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Third-order nonlinear optical properties of silver nanoparticles mediated by chitosan

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ABSTRACT

Silver nanoparticles in chitosan medium were prepared by the chemical reduction method. Silver nitrate and hydrazine were used as the precursor and reducing agent in the present of chitosan as a natural host polymer. The samples are characterized by UV–visible spectroscopy, X-ray diffraction (XRD) and transmission electron microscopy (TEM). The measurements of nonlinear optical properties were defined by Z-scan technique using green CW laser beam operated at 532 nm wavelengths. Thermal effect has a dominant role in the overall material nonlinearity with CW laser. It is shown that the synthesized samples have a negative nonlinear refractive index.

1. Introduction

Nanoparticles are interesting subject and have gained lots of attention since they are showing different properties than their bulk counterparts [1]. Among the different nanoparticles, silver nanoparticles have received high interest because of their diverse applications [2].

Polymers have been widely used in the synthesized process due to their unique properties. Usually metal-nanocomposites can be obtained by adding the metal ions in a polymer solution and then reduction of metal ions by an appropriate reducing agent [3]. To prevent from agglomeration, polymers play an important role; it serves as a capping agent. Chitosan is the most important derivative of chitin (poly β-(1-4)-N-acetyl-D-glucosamine) and is the second most abundant natural polymer [4,5]. There are many reports for synthesis of the silver nanoparticles in chitosan such as green method [6], gamma ray irradiation [7,8], thermal annealing [9] and chemical reduction [3].

Silver nanoparticles have found attractive application in optical signal processing, optical limiting and optical devices due to their optical nonlinear properties [10,11]. And photonic based on this nonlinear optical properties have been trying to develop very fast [12]. Different methods have been used for measuring the nonlinear optical properties but among them Z-scan technique have been used widely in most research groups because of its simplicity and accuracy in measurement [13–15]. Also it was proved that by this technique the nonlinear refractive index and the nonlinear absorption can be evaluated, including the sign and the magnitude. There are various mechanisms that independently contribute to optical nonlinearities of the materials. The electronic nonlinearity is an important mechanism and it appears in most of the dielectric materials, while non-electronic nonlinearities are nonradiative interactions such as in density and temperature [16]. Until now there are several reports on the electronic and non-electronic nonlinear properties of materials; He et al. reported nonlinear optical properties of azo dye under CW and pulse excitation, and the nonlinear origin was discussed in the terms of laser heating and resonant electronic effect [16]. Ganeev et al. studied the nonlinear optical properties of GaAs nanoparticles under the high pulse repetition rate and nanosecond pulses and it was shown that the thermal effect was dominant [17]. Andrade et al. developed a technique which the thermal nonlinearity contribution can be subtracted [18].

In this work we report the synthesis of silver nanoparticles in chitosan solution by the chemical reduction method. Also the experimental measurement of third-order nonlinear refractive index and absorption coefficient is reported using by the well-known Z-scan technique with continues wavelength laser beam operated on 532 nm. The close aperture and open aperture Z-scan measurement were both carried out at the laser power of 180 mW. The experiments were repeated for different concentration of silver nanoparticles.

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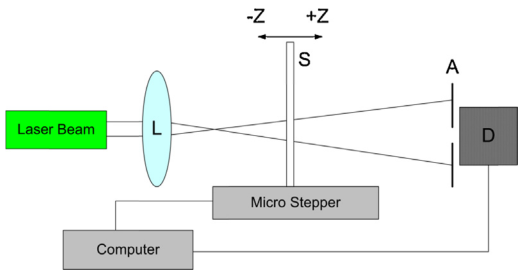

Fig. 1. Schematic diagram of Z-scan measurement setup: lens (L); sample (S); aperture (A); detector (D).

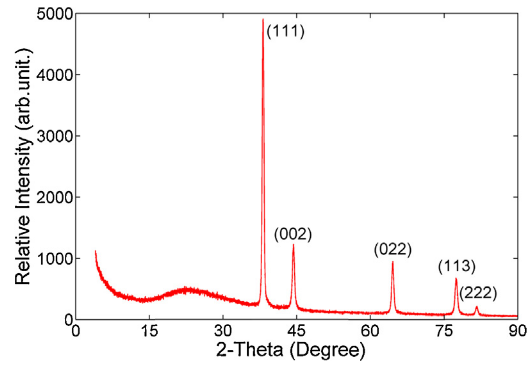

Fig. 2. XRD diffraction pattern of silver nanoparticles in chitosan solution for sample with 5 ml reducing agent.

2. Experimental works

2.1. Materials

Silver nitrite ($AgNO_3$) was obtained from MERK and chitosan with the average molecular weight number of 3,45,500 g/mol was obtained from the Malaysian nuclear agency. Hydrazine (N_2H_4), which has been used as a reducing agent, was purchased from ACROS.

2.2. Synthesis of silver nanoparticles

The silver nanoparticles in chitosan solution were synthesized by the following steps: 0.1 wt% chitosan solution was prepared by dissolving 0.1 g of chitosan in 1 ml acetic acid in 100 ml deionized water at room temperature and contentiously stirred for 2 h to make sure that all the chitosan is completely dissolved. The solution of chitosan was divided equally into five bottom flasks. Silver nitrate was added to the chitosan solution at the concentration of 0.1 M. After stirring for 30 min, 0.1 M hydrazine (N_2H_4) as a reducing agent in amounts of 5, 10, 15, 20 and 25 ml was added drop wise while the samples were still stirring. The samples were allowed to be stirred for the next 24 h. The major role of the chitosan in this synthesis is to prevent the aggregation of silver nanoparticles.

2.3. Characterization

The optical spectra of silver nanoparticles in chitosan solution were recorded by UV-3600, Shimadzu spectrophotometer over the range of 300–800 nm. X-ray diffraction measurement was done by XRD 6000 Shimadzu diffractometer by using Cuk$_\alpha$ (0.154 nm) radiation at the room temperature. The morphology of the silver nanoparticles in chitosan solution was investigated by transmission electron spectroscopy (JEOL 2010F UHR) operated at 200 kV. For preparation, the sample was first diluted in water and after 10 min ultrasonic, a drop of nanoparticles suspension was put on the copper grid and was left to evaporate overnight at room temperature under vacuum in the desiccators. The size distributions obtained by the UTHSCSA image tool program.

2.4. Nonlinear optical properties measurement

The Z-scan experiment is a sensible and reliable tool for investigation of nonlinear properties of different kind of samples [19,20]. Fig. 1 shows the schematic diagram of a single beam Z-scan experiment set up which was used in our experiment to measure the nonlinear properties of silver nanoparticles in chitosan solution. The experiment was carried out by 532 nm laser beam and power of 180 mW, which was focused to a spot by using a 10 cm focal length lens. The beam waist at the focus length was ~47 μm. The sample was located in the quartz cell with the thickness of 1 mm and was mounted on BSC101 micro stepping controller from Thorlabs which was moving across the focal point of the lens. The micro stepper was controlled by lab view program. In this experiment the sample can be considered as a thin medium due to the condition of:

$$\frac{\pi\omega_0^2}{\lambda > L},$$

where ω_0 is the beam waist at the focal point, L is the thickness of the sample and λ is the wavelength of the beam. The input and output powers were measured by 1936-C power meter from Newport. The detected power has been normalized by the power value observed when the quartz cell located at the focal point of the lens. The distance between the detector and the lens is about 60 cm, which is far enough to be considered as far-field. There are two different modes in Z-scan technique. In close aperture Z-scan, by having an aperture in front of the detector, the nonlinear refractive is disassociated from nonlinear absorption. An open aperture Z-scan captured all the transmitted power by omitting the aperture or enlarges it and focused onto the detector by using another lens. All the measurement was carried out at room temperature.

3. Results and discussion

3.1. Characterization of silver nanoparticles

Fig. 2 shows the XRD pattern of Ag nanoparticles in chitosan solution. All the refractions corresponded to the pure silver metal with cubic symmetry. The refractions presented by five main peaks at $2\theta = 38.11°$, 44.30°, 64.44°, 77.40° and 81.54° which are assigned to the lattice planes (1 1 1), (0 0 2), (0 2 2), (1 1 3) and (2 2 2). The broad peak at $2\theta = 22.17°$ is due to the existence of chitosan [7]. Synthesized of silver nanoparticles in chitosan solution was confirmed by JCPDS 98-006-1079. The X-ray diffraction was analyzed in all five samples and there is no distinct difference observed which suggests that the crystalline phases do not change while the amount of reducing agent increases.

Silver nanoparticles have absorption maximum at 400–430 nm which can be detected by UV–visible spectroscopy [2]. Fig. 3 shows UV–visible spectra of silver nanoparticles in chitosan solution. Silver plasmon resonance appears at 420 nm, which indicates the formation of nanoparticles in chitosan solution. In the ratio of 10 ml and 15 ml of reducing agent we observe a blue shift, it slightly went to lower wavelength by increasing the amount of reducing agent. It shows that the size of nanoparticles is decreasing. In sample with 20 ml of reducing agent, it can clearly be seen that the intense peak went to higher wavelength (red shift), this means that the size of