Nano-Structures & Nano-Objects 11 (2017) 32–38

Contents lists available at ScienceDirect

Nano-Structures & Nano-Objects

journal homepage: www.elsevier.com/locate/nanoso

Plasmon enhanced two-photon absorption in modified Styrene–Maleic Anhydride Silver nanocomposites

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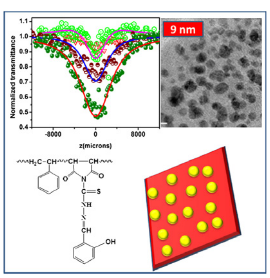
GRAPHICAL ABSTRACT

The Anhydride group in the Styrene-Maleic Anhydride modified with Salicylaldehyde Thiosemicarbazone and its Silver nanocomposites were prepared. Exploration of the nonlinear optical properties of the polymer with different weight percentage of Silver nanoparticles provide a platform for the development of practical nonlinear optical devices with good optical limiting properties.



ARTICLE INFO

Article history:
Received 5 January 2017
Received in revised form 19 April 2017
Accepted 26 May 2017

Keywords:
Copolymer
Modified copolymer
Silver nanocomposites
Optical limiting

ABSTRACT

Styrene–Maleic Anhydride (SMA), a synthetic copolymer, possess aromatic and anhydride functionalities with interesting thermal and membrane properties. In this work, we report on the nonlinear optical studies in Schiff base modified SMA by open aperture Z-scan experiments with 532 nm, 5 ns laser pulses. In addition, we incorporate Silver nanoparticles in the polymer SMA so as to enhance the nonlinear absorption. The nonlinear absorption coefficient is found to be nearly 0.8×10^{-11} m/W for the neat polymer. On incorporation of Silver nanoparticles in SMA, the nonlinear absorption coefficient is found to be increasing to 0.1×10^{-8} m/W, which is nearly three orders higher than SMA. The enhanced nonlinear absorption coefficient in polymer–metal nanocomposites is attributed to local field effects induced by metal nanoparticle. We also observed that the optical limiting threshold of the synthesized polymer nanocomposite can be tailored as a function of Silver nanoparticle concentration. Our observations indicate that the incorporation of metal nanoparticles, with the excitation wavelength non-resonant with the surface plasmon peak, offer a strategy to control the third order nonlinear optical properties of the polymer nanocomposite, making it suitable for various optoelectronic applications.

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http://dx.doi.org/10.1016/j.nanoso.2017.05.011
2352-507X/

1. Introduction

Polymers and polymer nanocomposites have promising applications in a wide spectrum of areas ranging from electronics to photonics, conducting materials to sensors, medicine to biotechnology [1–4]. Along with the application performance, these materials have shown peculiar and attractive mechanical strength, toughness, heat resistance, flame retardancy and barrier properties superior to those of their bulk counterparts [5–7]. The application window of the polymers can be broadened by enhancing particular characteristics such as modulus strength, thermal and electrical properties, resulting in the generation of advanced polymeric materials [8] Styrene–Maleic anhydride copolymer has interesting properties which include transparency, high heat resistance and high dimensional stability and the specific reactivity [9,10]. The convenient preparation of SMA can be seen as the advantage that has led to its well-known commercialization [11,12]. It can be used in applications like engineering plastics, drug delivery systems, paper making industry, paint industry etc. [13,14]. Modified polymers can be used to promote a wide range of transformations and applications in photonic devices, data storage, display devices etc. [15,16]. The versatility of SMA polymer is specific reactivity of the anhydride groups which can be modified by using hydroxyl, amine groups, Schiff base etc. [17,18]. Modified Styrene–Maleic anhydride copolymer can be used for polymer drug interactions, compatabilizer in thermoplastics and copolymers to improve thermal performance, removal of toxic metal cations from aqueous solutions etc. [19,20]. It was reported that the polyimide of the Schiff base modified styrene–Maleic anhydride form stable monolayers, to produce a large range of thermally stable Langmuir Blodgett films, and these thin films are regarded as promising system for functional applications such as molecularelectronics, optoelectronics [21]. Functionalization of SMA with the Schiff base improve the thermal stability of these polymers, however, the optical nonlinear absorption of SMA and Schiff base modified SMA is negligibly small. Materials with high nonlinear optical properties such as reverse saturable absorption, two-photon absorption, saturable absorption are found to be suitable for applications such as optical limiters, in optical switching, optical signal processing, multi-photon microscopy etc. [22–27]. Nonlinear optical properties of composite materials are found to be enhanced compared to monocomponent materials [28]. It has been reported that the third order optical nonlinearity of the polymer matrices can be modified by the incorporation of dyes, metal nanoparticles, semiconductor nanoparticles etc. [29,30]. Enhancing the nonlinear absorption of polymers is an interesting problem, in view of their improved thermal stability and potential applications. Noble metal nanoparticles have attracted a lot of interest for application in optical devices due to their enhanced third order nonlinear optical response, making it a suitable candidate for different photonic applications such as optical limiting, optical data storage, biophotonics applications [31–34]. Saturable absorption in metal nanoparticles have been reported by many groups [35,36], owing to the population bleaching of the ground state, when the population of the excited state cannot relax fast at a large pump rate [37]. At higher intensities, a switching over to reverse saturable absorption have been observed and is attributed to process such as interband transition resulting in multi-photon absorption, electron-ejection etc. The incorporation of metal nanoparticles have been widely used to enhance the third order nonlinearity of semiconductor nanoparticles, dyes, polymers etc. The surface plasmon resonances of the metallic nanoparticles can strongly enhance the local electric field and thereby increasing the one-photon and two-photon absorption [38,39]. The largest enhancement in the nonlinear optical properties is expected on excitation at the peak position of SPR, because of the giant local electric field. In our earlier work on Schiff base modified Styrene–Maleic anhydride polymer incorporated with Au nanoparticles, we have addressed the resonant excitation regime, where the incident frequency 532 nm lies in the SPR peak [40]. We observed that the two-photon absorption gets enhanced in the polymer–metal nanocomposite on the incorporation of metal nanoparticles. However, the linear absorption also reaches a maximum at this wavelength, which is not desirable for the applications such as optical limiting, three-dimensional data storage etc.

In this work, we have incorporated Silver nanoparticles in the modified polymer so that the excitation wavelength is away from the SPR band (off-resonant regime). Specifically, we investigate the effect of incorporation of Silver nanoparticles on the two-photon absorption of the polymer. We also investigate the optical limiting properties of the polymer–metal nanoparticle as a function of Silver nanoparticle concentration.

2. Experimental section

2.1. Synthesis of modified SMA and Silver nanocomposites

For the present synthesis, chemicals were purchased from Aldrich Chemie. Modified Styrene–Maleic anhydride copolymer with Schiff base (SMA-1) was prepared by the reaction of the copolymer with SalicylaldehydeThiosemicarbazone [41]. The diimide was formed by heating the synthesized polymer at 140 °C by using DMF as a solvent. Schematic representation of the preparation of SMA-1 is given in the Figure S.I 1 (Supporting Information). Silver nanoparticles of approximately 7 nm average diameter (20% size distribution) were synthesized via wet chemical reduction method [42]. In this method trisodium citrate (stabilizing agent) was dissolved in 0.01M solution of Silver nitrate by sonication for 10 min. An aqueous solution of $NaBH_4$ (0.001%), cooled at 0 °C, was added rapidly to this mixture under vigorous stirring. Rapid color change from colorless to yellowish was observed on sonication for 5 min indicating the formation of Silver nanoparticles, which was further confirmed by UV–Vis spectroscopy. The synthesized nanoparticles were dispersed in the modified polymer matrix and sonicated for 30 min to get a uniform distribution. Polymer–metal nanocomposites (PMNC) were synthesized with different wt% of Silver nanoparticles. Polymer Silver Nanoparticles (PSNC) with 0.05%, 0.1%, 0.15% were named as PSNC-1, PSNC-2, PSNC-3 respectively. The prepared solution was dried by using Rotary evaporator and redispersed in DMF was used for further characterization.

2.2. Characterization

The linear optical properties of all the samples were recorded, dispersing the samples in DMF using a UV–Visible spectrophotometer (wsp-UV-580pc). The elemental analysis and morphological characterization of the polymer and silver nanocomposites were done using Energy Dispersive Analysis of X-ray (EDAX) integrated with Scanning Electron Microscopy (SEM) (F E I Quanta FEG 200) Size of the Silver nanoparticles in the polymer matrix were examined using High Resolution Transmission Electron microscopy (HR-TEM) (JOEL 3010). The non-linear optical (NLO) properties were investigated by open aperture (OA) Z-scan technique.

OA-Z-scan technique was employed for the investigation of the effect of incorporation of Silver nanoparticles on the third order nonlinear optical properties of the polymer. Non-linear absorption properties and optical limiting response of the samples were