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Nonlinear optical properties of Au/PVP composite thin films*

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Colloidal Au and poly(vinylpyrrolidone) (PVP) composite thin films are fabricated by spin-coating method. Linear optical absorption measurements of the Au/PVP composite films indicate an absorption peak around 530 nm due to the surface plasmon resonance of gold nanoparticles. Nonlinear optical properties are studied using standard Z-scan technique, and experimental results show large optical nonlinearities of the Au/PVP composite films. A large value of $\chi^{(3)}/\alpha$ up to 0.56×10^{-10}esu·cm is obtained, which is comparable to the best values reported in metal/oxide composite films.

Keywords: Au/PVP, third-order optical nonlinearities, third-order susceptibility
PACC: 4265,4270F, 4270J

1. Introduction

Metal nanoclusters embedded in dielectric matrices exhibit a variety of linear and nonlinear optical properties, and have been attracted much attention for their potential applications in optical switching and signal processing.[1−3] Large third-order nonlinear optical response can be obtained from such kind of composite materials with proper choice of metal and matrix, which makes the composite system worthy of investigation. Composite films comprising metal nanoclusters embedded in oxide matrix, such as Au/SiO_2,[4−6] Au/TiO_2,[7] and $Au/BaTiO_3$[8,9] have been widely investigated, and large third-order susceptibility $\chi^{(3)}$ with values of 10^{-7}–10^{-6} esu were obtained. In addition to the considerations on inorganic materials, importance of organic molecular and polymeric materials have been considered in recent years due to their large and fast nonlinear optical response, as well as relatively low cost, architectural flexibility and ease of fabrication.[10−15] Furthermore, CdS nanocrystals doped PMMA films were investigated, by incorporating nanoparticles into the polymer, the nanocomposite structures provide a new method to improve the processability and stability of materials for applications in optical devices.[16] To our knowledge, however, optical nonlinearities of organic films containing zero-valent metal nanoparticles have been rarely reported up to now. In this letter, PVP and colloidal Au composite films are fabricated by spin-coating method in order to combine the large nonlinear optical response of gold colloids[17,18] with the excellent processibility of PVP. Nonlinear optical properties of the metal-polymer films are investigated using Z-scan technique,[19] and the results show large third-order optical nonlinearities, and a promising value of the figure of merit, $\chi^{(3)}/\alpha$ (α is the absorption coefficient).

2. Samples and experiments

Colloidal gold nanoparticles were prepared by the method proposed by Grabar.[20] Briefly, a 1L flat-

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bottom flask was equipped with a condenser, 200mL of 1mM $HAuCl_4 \cdot 3H_2O$ was added to the flask and heated to boil with vigorous stirring. Then 20mL of 38.8mM sodium citrate was rapidly added to the vortex of the solution. A colour change from pale yellow to wine red occurred within 2min. Boiling was continued for 10min, the heating was then stopped, and stirring was continued for an additional 15 to 20min until the solution reached room temperature. The resulting nanoparticles were characterized by scanning electron microscopy (SEM) and UV–visible absorption. SEM observation (not shown here) indicated that the colloidal nanoparticles are approximately spherical in shape with a very narrow distribution of particle size. The average diameter of the colloids is about 12±2nm.

PVP has good film-forming properties and excellent solubility in water. For the fabrication of composite films, the PVP (molecular weight 30000) was firstly dissolved in purified water, then, Au colloids was added into the PVP solutions and dispersed by ultrasonic agitation to ensure homogeneous distribution of nanoparticles. A transparent wine red gel was obtained with concentration of about 12mg/mL. Subsequently, the Au/PVP composite films were prepared on MgO (100) substrates using spin-coating method. After coating, the composite films were dried at 90° for 1h in vacuum oven. With Au concentrations varying from 0 to 2 wt%, transparent composite films can be obtained with colloidal nanoparticles distributed homogeneously in the polymer matrix. Thickness of the composite films for Z-scan investigation was measured to be 80–100nm with the Dektak 8 surface stylus profiler (Veeco company). Atomic force microscopy (AFM) was performed to characterize the surface morphology of the composite films.

The UV–visible absorption spectrum of the as-prepared aqueous Au colloids was measured with a U-3010 spectrophotometer. Optical absorption properties of Au/PVP composite films in the range from 350 to 800 nm were investigated with a Spectrapro500i spectrophotometer (Acton Research Corporation). Absorption spectra were corrected automatically taking into account the absorbance from MgO substrates. Nonlinear optical properties of the composite films were investigated by Z-scan technique. One of the advantages of Z-scan is that it can separate the contributions of refractive and absorptive nonlinearities when both are present in the samples simultaneously. In the experiments, the Nd:YAG Q-switched laser with a wavelength of 532nm and the pulse width of 10ns was used as the light source, and the repetition rate was set to 1Hz to reduce accumulative thermal effect. The laser beam was focused on the sample by a 120mm focal length lens. The beam waist (ω_0) at the focus was measured to be 25μm, corresponding to a Rayleigh length of Z_0=3.7mm, that was much longer than the total thickness of the film and the 0.5mm-thick MgO substrate. On-axis transmitted beam energy, the references beam energy, as well as the ratios of them were measured by an energy ratiometer simultaneously.

3. Results and discussion

Figure 1 shows a typical AFM image of 5×5 μm^2 area of an Au/PVP composite film on MgO substrate. The root-mean-square surface roughness is 0.600nm, indicating an excellent smoothness and uniformity of the composite film. The UV–visible absorption spectrum of aqueous Au colloids shown in Fig.2 demonstrates an absorption peak at 518nm, which is due to the surface plasmon resonance (SPR) of colloidal Au nanoparticles. However, the absorption properties of the composite films shown in Fig.3 exhibit a peak at 530nm, indicating a red shift of the SPR of gold nanoparticles relative to that in solution. The absorption properties of the composite film demonstrate that the colloidal gold nanoparticles were successfully mixed into and stabilized in the PVP matrix.

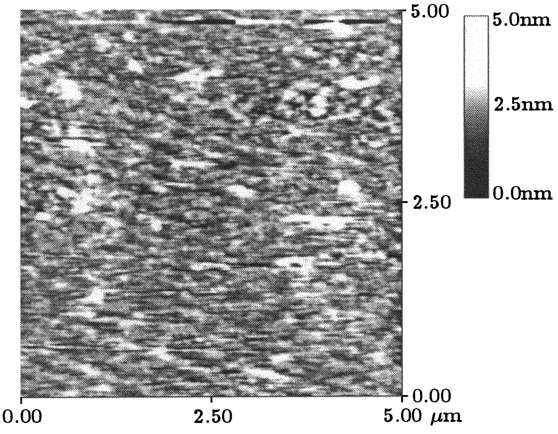

Fig.1. AFM image of Au/PVP film.

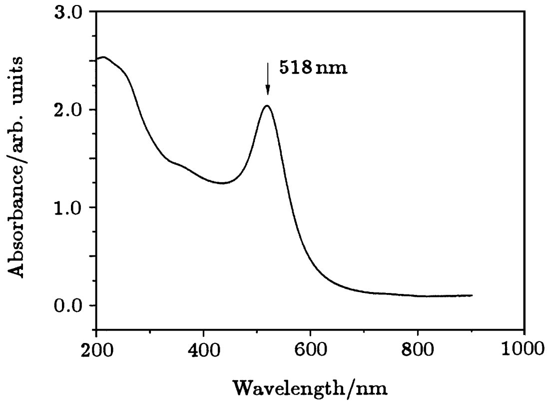

Fig.2. UV–visible absorption spectrum of the prepared colloid Au solution.

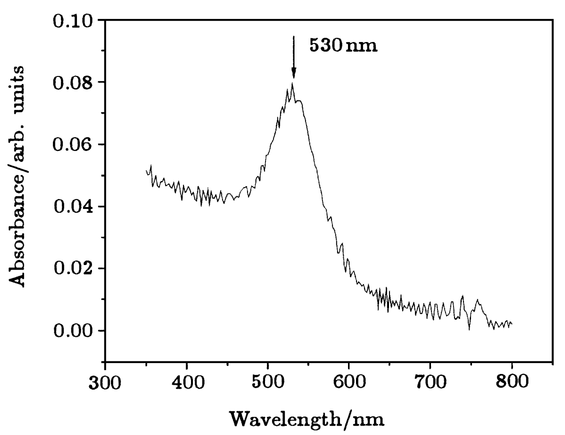

Fig.3. UV–visible absorption spectrum of Au/PVP composite film with Au concentration of 2wt%.

Figure 4 gives the typical Z-scan results of the composite film with relatively high Au doping concentration of about 2 wt%. The open circles indicate the measured data with each point corresponding to the average value of 15 measurements, and the solid line represents a theoretical fit.[19] Since MgO substrate has only very weak nonlinear optical response at 532 nm, as measured by the same Z-scan set-up, the observed large optical nonlinearities result certainly from the Au/PVP composite film. Open-aperture (OA) curve a in Fig.4 exhibits a normalized transmittance valley, indicating the presence of nonlinear absorption in the composite film. In the case of closed-aperture (CA) measurements, curve b in Fig.4 gives a valley–peak shape, representing a positive value for the nonlinear index n_2. It also can be seen in curve b that the distance between the peak and valley ($\Delta T_{\rm p-v}$) is about 6.3 mm as compared to 1.7 Z_0, which indicates the nonlinear effect is a third-order response. Nonlinear absorption coefficient β and nonlinear refractive index n_2 are calculated, according to the Z-scan theory,[19] to be 3.90×10^{-7}m/W and 7.37×10^{-14} m^2/W. The corresponding values of Im$\chi^{(3)}$ and Re$\chi^{(3)}$ are calculated to be 9.85×10^{-9}esu and 4.38×10^{-8} esu, respectively. With the calculated absorption coefficient α =800 cm^{-1}, the figure of merit, defined as $\chi^{(3)}/\alpha$, is determined to be 0.56×10^{-10}esu·cm. Also, Z-scan results of the composite film with Au concentration of 1 wt% gives $\chi^{(3)}$ value of 2.97×10^{-8}esu, and the corresponding value of $\chi^{(3)}/\alpha$ is calculated to be 0.50×10^{-10}esu·cm. The measurements are repeated on different spots of the film under the same condition to check the uniformity of the film, and the relative uncertainty in the results is estimated to be 10%–20%, which is within the limits of measurement uncertainty of a typical Z-scan. The reproducibility of the Z-scan results also demonstrates that there has no detectable destruction of the Au/PVP films occurring during the measurements.

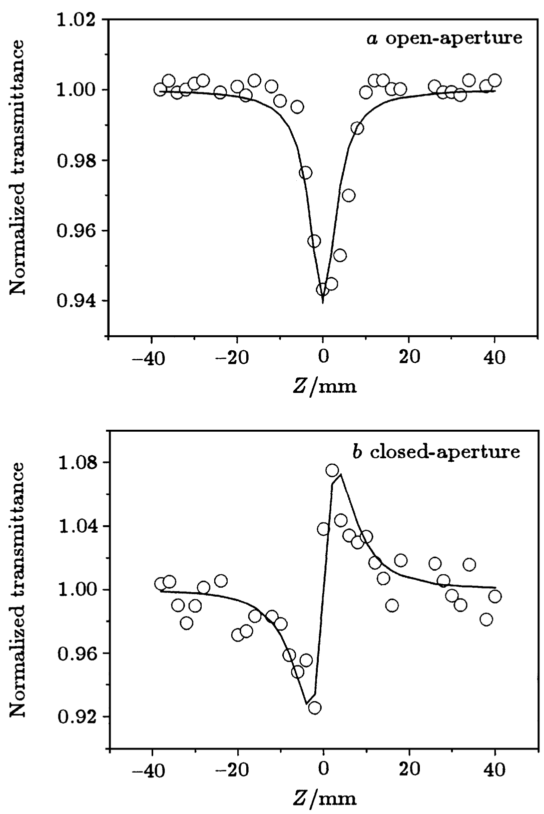

Fig.4. Z-scan data of Au/PVP composite film with 2 wt % Au; curve a Data for open aperture. curve b Data for closed aperture divided by those of open aperture. The solid lines are the theoretical fit.

It is worth noting that the third-order susceptibility $\chi^{(3)}$ of the composite films is three orders of magnitude higher than that of the aqueous gold colloids. The enhancement of $\chi^{(3)}$ for the present composite films is believed to stem from two mechanisms. One is the relatively high concentration of gold nanoparticles in the film compared with that in solution. It is known that the gold nanoparticles have very large optical nonlinear susceptibility $\chi_m^{(3)}$ of 10^{-7} esu,[21] and the values of $\chi^{(3)}$ in composite films can be significantly enhanced by increasing the concentration of metal nanoparticles.[5,7] Another mechanism for the large value of $\chi^{(3)}$ is the surface plasmon excitation. Usually, the third-order susceptibility $\chi^{(3)}$ exhibits a peak value at the plasmon frequency due to the SPR effect.[2,4] In our Z-scan measurements, the excitation wavelength of 532 nm is just at the SPR frequency of the gold nanoparticles in the composite films as shown in Fig.3. Furthermore, it needs to be noted that the gold nanoparticles embedded in PVP films exhibit a very narrow distribution of particle size. The narrow distribution of particle size may also contribute to the enhancement effects of optical nonlinearities.[22] Here, it is worth to point out that the figure of merit, $\chi^{(3)}/\alpha$, which is more important for practical applications, reaches the value of 0.56×10^{-10}esu·cm for the Au/PVP film. Such a value of $\chi^{(3)}/\alpha$ is comparable to the best values reported in metal/oxide composite films fabricated by co-sputtering or pulsed-laser deposition (PLD) method.[5,9]

5. Conclusions

In summary, colloidal Au/PVP composite films have been prepared by spin coating. The composite films show high linear transmittance in visible frequency range and large third-order optical nonlinearities. The enhancement of $\chi^{(3)}$ of the composite films can be explained by the effect of the relatively high concentration of gold nanoparticles in the film and the surface plasmon excitation. The value of $\chi^{(3)}/\alpha$ up to 0.56×10^{-10}esu·cm is achieved, comparable to the best values obtained in metal/oxide composite films fabricated by PLD or the co-sputtering method. And the present reported easy fabrication and relatively low cost make the metal-polymer composite film a valid candidate for applications in optical devices.

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