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Synthesis and nonlinear optical response of silver nanoparticles decorated polydiacetylene composite nanovesicles

B. Bhushan*, T. Kundu, B.P. Singh

Department of Physics, Indian Institute of Technology Bombay, Powai, Mumbai 400076, India

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ABSTRACT

We have synthesized, characterized and studied the third-order nonlinear optical properties of polydiacetylene (PDA) nanovesicles decorated by silver nanoparticles. The second molecular hyperpolarizability $\gamma(-\omega;\omega,-\omega,\omega)$ of the sample was investigated by the antiresonant ring interferometric nonlinear spectroscopic (ARINS) technique using femtosecond modelocked Ti:sapphire laser in the spectral range of 720–820 nm. The observed dispersion of γ has been explained in the framework of three-essential states model involving the ground state, a one-photon excited state and a two-photon excited state. The energy of two-photon state, transition dipole moments and line width of the transitions have been estimated. Our investigation reveals that the spectral dispersion characteristic of γ for coated PDA nanovesicles is qualitatively similar to that observed for uncoated PDA nanovesicles but bears no resemblance to that observed in silver nanoparticles. The presence of silver nanoparticles increases the γ values of coated nanovesicles slightly as compared to that of uncoated nanovesicles, suggesting a definite but weak coupling between free electrons of metal nanoparticles and π -electrons of polymer in the composite system.

1. Introduction

The rapid progress of optical communication network has increased the focus of research on the development of efficient nonlinear optical materials with large third-order nonlinear susceptibility for photonic devices such as ultrafast optical switching, optical data storage, optical limiting etc. In this direction, conjugated polymers have received considerable attention due to their inherently large ultrafast nonresonant nonlinearity and scope for improvement by way of molecular engineering. Among the varieties of conjugated polymers, polydiacetylenes (PDA) exhibit large potential for photonic device applications due to the ease of processibility, variety of morphologies – crystalline or amorphous, large damage threshold and environmental as well as mechanical stability. Polydiacetylenes have been extensively explored for their nonlinear optical studies. This includes polytoluene sulfonate polydiacetylene (PDA-PTS) [1–4], poly [4, 6-decadiene-1, 10-diol-bis (3-butoxycarbonyl-methyl-urethane)] (PDA-3-BCMU) [5], poly[5,7-dodecadiene-1, 12-diol-bis (4-butoxycarbonyl-methyl-urethane)] (PDA-4-BCMU) [6,7] and poly[4, 6-decadiene-1, 10-diol-bis (9-butoxycarbonyl-methyl-urethane)] (PDA-9-BCMU) [8] etc. However, none of the existing conjugated polymers so far possesses the requisite figure of merit for the practical realization of all optical signal processing devices. The device grade nonlinear optical polymers still remain a distant dream and new avenues are needed to be explored.

Apart from conjugated organic polymers such as PDAs, nonlinear optical properties of metal nanoparticles embedded in a dielectric host have also attracted considerable interest by a number of physicists [9–11]. Metal nanoparticles are of special interest as nonlinear materials for optical switching and computing because of their relatively large third-order nonlinearity $\{\chi^{(3)}\}$ and ultrafast response time [9]. Hache et al. [12] developed a theoretical formalism for the third-order nonlinear optical response of metal nanoparticles. In a system of metal nanoparticles such as gold and silver dispersed in a transparent matrix, an absorption peak due to the surface plasmon resonance (SPR) is usually observed in the visible spectral region [13]. SPR is associated with the collective oscillation of free electrons of metal nanoparticles which leads to the enhanced local electromagnetic fields. Due to the local field enhancement near the SPR, the third-order nonlinearity of metal nanoparticles can be enhanced substantially [9]. Silver nanoparticles have an advantage over other metal nanoparticles because of the location of their surface plasmon resonance energy quite far from the interband transition energy [14]. Therefore, in a sample containing silver nanoparticles

* Corresponding author. Present address: Department of Applied Physics, Birla Institute of Technology, Mesra, Patna Campus, Near BV College, Patna 800014, Bihar, India. Tel.: +91 9471859469; fax: +91 612 2227050.
E-mail addresses: binaybhushan@gmail.com, binay.bhushan@bitmesra.ac.in (B. Bhushan).

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embedded in a dielectric host, we can investigate the nonlinear optical effects focusing on the surface plasmon contribution.

Considering that both polydiacetylene as well as metal nanoparticles have been shown to exhibit considerable optical nonlinearity, it would then be very interesting to explore the nonlinear optical response of polydiacetylene-metal nanoparticle composite systems. Neeves and Birnboim [15], Kalyaniwalla et al. [16] and Haus et al. [17] have, in fact, theoretically predicted much larger enhancement of third-order nonlinearity of metallic shell coated semiconductor arising from surface plasmon enhanced local field. PDA-metal nanocomposites thus offer potential for enhanced nonlinear optical properties. However, nonlinear optical properties of such composite systems have not been explored too much so far. More recently, some composites of PDA have been reported to have excellent nonlinear optical properties [18–21]. However, it is to be noted that all these reported studies have been performed at a single resonant wavelength and hence did not offer any useful insight into the nonlinear response of these composite systems. On the other hand, spectral dispersion characteristic of second molecular hyperpolarizability $\{\gamma\}$ in a given spectral range is the key to understand the electronic structure-nonlinearity relationship in a given class of molecule. Chen et al. [21] have probed the spectral response of $\chi^{(3)}$ for nanometer size silver coated PDA nanovesicles but did not correlate it to the electronic structure of the samples. Moreover, they have investigated the nonlinearity by *Z*-scan technique using nanosecond pulse duration at 532 nm available from a frequency-doubled Q-switched Nd: YAG laser. However, the Z-scan technique, although being very popular because of the simple and single beam technique, can sometimes give misleading results because it does not differentiate between the electronic and other mechanism of nonlinearity. Also, it does not provide high enough sensitivity for the measurement of nonlinearity at moderate and safe intensity levels. On the other hand, the antiresonant ring interferometric nonlinear spectroscopic (ARINS) technique [22] based on Sagnac Interferometer [23], apart from being a highly sensitive technique, has the unique capability of discriminating electronic nonlinearity against other mechanisms of nonlinearity based on the response time of different types of nonlinear processes. In our investigation reported here, we have used transform limited, 80 fs pulses (repetition rate 100 MHz and energy per pulse 5 nJ) from a self mode-locked Ti:sapphire laser to measure the nonlinear optical response of our sample using ARINS technique. Because of use of femtosecond pulse and establishing the ARINS setup to measure nonlinearity faster than 3 ps (described below), the nonlinearity reported in this paper is purely of electronic origin. Moreover, instead of investigating the nonlinear response at a single wavelength, we have measured the third-order susceptibility in the spectral range of 720–820 nm. The subsequent spectral dispersion of second molecular hyperpolarizability has been analyzed in the framework of three-essential states model and a correlation with the electronic structure of the sample has been discussed. The energy of two-photon state, transition dipole moments and the line width of transitions have also been estimated.

2. Synthesis and characterization

Although Zhou et al. [24] have reported the route for the synthesis of silver nanoparticles decorated polydiacetylene nanovesicles, but we have synthesized the same by a little bit different method. High purity diacetylene monocarboxylic acid, 10,12-pentacosadiynoic acid (PCDA) was purchased from Alfa Aesar and used without further purification. A 2 ml volume of 1 mM PCDA solution in ethanol was rotaevaporated to dryness leaving a very thin uniform film of lipid layer on the wall of the flask. A 15 ml volume of electronic grade deionized water was then added and heated to 60 °C in constant temperature bath while rotating the flask to absolve the lipid layer in water. A 6 ml aqueous solution of $AgNO_3$ of 10^{-2} M concentration was then added to it and the resulting solution was again sonicated in the ultrasonic bath for about 15 min. At last a semitransparent solution was obtained and stored at 4 °C in a refrigerator overnight. This solution was then irradiated with UV light (254 nm) for 45 min. For monitoring the growth of silver coated nanovesicles, UV–vis absorption spectrum was recorded at regular intervals of UV exposure. Fig. 1 shows the absorption spectrum of the sample after 5 min, 15 min, 30 min and 45 min of UV exposure. It can be seen that while the optical density (OD) at 265 nm corresponding to the monomer decreases, the peak at 659 nm develops with the exposure of UV radiation. This peak at 659 nm corresponds to the exciton peak of polydiacetylene and its emergence implies the conversion of monomer into polymer. It can also be seen that another peak at 383 nm grows with the increasing dose of UV radiation. This peak corresponds to the surface plasmon band of silver and its growth implies the growth of silver nanoclusters due to photoreduction of Ag ions. The surface plasmon band at 383 nm suggests diameter of silver nanoparticles to be <20 nm [25]. As the exposure continues, the peak height stops growing further. In fact, a reduction in OD of PDA exciton peak becomes visible, presumably due to the increased thickness of the coating of silver nanoparticles on the vesicles. At this stage, exposure was stopped. It can be seen that there still remains a residual absorption at 265 nm (OD$\sim$0.25) as against initial $\sim$0.96 OD of unexposed sample. This implies that all monomer units did not get polymerize. The polymer concentration in terms of polymerized monomer units is $\sim$0.73 mM corresponding to $4.42 \times 10^{17}/cm^3$. The schemes of polymerization of diacetylene monomers, photoreduction of silver ions and formation of the silver coated nanovesicles have been explained in detail in Ref. [24].

The microstructure of the resulting silver coated nanovesicles was investigated by transmission electron microscope (TEM) and electron diffraction (ED). The TEM image, displayed in Fig. 2, shows that the silver-coated PDA nanocomposite sample has a vesicle shell structure of outer diameter 200 nm. The thickness of the vesicle shell is about 20 nm and the core size is about 180 nm. The TEM image reveals the presence of silver nanoparticles on the inner as well as on the outer surface of the vesicle. The presence of these silver nanoparticles on the surfaces of vesicle is further revealed by the ED pattern, displayed in Fig. 3, which shows four strongest fringes resulting from the diffraction by silver planes [220], [311], [331] and [440] with plane distances of 1.47 Å, 1.27 Å, 0.94 Å and 0.71 Å respectively.

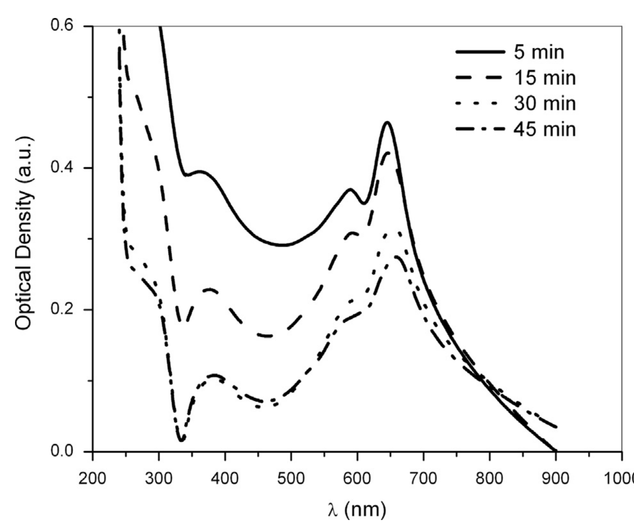

Fig. 1. Linear absorption spectrum of silver nanoparticles coated PDA nanovesicles at 5, 15, 30 and 45 min interval of UV exposure.