Optical power limiting in the femtosecond regime by silver nanoparticle–embedded polymer film

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A simple methodology is developed for the fabrication of freestanding polymer films with embedded silver nanoparticles grown in situ. Strong nonlinear absorption, positive nonlinear refraction, and efficient optical limiting in the femtosecond regime are demonstrated with these films. Additional investigations with supported films as well as parallel studies in the nanosecond regime are also presented. The freestanding nature of the films is not only of potential interest from the application perspective but also facilitates the unambiguous determination of the nonlinear coefficients of the metal nanoparticles embedded in polymer matrix without complications arising due to the contributions from the substrate. © 2007 American Institute of Physics.

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I. INTRODUCTION

Noble metal nanoparticles exhibit characteristic size and shape-dependent electronic structure leading to unique optical and nonlinear optical (NLO) properties. These attributes find application in a wide range of fields including electronics,1 photonics,2 plasmonics,3 and sensing.4 The plasmon absorption of metals such as copper, silver, gold, and palladium occurs in the UV-visible region of the spectrum. Multiphoton excitations in this energy range and further excited state absorptions can be exploited to elicit NLO responses from these nanomaterials. From a material point of view, it is advantageous to embed the metal nanoparticles in thin polymer films for optical and nonlinear applications.5,6 The polymer matrix serves not only as a medium to assemble the nanoparticles and stabilize them against aggregation but also with its characteristic mechanical properties should be uniquely suited for device applications. A methodology we have developed recently for the fabrication of metal nanoparticle–embedded polymer films6,7 involves further the advantage of in situ generation of the nanoparticles through the mediation of the functional groups on the polymer, preventing the need for external reducing agents as well as excluding potential hazards of inhalable free nanoparticles.8 Our protocol also facilitates the liberation of freestanding nanoparticle-embedded polymer films; choice of appropriate film thickness allows direct imaging in a transmission electron microscope and other materials characterizations as well as applications.

Optical power limiting, a phenomenon to which a range of processes including nonlinear absorption and nonlinear scattering can contribute, is an important area of application where metal nanoparticles are promising candidates.9,10 Optical limiters are ideally suited for the protection of human eyes and devices from damages that can be inflicted by high power lasers. Extensive studies have been reported on optical limiting in the nanosecond and picosecond time scales using metal nanoparticles;10 thermal effects may play a significant role in the optical limiting process at these time scales. Optical limiting of femtosecond pulses, involving higher input power in the terawatt regime and likely to be dominated by purely electronic responses, has been explored relatively less; some of the materials that have been investigated include semiconductor quantum dots,11 silver and gold nanocrystals,12,13 carbon nanostructures,14 fullerene functionalized polymers,15 and organometallics.16

We have reported earlier6 optical limiting in the nanosecond time scale by silver nanoparticle–embedded poly(vinyl alcohol) film layered over polystyrene (Ag-PVA/PS) supported on glass. It was demonstrated that films typically a few micrometers thick show characteristics comparable to colloidal silver with path lengths of a few millimeters. Nonlinear absorption in the nanosecond regime, of Ag/Au-PVA films typically 100 μm thick, has also been reported.17 We have now investigated the nonlinear absorption/refraction and optical limiting of femtosecond laser pulses by Ag-PVA coated directly on glass and more importantly, as freestanding films with the trilayer structure, PVA/Ag-PVA/PVA. The films with optimal concentrations of Ag show efficient responses and are quite stable against the high power laser irradiation. Unlike the case with nanosecond laser pulses, the high intensities associated with the femtosecond laser pulses can cause the substrates on which the films are coated to produce their own nonlinear responses. Open and closed aperture Z-scan experiments on the freestanding films allowed unambiguous estimation of the nonlinear absorption cross sections and nonlinear refraction due to the nanoparticles.
without the complications arising from the contribution of the glass substrate. Ag-PVA shows large nonlinear absorption ($\beta=2.2 \text{ cm/GW}$) and nonlinear refractive index ($n_2=1.20 \times 10^{-12} \text{ esu}$). Significantly, the $n_2$ dominated by electronic responses has a positive sign; experiments in the nanosecond domain revealed contrasting behavior, with negative nonlinearity possibly arising due to thermal contributions. The Ag-PVA films show nearly 90% linear transmission coupled with efficient optical limiting for femtosecond pulses; the freestanding nature of these composite films is a significant development from the point of view of device applications.

II. EXPERIMENT

A. Film fabrication

Required weight of silver nitrate ($\text{AgNO}_3$) dissolved in 1.0 ml water was mixed with 0.4 ml of a solution of polyvinyl alcohol (Aldrich, average molecular weight =13–23 kDa, % hydrolysis=86) in water (2.4 g PVA in 8 ml water) to prepare different compositions designated using the Ag/PVA weight ratio $x$ (for example, 5.5 mg of AgNO$_3$ gives $x=0.029$). The solution mixture was stirred for 5 min at 27–30 °C. Millipore MilliQ purified water was used in all operations. The glass substrate was cleaned by sonication with isopropyl alcohol, methanol, and finally acetone for 10 min each. The substrate required for fabricating freestanding films of Ag-PVA and samples for transmission electron microscopy (TEM) studies was prepared by spin coating a few drops of a solution of polyurethane, (average molecular weight=280 kDa) in toluene (1 g PS in 8 ml toluene) on glass, using a Laurell Technologies Corporation model WS-400B-6NPP/LITE/8K photoresist spinner, at 1000 rpm for 10 s followed by drying in a hot air oven at 85–90 °C for 15–20 min. Three kinds of AgNO$_3$-PVA films were prepared by spin coating at 6000 rpm for 10 s: (i) AgNO$_3$-PVA solution on glass substrate, (ii) AgNO$_3$-PVA solution on PS/glass substrate, and (iii) PVA, AgNO$_3$-PVA, and PVA solutions in succession on PS/glass substrate (scheme 1). The film coated plates were heated in a hot air oven at 130 °C for 60 min to generate the silver nanoparticles in situ inside the PVA matrix. Sample prepared using procedure (i) is referred to in the text as Ag-PVA film on glass. Samples from procedures (ii) and (iii) were immersed in toluene taken in a Petri dish to dissolve the PS layer and release free films. The free Ag-PVA film obtained via procedure (ii) was used directly for TEM imaging. The film obtained via procedure (iii) is referred to in the text as freestanding Ag-PVA or PVA/Ag-PVA/PVA film. Thicknesses of the films were measured using an Ambios Technology XP-1 profilometer. The values estimated for the different films are as follows. Ag-PVA on glass of ~0.5 μm; Ag-PVA/PS on glass of ~5.5 μm; freestanding PVA/Ag-PVA/PVA of ~10 μm.

B. Spectroscopy and microscopy

Electronic absorption spectra of the Ag-PVA films coated on glass or freestanding were recorded on a Shimadzu model UV-3101 UV-vis spectrometer. Ag-PVA films prepared following procedure (ii) described above were placed directly on a 100 mesh copper grid and examined in a TECNAI G$^2$ FEI F12 transmission electron microscope at an accelerating voltage of 120 kV.

C. Nonlinear optical studies

A Ti:sapphire laser (800 nm, ~110 fs, 1 kHz) and frequency doubled Nd:YAG (yttrium aluminum garnet) laser (532 nm, 6 ns, 10 Hz) were used as the excitation sources for the nonlinear optical studies. Open and closed aperture Z-scan measurements were carried out by moving the sample across the focus of the laser beam using a computer-controlled translation stage; the scans were repeated several times to ensure reproducibility of the data. Femtosecond (nanosecond) pulse laser was focused using a lens of 80 mm (60 mm) focal length; the beam waist was 27.1 μm (13.5 μm) at focus leading to peak intensity in the range of 0.15–1.73 TW/cm$^2$ (0.03–0.28 GW/cm$^2$), i.e., fluences in the range of 0.02–0.19 J/cm$^2$ (0.18–1.7 J/cm$^2$). The input intensity could be varied using calibrated neutral density filters; closed aperture experiments used an aperture of diameter of 1 or 2 mm after the sample. The transmitted output was collected using a calibrated fast photodiode (FND 100) and processed using a data acquisition system consisting of a lock-in amplifier or boxcar averager, adc and computer. The films were stable at all the intensities reported in the paper. Optical limiting studies were carried out using f/40 geometry (using 8 cm focal length lens and a beam diameter of 0.2 cm) with the femtosecond pulse laser in the same input fluence/intensity range as noted above.

III. RESULTS AND DISCUSSION

Ag-PVA films spin coated on glass substrate were fabricated with four different compositions ($x=0.029, 0.058, 0.087, 0.116$). In this paper we present the studies on films with $x=0.029$ and 0.058, since they showed superior damage thresholds compared to the films with higher content of silver; the data for the latter films are presented in Ref. 18. TEM images of the films are shown in Fig. 1. A uniform distribution of silver nanoparticles is observed with particle sizes ranging from 5 to 10 nm. The density of particles increases with the value of $x$. Figure 2(a) shows the electronic absorption spectra recorded for the different films. The intensity of the plasmon peak increases with increasing silver content.
Plots of the transmittance versus scan position for the open aperture Z-scan studies using the femtosecond pulse laser are shown in Figs. 2a–2d. Control experiment on glass and plain PVA coated on glass showed weak nonlinear absorption, possibly resulting from the large (∼1 mm) interaction length of glass involved, since both show nearly identical response. With comparable and higher input laser power, Ag-PVA films coated on glass exhibit strong nonlinear absorption. Films with \( x > 0.06 \) show perceptible damage at input intensity exceeding ∼1.3 TW/cm\(^2\).\(^{18}\) Earlier studies on silver nanoparticles in the form of suspensions and doped in glass matrices indicated saturable absorption;\(^{19}\) this could be due to longer lifetimes of the surface plasmon state in these environments. We have attempted to fit the Z-scan curves of the Ag-PVA films using models for nonlinear absorption. However, the fitting was not very satisfactory, possibly because of the non-negligible effect of the glass substrate at these high laser powers. Results of the optical limiting experiments are collected in Fig. 3. The films show high linear transmittance (∼87%) at low laser intensity. The plots of output versus input intensity indicate appreciable optical limiting with a threshold \( I_{1/2} \) of 1.62 TW/cm\(^2\) and output clamped at 0.70 TW/cm\(^2\) \( (I_{1/2} \) is defined\(^{20}\) as the input intensity at which the transmittance reduces to half of the linear transmittance). The dynamic range estimated as the ratio of the damage and limiting thresholds\(^{20}\) is ∼1.1. The ability of these polymer films to sustain high laser power is of practical interest. The contribution from nonlinear refraction was assessed using closed aperture Z-scan experiments with the femtosecond pulses. Traces of the transmittance of the Ag-PVA films coated on glass, divided by the corresponding values in the open aperture experiment so as to reveal the effect of nonlinear refraction alone, are shown in Fig. 4. The reduced transmittance before focus and increased transmittance after focus indicate that Ag-PVA possesses positive nonlinearity for refraction in the femtosecond regime. Thermal buildup would typically lead to negative non-
linearity; the positive nonlinearity of the films observed even with 1 kHz repetition rate therefore suggests that the responses are dominated by electronic effects. As in the case of the open aperture Z-scan curves, theoretical fitting of the closed aperture data is not dependable; the value of nonlinear refractive index obtained is comparable to that of glass alone.

Experiments using nanosecond laser pulses revealed interesting contrast with the nonlinear response for femtosecond pulses. Open and closed aperture Z-scan experiments with the nanosecond laser pulses were carried out on pure PVA on glass as well as Ag-PVA films on glass with two different compositions; the results are provided in Ref. 18. PVA film did not show any detectable nonlinear absorption or refraction with the nanosecond pulses. Ag-PVA films, however, showed appreciable nonlinear absorption (as reported earlier for Ag-PVA/PS films), and the closed aperture experiment clearly revealed a negative nonlinearity. The latter is a consequence of resonant absorption at 532 nm and considerable thermal effects operative with the longer laser pulses in the nanosecond regime. These experiments reaffirm that the strong positive nonlinear response of Ag-PVA films to femtosecond laser pulses arises primarily due to electronic effects. However, as noted above, the Z-scan experiments on the films supported on glass substrates do not permit an accurate evaluation of the nonlinear susceptibility of the Ag-PVA films. The reason for this is the following: the glass substrate, in spite of its weaker nonlinear susceptibility compared to Ag-PVA, is a couple of orders of magnitude thicker than the polymer film and hence exerts a comparable or even overwhelming impact on the total nonlinear response for the femtosecond pulses.

In order to unambiguously demonstrate the nonlinear ab-
absorption, quantitatively estimate the nonlinear susceptibility, and project the potential advantage from the point of view of device applications, we have fabricated freestanding films of Ag-PVA having no glass substrate and carried out the nonlinear optical studies on them. As noted earlier, these films were fabricated by successively spin coating PVA, AgNO₃-PVA, and PVA and generating the Ag nanoparticles by thermal treatment. Photographs of the glass supported ones; transparency of the film with the case of does not show any nonlinear absorption by spin coating PVA, AgNO₃-PVA, and PVA and generating the Ag nanoparticles by thermal treatment. Photographs of the glass supported ones; transparency of the film with the case of does not show any nonlinear absorption.

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The silver nanoparticle–glass supported ones; transparency of the film with the case of does not show any nonlinear absorption. The value of the Ag-PV A layer unambiguously with corroborating electron diffraction data. Therefore, it is likely to arise from an association of two and three photon absorptions, leading to reverse saturable absorption. At the highest input fluence of 1.22 TW/cm², we have studied, the values of β are found to be 2.0 and 2.2 cm/GW, respectively, for films with x = 0.029 and 0.058.

The plots of output versus input intensity (Fig. 7) indicate a limiting threshold (Iₜₙ) of 1.4 TW/cm², output clamped at 0.70 TW/cm², and dynamic range of ~1.2 for the film with x = 0.029; similar characteristics are observed in the case of x = 0.058 as well.

It may be noted that the linear transmittance of the freestanding films is higher than that of the glass supported ones; transparency of the film with x = 0.029 is quite significant. The silver nanoparticle–embedded films are quite stable for several months under ambient conditions; the stability of the material under laser irradiation is indicated by reproducible responses in Z-scan experiments repeated several times for up to ~10 min, keeping the peak intensities below the damage threshold. Closed aperture Z-scan experiments using femtosecond laser pulses on the freestanding films of Ag-PVA confirm that they exhibit positive nonlinearity (Fig. 8). More importantly, these Z-scan traces allow the direct estimation of the nonlinear refractive index n₂ and the real part of the third order susceptibility χ(3) of the Ag-PVA films. The data were fitted to the equation

\[ T(z) = 1 - \frac{4\Delta\phi_0(z/z_0)}{1 + (z/z_0)^2[9 + (z/z_0)^2]^2}, \]

where Δϕ₀ is the phase change. The values of Δϕ₀ estimated for Ag-PVA films with x = 0.029 and 0.058 are very similar, ~0.39 and ~0.41, respectively. These values provide directly n₂ = 1.20 × 10⁻¹² esu and χ(3) = 1.95 × 10⁻¹¹ esu for the Ag-PVA films. Based on the fabrication procedure, the active layer of Ag-PVA in the freestanding PVA/Ag-PVA/PVA films is likely to be ~1 μm thick. Even though TEM images of the film cross sections support this, in spite of several attempts we were unable to establish the thickness of the Ag-PVA layer unambiguously with corroborating elemental composition or electron diffraction data. Therefore, we have used the full thickness (10 μm) of the PVA/Ag-PVA/PVA films in the estimation of n₂ and χ(3) (even though the contribution of the PVA layer is negligible). Hence the values we report are likely to be the lower bounds for these materials. It is notable that even then they are comparable to the nonlinear susceptibility reported for silver nanoparticles in colloidal films on silicon substrates. The freestanding films which exhibit strong nonlinear response and optical limiting capability are highly advantageous from an application point of view.
IV. CONCLUSIONS

Silver nanoparticles are formed in situ inside poly(vinyl alcohol) film by a simple and convenient protocol leading to nanoparticle-embedded films supported on glass substrates. A protocol is developed for the fabrication of freestanding films, PVA/Ag/PVA/PVA. Nonlinear optical studies using femtosecond pulse laser reveal appreciable nonlinear absorption and optical limiting capability of these films at the ultrashort time scales. The positive nonlinearity observed is relatively rare and of potential utility in fabricating devices with graded nonlinear refractive indices. The freestanding films facilitate unambiguous estimation of the nonlinear refractive index and susceptibility which are comparable to those reported earlier for supported films under femtosecond laser irradiation. The current study establishes a convenient route to the realization of freestanding metal nanoparticle–embedded polymer film and demonstrates their optical limiting capability, serving as a step toward the development of optical power limiters.

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18See EPAPS Document No. E-JAP1AU-102-078715 for electronic absorption spectra, TEM images, and details of nonlinear optical studies. This document can be reached via a direct link in the online article’s HTML reference section or via the EPAPS homepage (http://www.aip.org/pubservs/epaps.html).