In situ synthesis and nonlinear optical properties of Au:Ag nanocomposite polymer films

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We report a simple *in situ* synthesis procedure for Au:Ag nanocomposite polymer (NCP) films using polyvinyl alcohol as the reducing agent. Optical measurements show absorption bands of varying strengths around 530 and 410 nm. The presence of nanoparticles is confirmed from Transmission Electron Microscopy (TEM). Nonlinear optical response is studied using 7 ns laser pulses, for near-resonant and off-resonant excitation wavelengths (532 and 1064 nm, respectively). Samples exhibit saturable as well as induced absorption. These materials have the potential to be used as saturable absorbers and optical limiters. © *2006 American Institute of Physics.*
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It is well known that noble metal nanoparticles show an absorption due to surface plasmon resonance (SPR) in the visible region.[1] The resonance frequency depends on parameters such as nanoparticle morphology, concentration, and dielectric constant of the host where the nanoparticles are embedded. Chemical reduction using different reducing agents will result in nanoparticles of different sizes. The use of polymers like poly(vinyl acetate), poly(methyl methacrylate), and poly(*N*-acylethylenimine) as reducing agents has been reported before. For example, recently, Porel *et al.*[2,3] showed that poly vinyl alcohol (PVA) can be used to produce monodisperse Ag nanoparticles and polygonal Au nanoplates. Such *in situ* synthesis techniques offer additional advantages, such as the production of freestanding films, which can be mechanically manipulated for device applications. Apart from this, the incorporation of nanoparticles in a polymer matrix is found to change the optical properties of both materials. From a device point of view, polymer nanocomposites (NCPs) have found many potential applications in the fields of optics, electrics, mechanics, and photoconductors.[4] In this letter, we present a simple method to synthesize Au:Ag bimetallic nanoparticles with PVA used as a stabilizer and a reducing agent. The interest in bimetallic nanoclusters stems from the fact that it is possible to tune their SPR band by varying the concentration of the constituents. The absorptive optical nonlinearity is investigated using nanosecond laser pulses at the near-resonant wavelength of 532 nm and off-resonant wavelength of 1064 nm. The results are compared with those obtained from pure Au and Ag nanocomposite films, synthesized by the same route.

Poly vinyl alcohol (PVA) was purchased from Aldrich chemicals (MW 19000, 98% solubility). High purity $AgNO_3$ and $HAuCl_4.3H_2O$ were used for the reaction. The preparation procedure is as follows. An aqueous solution of PVA, where 1 g of PVA is dissolved in 25 ml of water, is initially prepared. It is then mixed with a solution of silver nitrate [hydrogen tetrachloroaurate (III) hydrate] and stirred. The initial weight ratio of $AgNO_3(HAuCl_4.3H_2O)/PVA$ is 0.005. For the production of bimetallic nanoparticles $AgNO_3$ and $HAuCl_4.3H_2O$ are taken in the 4 mg:1 mg ratio, dissolved in water, and then mixed with the PVA solution. The solutions are poured into petry dishes, covered, and kept undisturbed in ambient conditions. The slow reduction of silver and gold ions results in the formation of nanoclusters of different sizes. Initially, the mixture of PVA and $AgNO_3/HAuCl_4.3H_2O$ looks colorless/pale yellow. After 24 h the Ag-PVA solution becomes pale green, and the Au-PVA solution becomes light red. After 20 days, the color changes to dark brown for Ag-PVA, dark red for Au-PVA, and dark blue for Au:Ag-PVA. The obtained films are approximately 100 μm in thickness. To obtain the alloy nanoclusters, the Au:Ag-PVA films are annealed at 120 °C in air for different time periods of 15, 30, and 60 min (named as Au:Ag-PVA_15, Au:Ag-PVA_30, and Au:Ag-PVA_60, respectively). It may be noted that in this *in situ* formation of gold/silver and bimetallic nanoparticles in the PVA matrix, no additional reducing agents are employed. PVA acts as the sole reducing agent, which reduces the Ag^+ and $AuCl_4^-$ ions. Samples were kept in airtight containers, and were taken out only while performing the experiments.

Optical absorption measurement is an initial step to observe the monometal and bimetallic nanoparticle behavior. Figures 1(a) and 1(b) show the absorption spectra measured on a Perkin-Elmer spectrophotometer. For Ag and Au, the
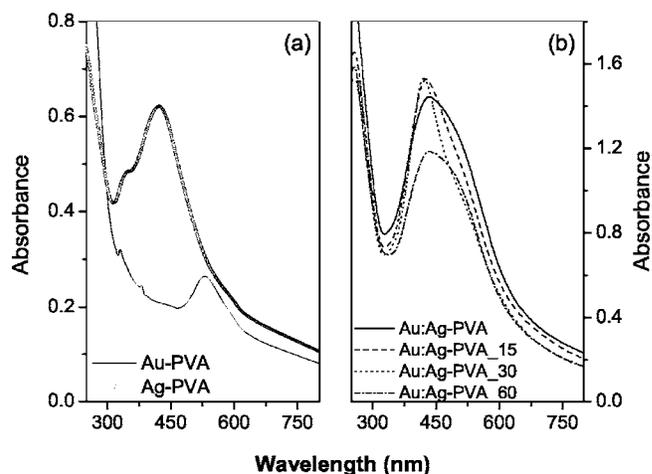

FIG. 1. Absorption spectra of (a) Au-PVA and Ag-PVA nanocomposites, (b) as-prepared and annealed Au:Ag-PVA nanocomposites.

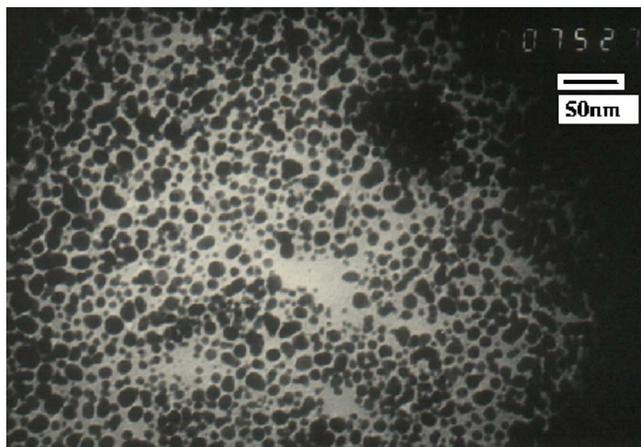[a)]Electronic mail: balkarin@yahoo.com
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FIG. 2. TEM image of the Ag-PVA film.

FIG. 4. (Color online) Z-scan curves of the samples at 1064 nm, 7 ns excitation. Solid lines are numerical fits to the experimental data, using Eq. (3). The laser pulse energy is 1 mJ.

SPR band lies in the 410 and 530 nm regions, respectively. On the other hand, the as-prepared Au:Ag nanoparticles show a broadened resonance showing bimetallic behavior. When annealed for 15 and 30 min, respectively, the peak at 410 nm grows, but when annealed for 60 min, the broadening reappears. We believe that with moderate annealing the Ag ions get reduced, forming a core-shell structure where an Au:Ag alloy core is enclosed by Ag shell.[5] When annealed for 60 min the shell disappears. A transmission electron micrograph (TEM) picture of the Ag-PVA film, recorded using a JEOL JM200CX micrograph, is shown in Fig. 2. The average particle size is seen to be about 10 nm.

The nonlinear transmission properties of the NCPs were investigated using 7 ns laser pulses at 1064 and 532 nm, available from a frequency doubled Q-switched Nd: YAG laser. The intensity dependent transmission was measured using an automated open aperture z-scan setup.[6] In our experiment we used a lens of 20 cm focal length. The pulse-to-pulse energy stability of the laser was found to be approximately ±5%. The pulse repetition rate was approximately 1 Hz.

Figure 3 shows the nonlinearity observed at 532 nm. An absorption saturation behavior is found in films containing only Au. However, the saturation changes over to induced absorption in all other films when the input intensity is in-
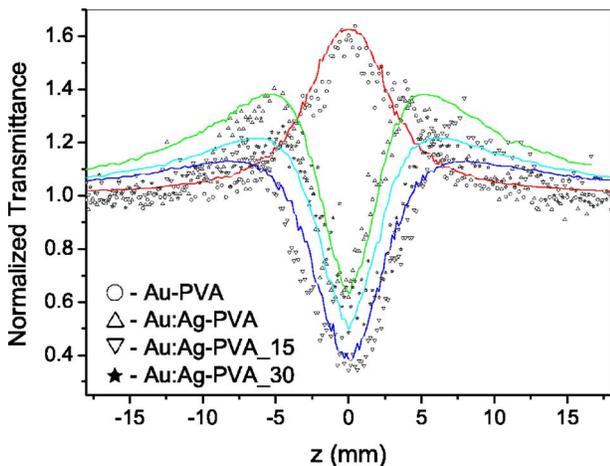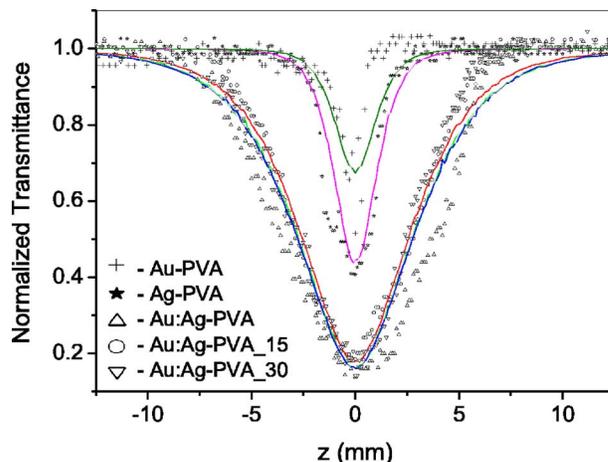
creased. Such a changeover in the sign of the nonlinearity is related to the interplay of plasmon band bleach and optical limiting mechanisms, as found from earlier studies of noble metal nanoparticles in liquid and glass media.[7,8] Such behavior can generally be modeled by defining a nonlinear absorption coefficient $\alpha(I)$, which is a sum of independent positive and negative transmission coefficients[9]

$$\alpha(I) = \frac{\alpha_0}{1 + (I/I_s)} + \beta I, \tag{1}$$

where α_0 is the linear absorption coefficient, I is the laser intensity, and I_s is the saturation intensity. Now the open aperture normalized transmittance can be written as[6]

$$T(z) = [1/\pi^{1/2}q(z)] \int_{-\infty}^{+\infty} \ln[1 + q(z)\exp(-\tau^2)]d\tau, \tag{2}$$

where $q(z) = \alpha I_0 L/[1 + (z/z_0)^2]$, with I_0 being the peak intensity at the focal point. L is given by $[1 - \exp(-\alpha_0 l)]/\alpha_0$, where l is the sample length, and $z_0 = \pi\omega_0^2/\lambda$ is the Rayleigh range, where ω_0 is the beam waist radius at focus and λ is the light wavelength.

Figure 4 shows the nonlinear absorption at 1064 nm. At this off-resonant excitation wavelength there is no local field enhancement within the particles, and hence, higher pulse energies up to 1 mJ are required to induce nonlinearity in the films. Such high pulse intensities do not seem to cause any damage to the films. Interestingly, films containing only Au or Ag nanoparticles show a minimum nonlinearity at this wavelength, while the alloy films clearly exhibit a larger induced absorption behavior. The obtained nonlinearity is found to be of the fifth order, as it fits only to a three-photon absorption process. The corresponding net transmission is given by[10]

$$T = [(1 - R)^2 \exp(-\alpha_0 l)/p_0\sqrt{\pi}]$$

$$\int_{-\infty}^{\infty} \ln[\sqrt{1 + p_0^2 \exp(-2t^2)} + p_0 \exp(-t^2)]dt, \tag{3}$$

where R is the surface reflectivity. p_0 is given by $2\gamma(1 - R)^2 I_0^2 L$, where γ is the three photon absorption coefficient and I_0 is the on-axis peak intensity. The calculated nonlinear coefficients given in Table I show fairly high values of non-

FIG. 3. (Color online) Z-scan curves of the samples at 532 nm, 7 ns excitation. Solid lines are numerical fits to the experimental data, using Eq. (2). Laser pulse energy is 30 μJ.

TABLE I. Values of the saturation intensity (I_s), two-photon absorption coefficient (β), and three-photon absorption coefficient (γ), calculated from numerical fits to Eqs. (2) and (3).

Polymer nanocomposite film	$\beta(\times 10^{-9})$(m/W) (532 nm excitation)	$I_s(\times 10^{11})$(W/m^2) (532 nm excitation)	$\gamma(\times 10^{-24})$(m^3/W^2) (1064 nm excitation)
Au-PVA	1	50	1.5
Ag-PVA	20	11	5
Au:Ag-PVA	70	8	200
Au:Ag-PVA_15	159	6	200
Au:Ag-PVA_30	70	8	240

linearity. The three photon absorption coefficient increases substantially in the bimetallic and core-shell nanocomposites, as compared to pure Au and Ag. More studies are required to find out the exact reasons for this behavior.

To estimate the stability of the samples over a period of time, the spectral and z-scan measurements were repeated about 80 days after the first set of experiments. Whereas in the first set of experiments laser-induced damage occurred in the films above 30 μJ (532 nm) and 1 mJ (1064 nm) pulse energies, in the second set, damage thresholds were found to be reduced for all films other than Au-PVA. The absorption spectrum of Au-PVA showed some amplitude change from the earlier spectrum, but the change for Ag-PVA was much more pronounced. Among the alloy samples, the absorption spectrum changed the most for Au:Ag-PVA_15, while the change was the least for Au:Ag-PVA_60. All films, however, retained the SPR features substantially in their spectra. Thus Au-PVA seems to be the most stable sample, and for the annealed samples, longer annealing times result in better stability.

In conclusion, we have synthesized Au, Ag, and Au:Ag nanocomposite polymers through a simple chemical reduction process employing PVA, and determined their nonlinear optical response to nanosecond laser pulses for near- and off-resonant optical excitations. For resonant excitation, the sign of the nonlinearity is dependent on sample composition and input laser fluence, while for off-resonant excitation the samples exhibit induced absorption caused by three-photon absorption. Hence these materials can be used either as saturable absorbers or optical limiters at the appropriate wavelengths and pump intensities.

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