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Nanoparticle-Embedded Polymer: In Situ Synthesis, Free-Standing Films with Highly Monodisperse Silver Nanoparticles and Optical Limiting

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Synthesis and assembly of nanoparticles are central themes in nanomaterials science and technology. Development of environment-friendly procedures[1] and control of particle size are important contemporary issues. The “bottom-up” approaches to metal nanoparticle synthesis are mostly based on the colloidal route.[2] However, assembly of nanoparticles in matrixes such as polymer or sol−gel films is of major interest in several optical, nonlinear optical, and sensor applications,[3,4] especially those requiring large area coating. The common approaches to such materials include casting of films from a mixture of preformed nanoparticles and polymer,[5] plasma deposition techniques[6] and in situ growth.[3,7,8] The latter mode of synthesis inside solid matrixes is of interest in the context of the current debate on potential health hazards of inhalable nanoparticles.[9] Free-standing thin films are useful for device applications, and have been fabricated at the air−water interface[10] and through layer-by-layer assembly;[11] however, preformed nanoparticles were used in both cases. We have sought to combine the advantages of the chemical reduction route to metal nanoparticles, environment-friendly reagents, and the stabilization of the particles in a polymer matrix, in the fabrication of silver nanoparticle-embedded poly(vinyl alcohol) (PVA) film. Optimal concentrations and thermal treatment for short periods of time are shown to lead to a homogeneous in situ generation of 2−3-nm diameter particles. A simple procedure involving a sacrificial layer[12] of polystyrene (PS) is used to obtain free-standing Ag−PVA films. This strategy facilitated the monitoring of particle size directly in a TEM, without the need for microtoming. To the best of our knowledge, this is the first report of in situ fabrication leading to free-standing polymer film incorporating silver nanoparticles. Further, the small sizes and narrow distributions achieved under such mild conditions and short processing time are very significant. Preliminary investigations of the optical limiting capability of these nanoparticle-embedded polymer films appear quite promising. Our methodology opens up a wide range of possibilities in terms of the choice of metals, polymers, and particle growth conditions and the feasibility of further mechanical or optical manipulations.[13]

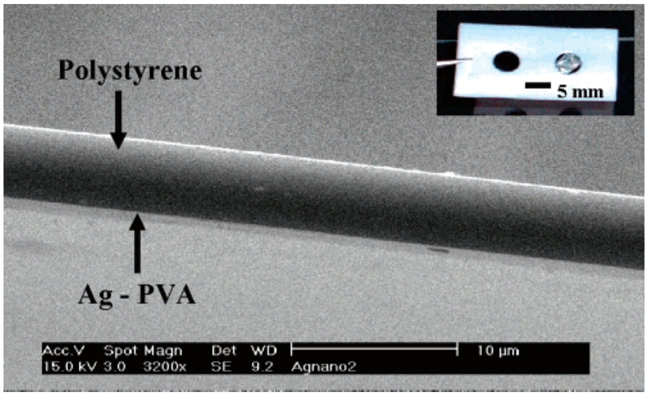

Figure 1. SEM of the cross-sectional view of Ag−PVA/PS film. Inset shows the Ag−PVA film on a Teflon support; the empty hole shows the contrast.

The fabrication procedure is outlined in Scheme 1. Aqueous solutions of silver nitrate and PVA (Fluka, average MW = 15 000, % hydrolysis = 88) were mixed and stirred; three initial weight ratios of Ag/PVA, 0.028, 0.042, and 0.058, were studied (see Supporting Information). The solution mixture was spin-coated either directly on quartz or on glass substrates previously coated with a PS layer. The thickness of the PS and PVA layers are 3−6 μm and 400−500 nm, respectively (Figure 1). Silver nanoparticles were generated by heating the solid films in a hot air oven under ambient atmosphere. PVA acts simultaneously as the reducing agent,[14] stabilizer for the nanoparticles, and the matrix for homogeneous distribution and immobilization. Heat treatment times from 5 to 60 min and temperatures from 50 to 110 °C were explored. The films obtained are fully transparent with no visible coloration; however when larger amounts of silver are involved, the films appear yellow. Interestingly, the photostability of AgNO$_3$−PVA and Ag−PVA films are considerably enhanced with respect to that of colloidal mixtures of AgNO$_3$ and PVA. The Ag−PVA

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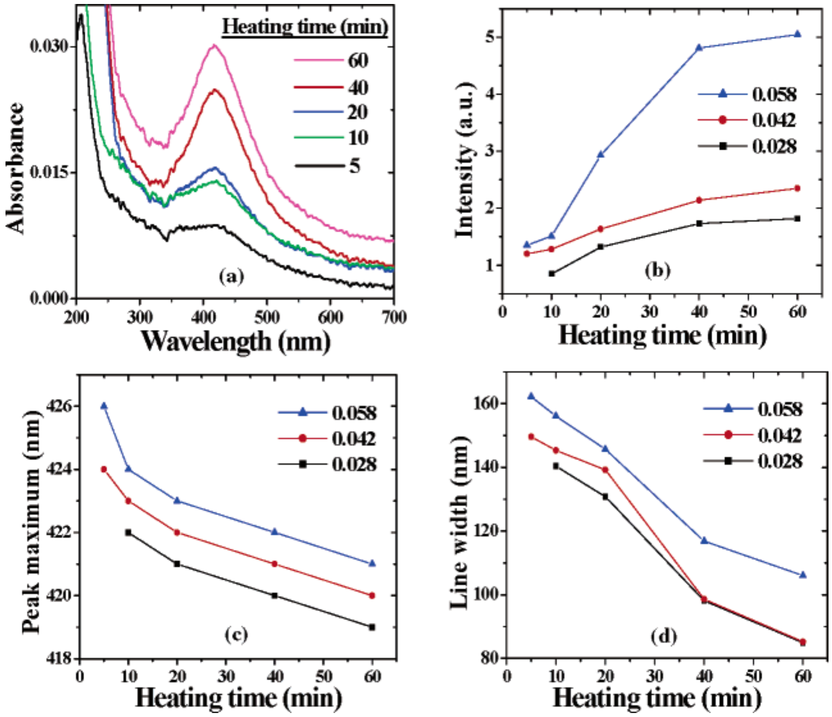
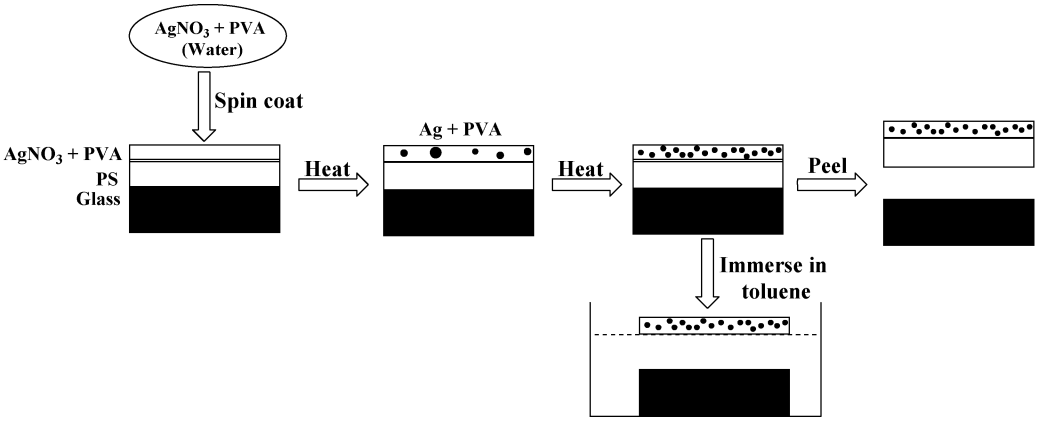


Figure 2. (a) Plasmon absorption of Ag−PVA (weight ratio = 0.042:1) heated at 90 °C for different periods of time. Variation of (b) intensity, (c) peak maximum, and (d) line width of the plasmon absorption with heating time for Ag−PVA with different weight ratios heated at 90 °C.

Scheme 1



films on quartz were used for optical absorption studies. The Ag−PVA/PS on glass could be peeled off to give free-standing films. Alternately, the glass substrate with Ag−PVA/PS was immersed in toluene whereupon the PS layer dissolved and the Ag−PVA layer floated to the surface; this film was collected on a 100-μm-mesh folded copper grid for TEM studies.

Plasmon absorptions of Ag−PVA films heated at 90 °C for different lengths of time are shown in Figure 2. The variation of intensity, peak maximum, and line width for different compositions are also shown. The intensity plots show that the nanoparticle production increases with time and saturates in about an hour; the progress is very prominent at the highest Ag/PVA ratio. The small but steady blue shift of the peaks with heating time indicates decrease of the particle size.[15] The marked line width reduction reflects the increasing monodispersity of the size.

An earlier study of silver nanoparticles in polymers[16] reported a broad size distribution (10−60 nm) and suggested possible increase of size with heating time. TEM (with electron diffraction) of our Ag−PVA films demonstrated the formation of smaller particles, tighter size distribution, and size decrease with heating time, fully consistent with the plasmon absorption data. Figure 3 shows TEM images of the roughly spherical silver nanoparticles in PVA matrix obtained by heating the films (Ag/PVA = 0.042) at 90 °C. The histograms illustrate the increase in particle density (average number of particles in unit area of the film), decrease in the mean diameter (d_{mean}), and narrowing of the size distribution with increasing heating time. Film heated for 60 min shows very small particles ($d_{\mathrm{mean}} = 2.6$ nm) and a tight distribution ($\sigma = 0.2$ nm). Other Ag/PVA compositions show similar trends, but the average size increases and

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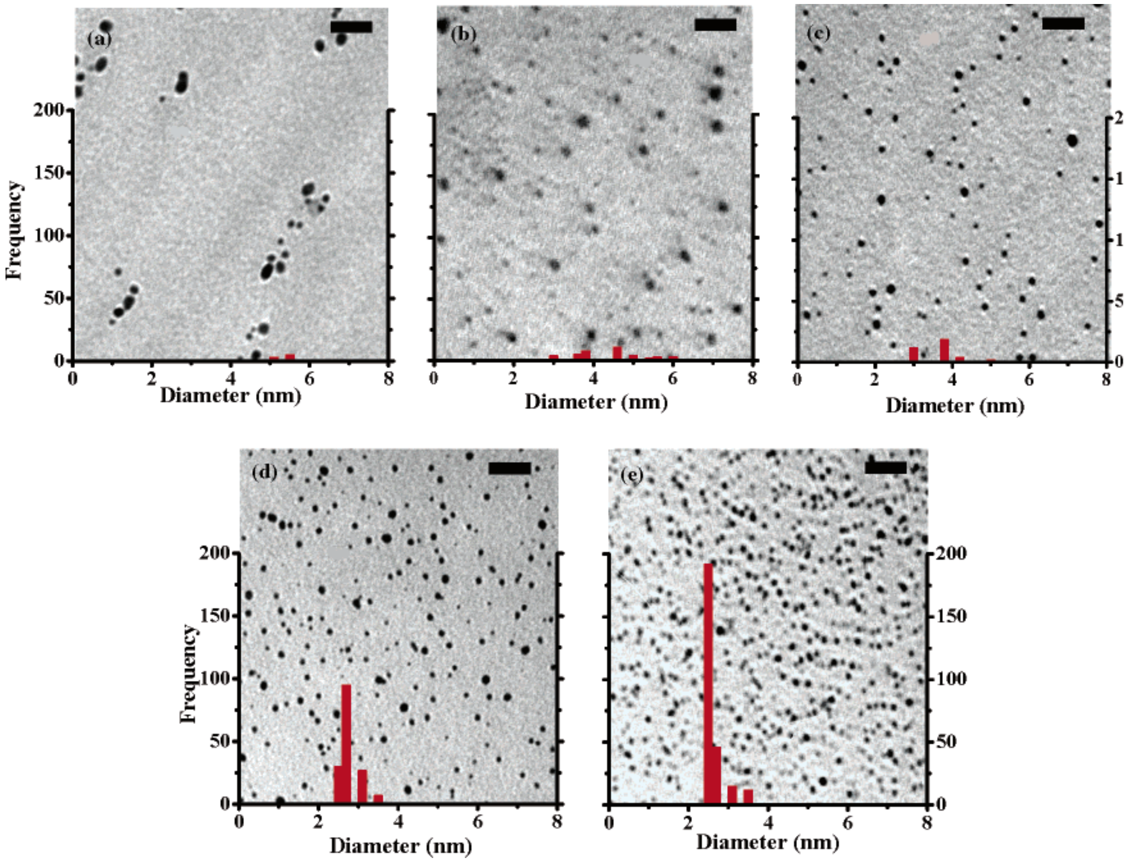

Figure 3. TEM images of Ag−PVA films (0.042:1) heated at 90 °C for (a) 5, (b) 10, (c) 20, (d) 40, and (e) 60 min (scale bar = 20 nm). Mean diameters (standard deviation) are (a) 5.4 (0.9), (b) 4.5 (1.0), (c) 3.8 (0.8), (d) 2.8 (0.3), and (e) 2.6 (0.2) nm. The histograms show the particle size distribution in the image area.

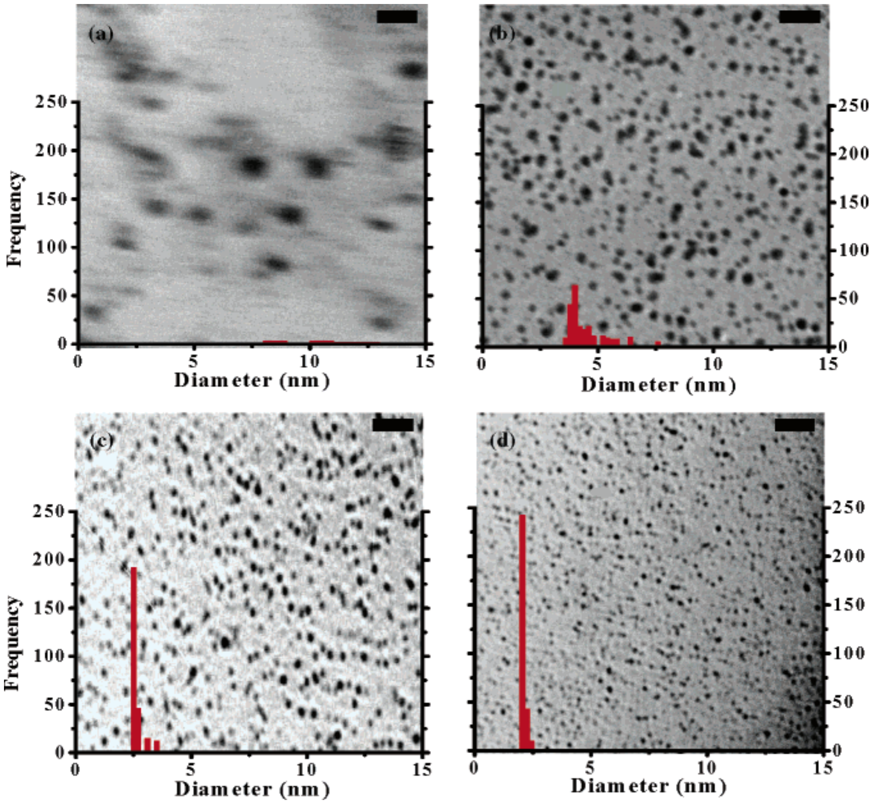

Figure 4. TEM images of Ag−PVA films (0.042:1) heated for 60 min at (a) 50, (b) 70, (c) 90, and (d) 110 °C (scale bar = 20 nm). Mean diameters (standard deviation) are (a) 10.2 (1.7), (b) 4.5 (0.8), (c) 2.6 (0.2), and (d) 2.1 (0.2) nm. The histograms show the particle size distribution in the image area.

size distribution broadens with concentration. Temperature also provides fine control on particle size. For Ag/PVA = 0.028, nanoparticles do not form at 50 °C even after 60 min. In the case of Ag/PVA = 0.042, few particles with variable

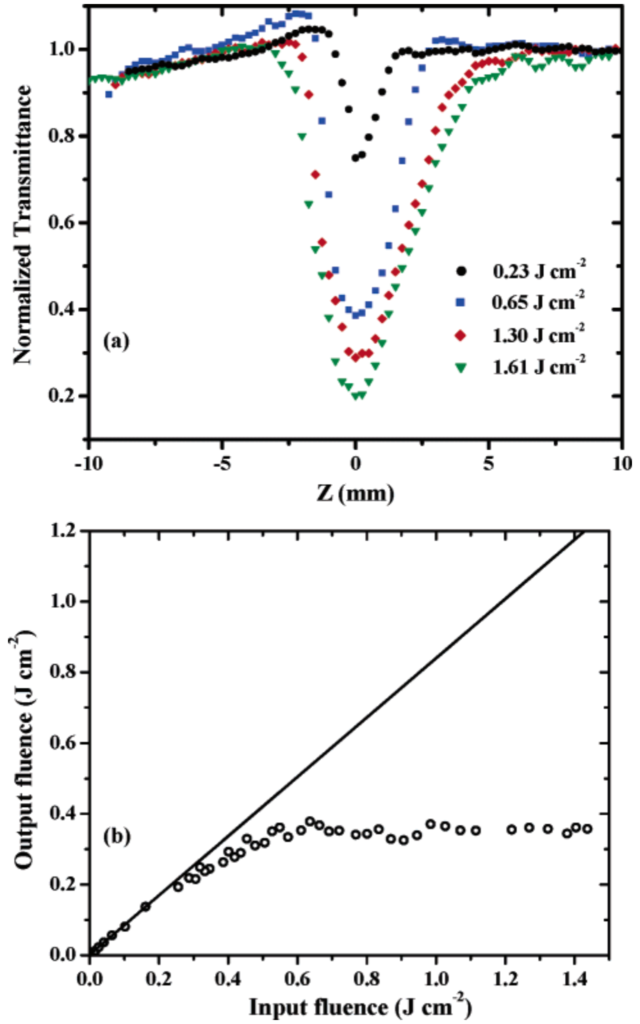

Figure 5. Optical limiting in Ag−PVA/PS film on glass substrate (Ag/PVA = 0.058, thermal treatment time, temperature = 60 min, 90 °C): (a) Z-scan curves at different input fluences, and (b) optical limiting response; the full line represents 84% linear transmission.

sizes are formed at 50 °C, but uniformly small particles (d_{mean} = 2.1 (0.2) nm) are obtained at 110 °C (Figure 4). At 110 °C, even 10-min heating leads to uniform size. Interestingly, the Ag/PVA = 0.058 film heated at 110 °C for 60 min showed appreciable ordering of the particles (see Supporting Information). The change in the particle density and size distribution with time, and more markedly with temperature of heating, appears to result from the varying extent of chemical reduction as well as a digestive ripening process. Digestive ripening observed with gold nanoparticles[15] has not been reported so far for silver nanoparticles. Longer heating time and higher temperatures lead to greater progress of reaction and faster rates, respectively. The concomitant decrease in the polymer viscosity possibly facilitates higher ion/atom mobility and homogeneous nucleation. The small sizes obtained suggest that the PVA matrix effectively suppresses particle aggregation.

We have examined the nonlinear absorption characteristics of the Ag−PVA/PS films using Z-scan measurements. Second harmonic (532 nm) of an Nd:YAG laser (10 Hz, 6 ns) was used in f/24 geometry.[17] Films $\sim$5 μm thick, with a linear transmission of 84% at low laser intensities, show strong reverse saturable absorption at higher intensities (Figure 5a). Plot of the output fluence versus the input fluence (Figure 5b) shows appreciable optical limiting with a threshold ($I_{1/2}$) of 0.83 J cm^{-2} and output clamped at 0.35 J cm^{-2} ($I_{1/2}$ is defined[18] as the input fluence at which the transmittance reduces to half of the linear transmittance). The dynamic range estimated[18] from the damage and limiting thresholds is approximately 2. Ag−PVA films showed similar behavior, however the damage threshold was lower. It is significant that this first report of optical limiting with silver nanoparticle-embedded polymer thin films indicates thresholds which are comparable or superior to those obtained earlier[19] for silver nanoparticles in colloidal medium with 1−2-mm path lengths. Investigations directed at optimizing the film characteristics to achieve even better optical limiting and unraveling the basic mechanisms involved are under way.

The present study of the Ag−PVA system illustrates the simple in situ process we have developed for the fabrication of free-standing metal nanoparticle-embedded polymer film and the fine control it provides on the particle size selection. These films with immobilized and size-tuned metal nanoparticles appear to be attractive candidates for optical limiting application. The polymeric constitution would facilitate future device development. The current protocol appears to be promising for the fabrication of other metal/semiconductor−polymer systems as well.

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Supporting Information Available: Details of synthesis, film fabrication, SEM, plasmon absorption, TEM, electron diffraction and nonlinear absorption studies (pdf). This material is available free of charge via the Internet at http://pubs.acs.org.

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