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Nonlinear absorption enhancement of AuNPs based polymer nanocomposites

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ABSTRACT

Au nanoparticles (AuNPs) based polymer nanocomposites with high nonlinear absorption coefficient were synthesized by UV-photocuring. AuNPs were synthesized by laser ablation method in liquid monomer isodecyl acrylate (IDA). In this research, two colloids with 70 nm and 20 nm nanoparticles average sizes were studied. Size control was performed with SEM and STEM. Prepared nanomaterials exhibit strong third-order nonlinear optical responses under CW laser irradiation at 532 nm, which was estimated by using z-scan technique performed with open aperture. It was found experimentally that nonlinear absorption β is almost twice higher for nanocomposites with smaller AuNPs.

1. Introduction

Composites of polymers and nanoparticles are finding great interest for their potential applications in molecular electronic devices, sensors, biosensors etc. [1–4]. Nanocomposites composed of noble metal nanoparticles (such as Pt, Au, Ag, and Pd) are currently of great research interest due to the unique optical, charge storage and catalytic properties of metal nanoparticles [5,6]. Among those noble metals, Au nanoparticles are inorganic nanomaterials with excellent chemical and physical properties, and, also, show interesting nonlinear optical properties, such as high third order nonlinear susceptibility and self-defocusing [7].

Among nonlinear optical effects, optical limiting of laser radiation and light-induced changes in refractive index occupy a prominent position. A successful optical limiter should strongly attenuate intense, potentially dangerous laser beams, while exhibiting high transmittance for low intensity ambient light and protect delicate optical instruments, especially the human eye [8,9]. The mechanism of optical limiting is mainly attributed to various optical processes, such as multiphoton absorption, thermal heating, free-carrier absorption, light-induced scattering, reverse saturable absorption, and so on. The *Z*-scan method is a well-known and widely-used technique to characterize the nonlinear optical properties of materials, including nonlinear absorption, scattering, or refraction [10–15].

In the present study, we investigated nonlinear absorption of polymer nanocomposites based on gold nanoparticles (AuNPs), and its probable dependence on nanoparticles sizes. AuNPs were prepared by laser ablation and fragmentation (for size reduction) in a liquid monomer. The method is promising physical process of nanoparticles synthesis and their incorporation in polymer matrices [16–20]. Laser ablation in liquid consists of instantaneous material removing from target surface and form nanoparticles in liquid volume, so there is no need for chemical synthesis reactions, the method is universal and has no contamination of reaction products and allow to overcome nanoparticles synthesis difficulties of chemical methods. With this method, nanoparticles of various materials can be obtained, including nanoalloys of thermodynamically forbidden compounds [20].

2. Materials and methods

Chemically pure gold (Testbourne Ltd., G4-9000-D5, 99.99%) was used as a target for laser ablation.

The monomer isodecyl acrylate (IDA, Aldrich, number # 408,956, CAS # 1330-61-6) was used as a liquid for laser ablation. IDA is aliphatic monomer with long molecular chain and to produce IDA based solid films it is necessary to use cross-linking diacrylates (Fig. 1). In this study DIOL (1,6-Hexandiol diacrylate, Aldrich 246816, CAS Number 13048-33-4) was used.

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Fig. 1. Structural formulas of monomer isodecyl acrylate (IDA) and cross-linked monomer 1.6 Hexanediol diacrylate (DIOL).

For laser ablation and fragmentation Nd: YAG laser was used (Sol instruments LF117, 1064 nm, 532 nm) with a pulse repetition rate of 10 Hz, a pulse energy of 30–50 mJ, and 10 ns pulse width. In this case, a two-step approach can be followed for the generation of monodispersed NPs. In the first step, high laser energies are used for the production of NPs colloids of wide size distribution. While, in the second step the produced NPs colloids are further processed by a focused laser beam with certain parameters, providing the final monodispersed colloids [21,22].

The experimental setup for the laser ablation and fragmentation is shown in Fig. 2a. In first step, laser beam (wavelength 1064 nm) was focused on the target through the liquid layer of 5 mm thick with spot diameter about 200 μm. Irradiation of target endured for 5 min and accompanied by a homogeneous liquid staining in a characteristic purple color (Fig. 3b). Concentration of nanoparticles in solution was estimated by weight measurement of target before and after ablation. Approximate concentration rate for this study was about 1 mg/ml. Then, for second step, obtained colloidal solution was illuminated with 532 nm laser with constant magnetic stirring. During illumination color change of colloid was observed, this procedure endured till color of colloid became as red (orange) as possible and was not controlled by spectroscopy during experiment. Such wavelength choose is explained as fact, that forming colloid is more transparent for 1064 nm radiation, than for 532 nm, because of plasmon resonance band of AuNPs, thus lower laser intensity will be not enough to produce concentrated colloid.

Colloidal solutions obtained by first step only and after fragmentation were studied by UV–visible spectroscopy with UV-spectrometer Shimadzu UV-1800. Further, drops of colloidal solutions were placed on a silicon substrates and heated to the monomer evaporation temperature. Images of AuNPs obtained by laser ablation and fragmentation were received with a scanning electron microscope (SEM and STEM) Carl Zeiss Merlin.

In colloidal solutions (AuNPs + IDA) DIOL was added by intensive stirring with ultrasonic disperser. Then polymerization initiator 2,2-dimethoxy-2-fenilatsetofenol (0.5%) was injected into the monomer mixture as a methylene chloride solution. The composition was irradiated with UV lamp (365 nm) for 10–15 min. The surface of the obtained films was treated with isopropyl alcohol to remove residual monomer and put in thermostat for 12 h with temperature 50 °C to complete polymerization.

The refractive indices of the polymer matrices and polymerized nanocomposites were also measured for comparison by an Abbe refractometer.

Nonlinear absorption of polymer nanocomposites were studied by z-scan technique [10–15], the experimental setup is shown in Fig. 2b. In this work nonlinear optical properties of AuNPs based polymer nanocomposites were measured by z-scan technique with open aperture.

When the high-intensity laser radiation come through substance the Lambert-Beer linear absorption and transmittance T law becomes dependent on radiation intensity I. In this case, attenuation of laser radiation intensity can be found as

$$\frac{dI}{dz} = -(\alpha_0 + \beta I)I,$$

where α_0 and β are linear and nonlinear absorption coefficients, respectively.

The connection between β and substance parameters depends on nonlinear absorption mechanism. In the case of two-photon absorption this coefficient is related to imaginary part of third-order nonlinear susceptibility

$$\mathrm{Im}\{\chi^{(3)}\} = \frac{n_0^2 \varepsilon_0 c \lambda \beta}{2\pi},$$

where ε_0 is the vacuum permittivity, c is the speed of light in vacuum, and n_0 is the linear refractive index.

Calculations of the nonlinear absorption coefficients β from the open aperture Z-scan data were performed using the formula [12,15]:

$$\beta = 2\sqrt{2}\frac{\Delta T}{I_o L_{eff}}$$

where ΔT is the difference between nonlinear and linear transmittance of the sample. L_{eff} is given as follows:

$$L_{eff} = \frac{1 - e^{-\alpha L}}{a}$$

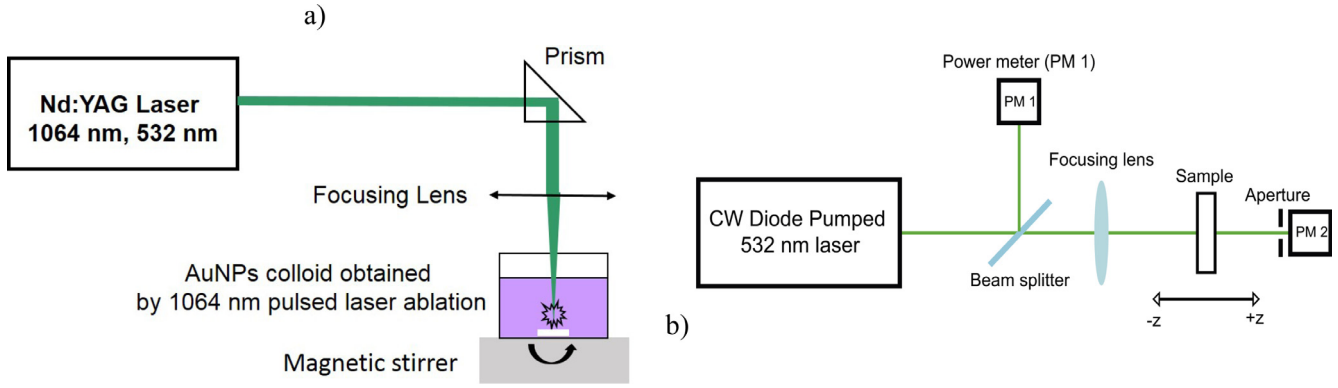

Fig. 2. Experimental setup: (a) Laser ablation and fragmentation, (b) Z-scan technique.