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Optical, structural and nonlinear optical properties of laser ablation synthesized Ag nanoparticles and photopolymer nanocomposites based on them

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ABSTRACT

In this work Ag nanoparticles (NPs) stable colloid solution were prepared by laser ablation of chemically pure silver rod in liquid monomer isodecyl acrylate (IDA). Sizes of obtained nanoparticles were determined by scanning electron microscope and vary from 27 to 120 nm. Nanocomposites films were prepared from obtained stable colloid solution of AgNPs by photocuring. For aliphatic polymer IDA long molecules cross-linking Diurethane dimethacrylate, 1,6-Hexandiol diacrylate and Tetra (ethylene glycol) diacrylate were used. Prepared nanomaterials exhibit strong third-order nonlinear optical responses, which was estimated by using z-scan technique. The third-order nonlinear optical coefficients of the studied nanocomposites were found to be up to $Re\chi^{(3)}=1.31\times10^{-5}$ (esu) and $Im\chi^{(3)}=7.64\times10^{-5}$ (esu).

1. Introduction

The widespread use of laser technology in various fields of human activities has led to the need for optical materials with specific properties, in particular, nonlinear optical properties. There are plenty of potential materials for this field - carbon nanostructures, organic dyes and metallic nanoparticles [1]. Metal nanoparticles in dielectrics exhibit large optical nonlinearity, are characterized by high polarizability, fast response, caused by effects such as two-photon absorption, self-focusing/defocusing, etc. In this regard, metal nanomaterials and nanocomposites are of great practical interest, for example, for the creation and improving of photonics devices, especially in the field of information transmission, and to an optical limiting [2]. Nonlinear optical properties of the nanocomposite with metal nanoparticles are caused by nonlinear polarization of matter under the influence of the light wave, in this case - a nonlinear dependence of the electrons shift in the plasmon resonance on peak value of the light field vector E [3].

In this study photopolymer nanocomposites based on aliphatic polymers and silver nanoparticles (AgNPs) are applied. Polymers elements allow to perform any desired size, shape and distribution of nanoparticles in the bulk. The main challenge for creating photopolymer nanocomposites based on metallic nanoparticles is the introduction of nanoparticles in the monomer composition.

Currently, there are several methods for metal nanoparticles synthesis based on carrying out chemical reactions and, hence, of having to remove the reaction products and the need to transfer the nanoparticles from the reaction medium, which is not always feasible. The method of laser ablation in liquids does not have these disadvantages, this method consists of instantaneous evaporation and condensation of vapor to form a nanoparticles. Since in this case there is no need for chemical synthesis reactions, the method is more universal and has no contamination of reaction products. Obtaining nanoparticles by laser ablation of metals in liquids is considered, for example, in [4–8].

Furthermore, this method carrying out in liquid monomer, it allows monomer adsorption on the surface of the newly formed nanoparticles and the formation of stable colloidal solutions. Obtained colloidal solution of nanoparticles in the monomer can be used to form solid films of polymer nanocomposites by photocuring.

2. Materials and methods

Laser ablation in liquid method is instantaneous material removing (evaporation) from the surface of the irradiated target. Vapor bubbles produced during the ablation condensate and collapse leads to the formation of nanoparticles in the liquid.

Chemically pure silver (Kurt J Lesker Company ltd., EVMAG40SHOT1, 99.99%) was used as a target for laser ablation.

The monomer isodecyl acrylate (IDA, Isodecylacrylate, Aldrich,

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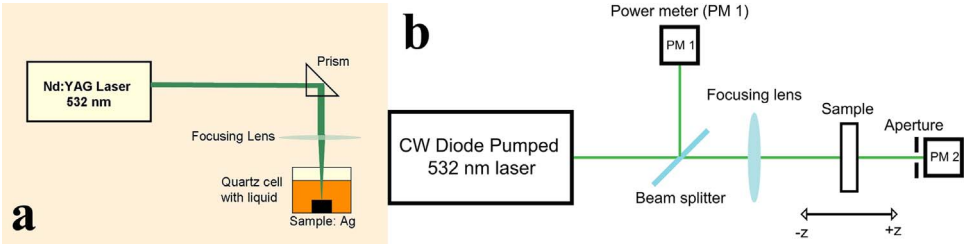

Fig. 1. Experimental setup a) laser ablation, b) z-scan. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

number # 408,956, CAS # 1330-61-6) was chosen as a liquid for laser ablation.

For laser ablation Nd: YAG laser was used (Sol instruments LF117, 532 nm) with a pulse repetition rate of 10 Hz, a pulse energy of 30 mJ, and 10 ns pulse width.

The experimental setup for the laser ablation is shown in Fig. 1a. The target was placed at the bottom of the quartz cell filled with liquid. The laser beam is focused onto the target through the liquid layer of 2–5 mm thick. Irradiation was carried out for 5 min and was accompanied by a homogeneous liquid staining in a characteristic red-brown color..

Obtained AgNPs in the form of a colloidal solution have been investigated by UV–visible spectroscopy with UV-spectrometer Shimadzu UV-1800. Further, the obtained colloidal solution was placed on a silicon substrate and heated to a temperature of the monomer evaporation to isolate the nanoparticles. Images of AgNPs obtained by laser ablation were received with a scanning electron microscope (SEM) Carl Zeiss Merlin.

IDA is a photocurable monomer; however, to produce solid films on its base diacrylates should be used for IDA molecules crosslinking. In this study following diacrylates were used: UDMA (Diurethane dimethacrylate, Aldrich 436909, CAS Number 72869-86-4), DIOL (1,6-Hexandiol diacrylate, Aldrich 246816, CAS Number 13048-33-4) and TEGDA (Tetra (ethylene glycol) diacrylate, Aldrich 398802, CAS Number 17831-71-9). Polymerization of AgNPs colloidal solution in IDA and diacrylates occurred by using a polymerization initiator 2,2-dimethoxy-2-fenilatsetofenol (0.5%). The initiator was injected into the monomer mixture as a methylene chloride solution. The composition was mixed thoroughly using an ultrasonic disperser. Further colloidal solution was placed on the surface of polyester between spicers height of 1 mm to form a film of a certain thickness, and cover the top in the same polyester for oxygen limitation that prevents photocuring. 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.

Nonlinear optical properties (nonlinear optical absorption and refraction) of colloidal solution (monomer IDA+AgNPs), polymer matrixes (IDA+DIOL, IDA+TEGDA and IDA+UDMA) and polymer nanocomposites (AgNPs+IDA+DIOL, AgNPs+IDA+TEGDA, and AgNPs+IDA+UDMA) were studied by z-scan technique [9], the experimental setup is shown on Fig. 1b.

The experiment used a collimated beam (5 mm diameter) of Diode Pumped laser (532 nm, 140 mW, 0.7 W/cm^2) radiation, operating in continuous mode (CW). The beam was focused by a lens with a focal length of 6 cm and waist length 6 mm. Scanning was performed on samples of 8–12 mm on both sides of focus.

This method consists of laser radiation transmitted by sample intensity registration as it (sample) moves along the laser beam, with the passage of the beam waist and the point of focus, where the light intensity is maximal (with the diameter of the laser beam 200 μm, 1.4 kW/cm^2). Magnitude of laser radiation intensity increased in orders at the point of focus allows to evaluate the nonlinear optical properties of the samples.

Calculations of the nonlinear absorption coefficients β from the open aperture Z-scan data were performed using the formula [9,10]:

$$\beta=2\sqrt{2}\frac{\Delta T}{I_0 L_{eff}} \quad (1)$$

where ΔT is the difference between nonlinear and linear transmittance of the sample.

Calculations of the nonlinear refractive indexes n_2 from normalized transmittance Z-scan curves were performed using the formula [9,10]:

$$n_2 = \frac{\Delta\phi_0\lambda}{2\pi L_{eff} I_0} \quad (2)$$

where λ is the wavelength, L_{eff} is the effective thickness of the sample, I_O is the laser radiation intensity at the focus spot, and $\Delta\varphi_O$ is the phase distortion given from the difference between peak and valley transmission ($\Delta T_{P\text{-}\upsilon}$) as follows:

$$\Delta T_{p-v} = 0.406(1-S)^{0.25}|\Delta\phi_0| \quad (3)$$

where S is the aperture linear transmittance. L_{eff} is given as follows:

$$L_{eff} = \frac{1-e^{-\alpha L}}{\alpha} \quad (4)$$

where α is the linear absorption of the sample and L is the sample thickness.

The experimental measurements of the nonlinear refractive index n_2 and absorption coefficient β were used for determination of the real and imaginary parts of the third-order nonlinear optical susceptibility ($\chi^{(3)}$) according to the following equations [9,10]:

$$Re\chi^{(3)}(esu) = \left(\frac{10^{-4}\varepsilon_0 c^2 n_0^2 n_2}{\pi}\right)\left(\frac{cm^2}{W}\right) \quad (5)$$

$$Im\chi^{(3)}(esu) = \left(\frac{10^{-2}\varepsilon_0 c^2 n_0^2 \lambda\beta}{4\pi^2}\right)\left(\frac{cm^2}{W}\right) \quad (6)$$

where ε_O is the vacuum permittivity, c is the speed of light in vacuum, and n_O is the refractive index.

3. Results and discussion

The main way to detect not agglomerated AgNPs is optical spectroscopy in the visible region. Plasmon resonance peak of AgNPs is in the range of 400–430 nm [11].

Fig. 2a shows that the optical absorption spectrum of laser ablation in IDA synthesized AgNPs has a maximum in the region 400–450 nm. SEM images of obtained nanoparticles are shown in Fig. 2b, the dimensional distribution of the nanoparticles in Fig. 3c.

Laser ablation does not lead to photocuring or photodegradation of liquid monomer. Ablation processes are similar to the processes in classical liquids (water, organic solvents), in which the obtaining of metal nanoparticles widely studied previously. Since in this case the nanoparticles are formed directly in the liquid medium of the surfactant monomer, so they are stabilized in it. A colloidal dispersion of metal nanoparticles is stable for a long time and can be transformed into a solid polymeric film with photocuring of monomer.

Fig. 3 shows the optical absorption spectra of the films IDA+UDMA and AgNPs+IDA+UDMA, IDA+DIOL and AgNPs+IDA+DIOL, IDA +TEGDA and AgNPs+IDA+TEGDA (concentration AgNPs 1 mg/mL,