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Synthesis and nonlinear optical behavior of Ag nanoparticles in PMMA

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ABSTRACT

In this work we have synthesized silver nanoparticles in Poly (methyl methacrylate) (PMMA). This was achieved by polymerizing the mixture of monomer and corresponding metal compound, followed by post-heating treatment. The linear absorption coefficient of the samples was measured using a spectrophotometer, where an absorption peak at 420 nm was observed. This peak grows up and shifts as a function of the concentration of the radical initiator. The linear refractive index was measured using the Fresnel equations and agrees with previous reported results. The nonlinear properties were obtained using the single lens *Z*-scan method, where the nonlinear absorption coefficient ($\Delta\alpha$) was found between 5.5975514 and 17.9483493 cm^{-1}. The nonlinear refractive index coefficient ($\Delta\eta$) was found to be negative and its value oscillates between 12.9099 E-06 and 22.4276 E-06. Finally, the third-order coefficient ($\chi^{(3)}$) was calculated in the range of 233–787 E-9 esu.

1. Introduction

In the last decades, photonics based on nonlinear optics have been trying to develop fast and integrated optical devices by using some nonlinear features such as nonlinear refractive index or nonlinear absorption coefficient, among others [1–6]. As a result, several groups have developed numerous studies at the molecular design level. The studies have shown that the hybrid materials (organic host with inorganic particles) have high nonlinear coefficients, more bandwidth, high damage threshold, nonlinear control with lower voltage, low fabrication costs, low insertion losses caused in a hybrid-device junction, high-energy conversion efficiency and of course, the nonlinear characteristics of the hybrid material can be modified as we change the inorganic dopant. One of the most important characteristics of these hybrid materials (metallo–organic) resides in its high-molecular hiperpolarisability, which is a consequence of the electronic transfer between metallic atoms and the interacting organic part [7].

As light travels through the material a variety of nonlinear optical effects may occur. The interaction of the light with such material will cause the material's properties to change, so the next photon will practically interact with another material. Particles in these nano-dimensions have very particular properties well described by the corresponding Mie electromagnetic theory [8], in particular metallic particles [9]. However, in the range of a few nanometers ~10 nm they show a characteristic nonlinear behavior that arises either from the confinement of its plasmon [10], a size dependent feature extensively discussed by Uchida [10], or from the size of the cluster [11]. In this work, we report the synthesis of Ag nanoparticles contained in Poly (methyl methacrylate) (PMMA) in order to study their nonlinear optical properties, their dependence on the post-heating treatment and the density of Ag nanoparticles as well.

2. Experiment

The preparation of nanometer-sized silver is done by using the reduction process of organometallic compounds in a polymer matrix. The fabrication process consists of the following four steps:

(1) Preparation of a solution for coating: An organometallic compound, a reducing agent, and an amorphous polymer are dissolved in organic solvents. These ingredients do not react with each other at room temperature.
(2) Casting this solution on a substrate.

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(3) Drying the cast film at room temperature: The film remains colorless and transparent.
(4) Heating the film at 120 °C for several seconds: The organometallic compounds are reduced to metal and the film becomes colored.

In order to obtain the silver coating, we used the solution: 0.2 g of silver heptafluorobutyrate, 0.2 g of Sumilizer GM (2-tbutyl-2hidroxy-5-methylbenzyl)-4-methylphenyl acrylate) and 4.5 g of polyvinyl butyral (BM-2 manufactured by Sekisui Chemical Co., Ltd.) dissolved in a mixture of 41.6 g of 2-butanone and 13.9 g of toluene. The coating solution was cast onto a PMMA film with a thickness of 125 μm. The cast layer was dried at room temperature and then heated at 120 °C. The chemical reaction results in the growth of the metal particles and could be understood as follows.

When the cast film is heated, the reduction of the organometallic compound is carried on throughout the homogeneous phase of the amorphous polymer matrix. At the initial stage of heat treatment, a large number of metallic silver are randomly formed. As the heat treatment progresses, the organosilver compound diffuses from the homogeneous phase and silver clusters grow to nanometer-sized particles. In the fabrication process of highly reflective recording materials reported in [12], they used palladium which reacts with organic silver salt as a catalyst. In our case, however, silver particles were synthesized uniformly without adding palladium. We assume that silver cluster itself acts as catalyst for the reduction. The reactions are expressed by the following scheme:

$$\mathrm{nRCOOAg} + \mathrm{n}\phi\text{-OH}\text{----------------}(\mathrm{Ag}^0)_\mathrm{n} + \mathrm{nRCOOH} + \mathrm{n}\phi = 0 \quad (1)$$

In order to investigate the dependence of the optical properties of the material with respect of the fabrication parameters, we prepared six samples (films) by varying Ag concentration and time duration of heat treatment as is stated in Table 1.

Linear optical properties were first obtained for each sample. The linear transmission spectra were obtained using a UV–visible spectrophotometer Lambda 3B (Perkin Elmer) from 350 to 850 nm by 2 nm step. We observed an absorption band peak at 420 nm for all the silver-dispersed films and the amplitude of this peak increases, shifts and get wider as heat treatment increases. We used the results obtained by this technique, as well as those obtained by the transmittance technique (i.e. measuring transmitted and reflected intensity of an incident beam) and the Z-scan technique (i.e. focusing a beam over the sample and measuring the far field intensity) in order to estimate the linear absorption coefficient of each sample, and the results are shown in Table 2. Linear refractive index estimations were obtained by using Fresnel coefficients and Table 3 shows the obtained values.

Table 1
Description of the features of each of the six samples reported here, where we have varied the Ag concentration and the post-heating treatment

Sample number	Sample	Ag concentration (μmol)	Heat treatment temperature (120 °C) Time (*s*)
1	Ag(10)/90	10	5400
2	Ag(10)/120	10	7200
3	Ag(10)/30	30	1800
4	Ag(10)/120	30	7200
5	Ag(10)/180	50	10,800
6	Ag(10)/120	50	7200

Table 2
Linear absorption coefficient for each sample obtained by using three different methods; a spectrophotometer, a transmitted/reflected intensity and the *Z*-scan technique

Sample	Spectrophotometer technique	Transmittance technique	*Z*-scan technique
1	1.54733	1.5751	1.9396
2	2.4405994	2.4231	2.4216
3	2.006047265	2.08266	2.2001
4	3.54137587	3.6264	3.6299
5	4.960343936	4.6745	4.6266
6	5.129537889	5.6266	5.5109

Table 3
Linear refractive index obtained for each sample by using Fresnel coefficients

Sample	Transmittance (T)	Reflectance (R)	Refraction index (n_0)
1	0.837736178	0.06199864	1.663584666
2	0.77025242	0.06088080	1.655610249
3	0.779050379	0.05912902	1.643062151
4	0.67388240	0.05682148	1.626430606
5	0.609554124	0.050713626	1.58176269
6	0.577734112	0.046846684	1.552909312

Table 4
Nonlinear absorption coefficients and nonlinear refractive index for each sample using *Z*-scan method

Sample number	Nonlinear absorption coefficient $\Delta\alpha$ (cm^{-1})	Nonlinear refraction index ($\Delta n \times 10^{-6}$)
1	6.045379	3.0004
2	6.267247	3.0929
3	6.173444	4.1766
4	13.080480	5.7220
5	17–234714	8.5762
6	23.402806	9.8348

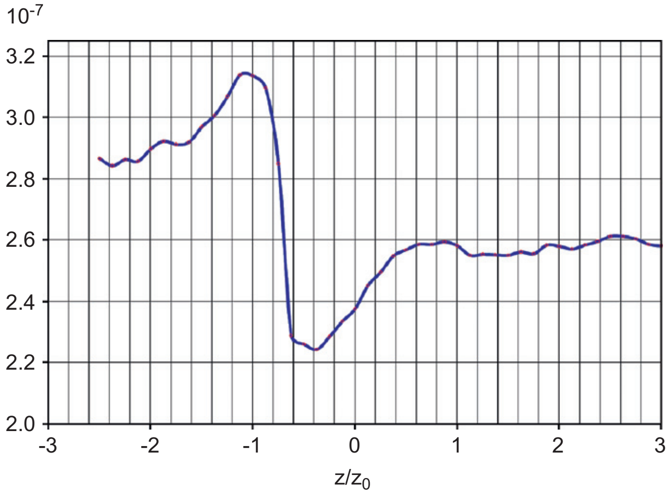

Fig. 1. A *Z*-scan plot from sample 5. The graph denotes a nonlinear negative optical behavior of the sample. The far field intensity detector was blocked with a 10% pinhole.

Nonlinear optical characterization was developed using the Z-scan method with the following experimental parameters: lens focal length $F = 25.4$ mm, focal back length $Fb = 17.9$ mm, beam wavelength $\lambda = 632.8$ nm, beam diameter $D = 0.63$ mm, and beam divergence $\varphi = 1.3$ mrad. Later on, we calculated the minimal beam waist (w_o) and the diffraction length (Z_o) which are 16.242 μm and 2.619 mm, respectively. Finally we can obtain the peak valley (Z_{pv}) value and the initial beam intensity (I_{o}) as 4.5 mm and 917×10^{-6} MW cm^{-2}.

For each sample, we have recorded the far field normalized transmittance by using a non blocked detector to estimate the nonlinear absorption coefficient and by using a blocked (4.5% and 10% of the total intensity) detector for nonlinear refractive index estimation. We calculated the nonlinear absorption for each sample and are shown in Table 4, while Fig. 1 shows one of the obtained plots for the nonlinear refractive index, in particular from sample #5. Third column of Table 4 also shows the obtained values for nonlinear refractive index in each sample for a 10% transmittance detector aperture. Our results claim a linear response of the nonlinear absorption coefficient respect the heat treatment as well as a linear response of the nonlinear absorption coefficient respects of the Ag concentration. By plotting the dependence of the nonlinear refractive index of the samples we found that it also has a direct relation with respect to the heat treatment and the Ag concentration, nevertheless the dependence of the heat treatment is not exactly linear.

4. Conclusions

Z-scan results show a negative nonlinear behavior for all samples. We also obtained the values of $\chi^{(3)}$ for samples 1 and 6, resulting 23.384×10^{-8} and 78.773×10^{-8} (esu), respectively. The nonlinear absorption coefficients for samples 1 and 6 were 6.045 and 23.402 (cm^{-1}), respectively. All these results agree with previous experimental reports for similar materials [13]. We can conclude that the nonlinear parameters, i.e. absorption coefficient and refractive index have a strong dependence on the time of the heat treatment as well as the concentration of the Ag particles. The linear parameters were calculated by using different methods and even when, in some of the samples they were similar, we noticed that either an increment in the concentration of Ag particles or extending the heat treatment time will increase the dispersion and reducing the sample optical quality. This last result implies that we have to be very careful if we plan to increase the nonlinear characteristics of the material by increasing the concentration of Ag nanoparticles or heat treatment duration.

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