and Molecular Materials, Wake Forest University [25]. The MWBNs were grown using an arc generator method. The starting material for the tube growth was hexagonal boron nitride (h-BN). The nanotubes were relatively free from catalysts and the diameters ranged from 5 nm to 20 nm

* Corresponding author.
E-mail address: kuthirummaln@cofc.edu (N. Kuthirummal).

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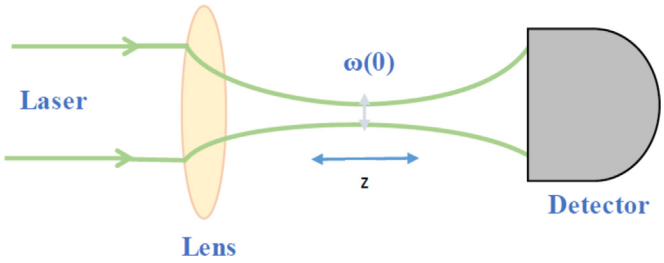

Fig. 1. Conceptual diagram of the open aperture Z-scan experiment. Transmission of the sample is measured at different positions on the z axis, in a region close to the focal point of the converging lens. Maximum laser intensity will be experienced at the focus, where the nonlinearity of the sample will be clearly evident.

as described in [25]. Chitosan (low molecular weight) was purchased from Aldrich (#448869). A 1% solution of chitosan in water with 2% glacial acetic acid was used. Boron nitride nanotubes were added to the chitosan solution at specified amounts and the solution was sonicated to disperse the nanotubes. Thin films were prepared by pouring the boron nitride nanotubes in chitosan solution into 100 mm petri dishes and evaporating the water acetic acid mixture.

Nonlinear optical measurements were carried out using the open aperture Z-scan technique [26]. A conceptual diagram of the open aperture Z-scan experiment is shown in Fig. 1. A regeneratively amplified Ti:Sapphire laser producing 100 femtosecond (FWHM) laser pulses at 800 nm was used as the excitation source. The laser was run at 10 Hz for thermal stability, but by using a fast, electronically synchronized mechanical shutter in the beam path, single pulses were selected from the 10 Hz pulse train for the experiment. Thus the effective pulse repetition rate of the experiment was lower at about one pulse in five seconds, allowing complete thermal relaxation of the sample before the arrival of the following pulse. The pulses were focused using a plano-convex lens of 20 cm focal length, and the focal spot radius (ω_0) was 16 μm. The laser pulse energy used was 11 μJ.

For measuring the nonlinear optical transmission, CS–MWBN samples (having a linear transmittance of 77% at the excitation wavelength) were mounted on a stepper motor controlled linear translation stage and translated in the z direction in small steps of 200 μm each, through the focal region of the lens. At each step a laser pulse was fired, and the transmitted energy was measured using a pyroelectric laser energy detector (Laser Probe Inc.). No visible emission or breakdown of the sample was observed during the experiment.

Fourier transform infrared (FTIR) photoacoustic spectra in the 400–4000 cm^{-1} were acquired by co-adding 256 scans at a resolution of 8 cm^{-1} using a Varian 7000 FTIR spectrometer equipped with a MTS300 photoacoustic module from MTEC Photoacoustics, Inc. USA. The photoacoustic module consisted of a microphone with a nominal sensitivity of 50 mV/Pa and a sample cup of 10 mm diameter. The sample cup contained helium gas to enhance the signal amplitude. The spectrometer included a water cooled mid-IR source and KBr beamsplitter. Rapid scan was used to obtain the spectra of CS–MWBN samples in the solid state. The polymer composite samples were used as is without mixing it with KBr. The final spectra were light intensity normalized using photoacoustic signals from a carbon black pellet under the same experimental conditions.

3. Results and discussion

In the open aperture Z-scan technique the laser beam is focused using a lens, and the sample transmission is measured as it

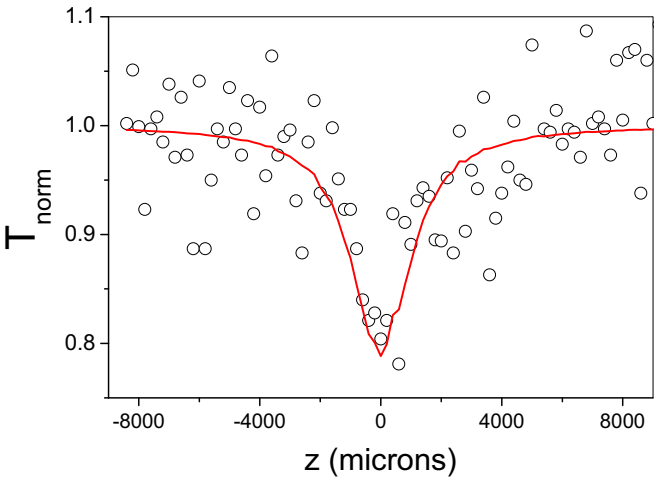

Fig. 2. Open aperture Z-scan measurement of chitosan doped with 0.01% MWBN. Circles are data points while the solid curve is a numerical fit to the data using Eq. (3).

is moved along the beam axis (z-axis) from one side of the focus to the other through the focal point (which is taken as $z=0$). For a spatially Gaussian laser beam which is focused by a converging lens, the beam radius $\omega(z)$ at each position z is given by

$$\omega(z) = \omega(0)\sqrt{1 + (z/z_0)^2}, \tag{1}$$

where $\omega(0)$ is the beam radius at the focus, and $z_0 = \pi\omega_0^2/\lambda$ is the Rayleigh range (diffraction length). The corresponding input light intensity is given by [27]

$$I_{in}(z) = 4\sqrt{\ln 2}\,E_{in}/\pi^{3/2}\omega(z)^2\tau, \tag{2}$$

where E_{in} is the input laser pulse energy, and τ is the laser pulsewidth. Thus at each position z the sample sees a different laser intensity, and the intensity will be a maximum at the focal point. For a sample showing nonlinear behavior the transmittance $I_{out}(z)/I_{in}(z)$ will be a function of $I_{in}(z)$. The normalized transmittance of the sample plotted against z gives the open aperture Z-scan curve. The curves thus plotted from the present measurements are given in Figs. 2 and 3, for the samples with 0.01% and 1% MWBN doping, respectively.

The best numerical fits to the above Z-scan curves were obtained for a two-photon absorption (2PA) process. For 2PA the normalized transmittance is given by [26]

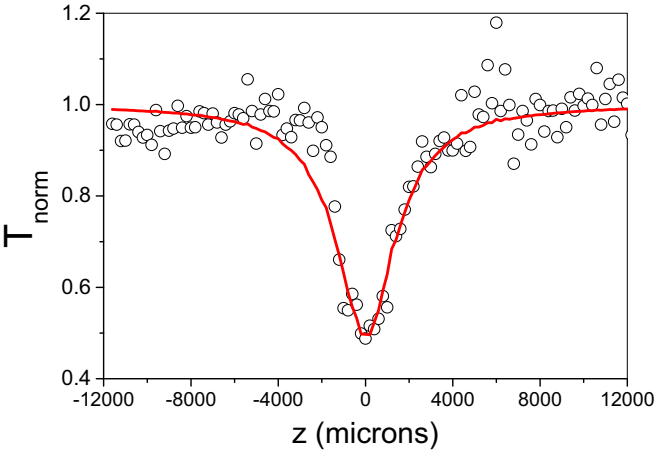

Fig. 3. Open aperture Z-scan measurement of chitosan doped with 1% MWBN. Circles are data points while the solid curve is a numerical fit to the data using Eq. (3).