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# Picosecond nonlinear optical responses of Au/PVP composite films

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**Abstract**
Nonlinear optical properties of colloidal Au and poly(vinylpyrrolidone) (PVP) composite films were investigated using the Z-scan technique with 25 ps pulses at 532 nm near the surface plasmon resonance frequency of Au nanoparticles. Experimental results show large optical nonlinearities of the composite films with the real and imaginary parts of the third-order nonlinear optical susceptibility $\chi^{(3)}$ being $4.7 \times 10^{-10}$ esu and $2.5 \times 10^{-10}$ esu, respectively. The obtained $\chi^{(3)}$ value of Au/PVP composite films is comparable or higher than that of the organometallic complexes reported. Furthermore, a strong optical limiting response was observed and a possible application of the composite films as an optical limiter of picosecond laser pulses was discussed.

## 1. Introduction

Materials with large third-order optical nonlinearities and fast time response are essential for potential applications in optical signal processing, optical limiting (OL) and optical devices [1,2]. In noble-metal nanoparticle composite systems, large third-order nonlinear optical susceptibility $\chi^{(3)}$ and ultrafast time response have been observed near the surface plasmon resonance (SPR) peak of metal nanoparticles as a result of local-field enhancement [3–5]. Composite films comprising metal nanoclusters embedded in an oxide matrix, such as $SiO_2$ [3, 4], $TiO_2$ [5] and $BaTiO_3$ [6, 7] have been widely investigated for their large values of third-order susceptibility $\chi^{(3)}$. In addition to many considerations on inorganic materials, organic molecular or polymeric materials have attracted more and more attention in recent years, not only due to their large nonlinear optical susceptibilities and fast response time, but also due to their relatively low cost, architectural flexibility and simple fabrication process [8]. Furthermore, by incorporating semiconductor nanoparticles into the polymer, the nanocomposite films provide a new method to improve the processability and stability of nonlinear materials for applications in optical devices [9]. In this paper, poly(vinylpyrrolidone) (PVP) and colloidal Au composite films are fabricated by the spin-coating method to combine large optical nonlinearities of gold colloids [10, 11] and excellent processability of PVP. Third-order nonlinear optical properties of the metal–polymer films are investigated using the Z-scan technique [12] at a wavelength of 532 nm with pulse duration of 25 ps. In the OL experiments, strong OL behaviours have been observed in the Au/PVP films. To our knowledge, this is the first investigation of the nonlinear optical properties of Au/PVP films induced by picosecond laser pulses.

## 2. Samples and experiments

Colloidal gold nanoparticles were prepared by the chemical reduction of chloroauric acid ($HAuCl_4$) as proposed by Grabar *et al* [13]. SEM observation by XL30 S-FEG indicates that the colloidal nanoparticles are approximately spherical in shape with a very narrow distribution of particle size, and the average diameter of the colloids is about 12 ± 3 nm.

For the fabrication of composite films, PVP (molecular weight 30 000) was firstly dissolved in purified water; subsequently, Au colloids were added to the PVP solutions and dispersed by ultrasonic agitation to ensure a homogeneous distribution of nanoparticles. A transparent wine red gel was obtained with a concentration of about 12 mg ml$^{-1}$. Au/PVP composite films were prepared on MgO (100) substrates by

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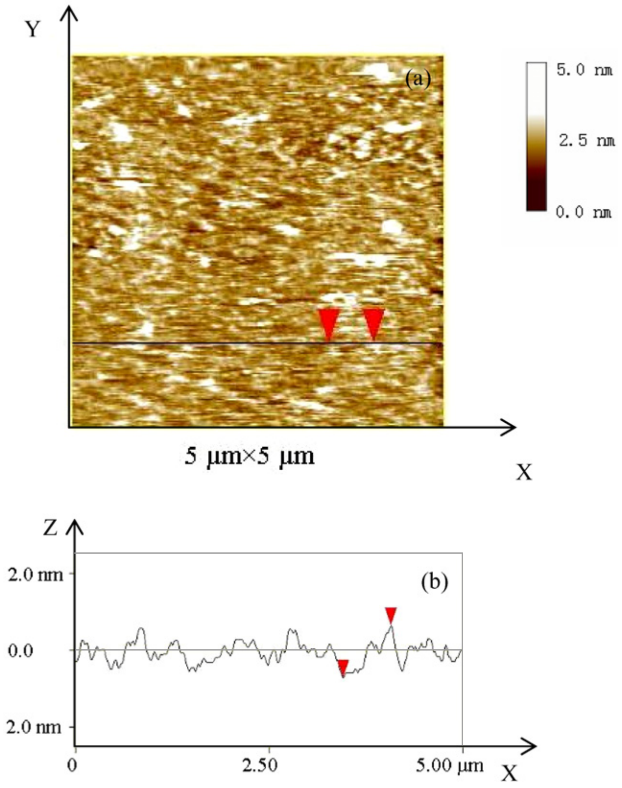

**Figure 1.** AFM image of Au/PVP film (*a*), height profiles along the dark line (*b*).

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spin coating, and then the composite films were dried at 90 ˚C for 1 h in a vacuum oven. Au concentration in the composite films was estimated to be about 1.0 wt%. The thickness of the composite films was measured by Dektak 8 surface stylus profiler (Veeco company). Atomic force microscopy (AFM) was performed to characterize the surface morphology of the composite film.

Linear optical absorption properties of Au/PVP composite films were investigated in the range of wavelength from 200–800 nm at room temperature with a Spectrapro500i spectrophotometer (Acton Research Corporation). The absorption spectrum was corrected automatically taking into account the absorbance from MgO substrates. The nonlinear optical properties of the Au/PVP composite films were investigated using the Z-scan technique with the advantage of separating the contributions of refractive and absorptive nonlinearities in the samples. In the experiments, a mode-locked Nd : YAG laser with a frequency doubled at 532 nm and characterized by a pulse duration of 25 ps at a repetition rate of 1 Hz was used as the light source. The laser beam was focused on the sample by a 120 mm focal length lens, leading to a measured beam waist ($\omega_0$) of 25 $\mu$m. In the OL experiments, the sample was kept at the focus and the dependence of transmittance on the intensity of laser radiation was measured with the open-aperture (OA) Z-scan scheme. On-axis transmitted beam energy, the reference beam energy as well as their ratios were measured by an energy ratiometer (Rm 6600, Laser Probe Corp.) simultaneously.

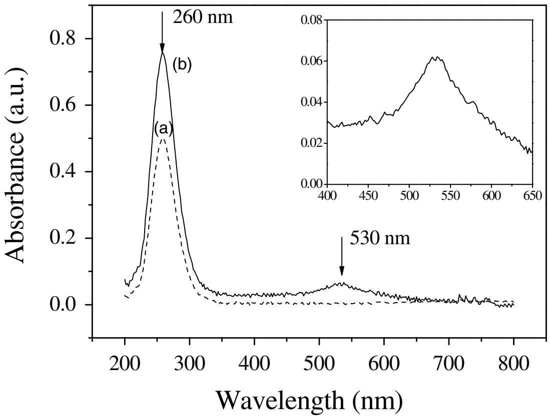
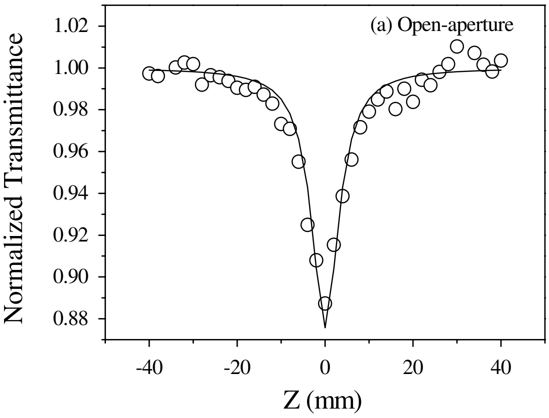


**Figure 2.** UV-visible absorption spectra of Au/PVP composite films (film thickness $L = 1\ \mu$m): (a) undoped PVP thin film, (b) composite films with 1 wt% Au (inset: absorption spectra of composite film from 400–650 nm).

## 3. Results and discussion

Nonlinear optical measurements are performed on five composite films with thickness varying from 80–120 nm. Figures 1, 3 and 4 are typical results for one composite film with a thickness of 107 nm. Because the optical absorption of the composite films is very weak, we note that for the absorption measurements shown in figure 2 the film thickness is about 1 $\mu$m. Figure 1(*a*) shows the AFM image of $5 \times 5\ \mu\mathrm{m}^2$ area of Au/PVP composite film on MgO substrate. The height profiles along the dark line in (*a*) give the maximum height fluctuation of 1.35 nm, as shown in figure 1(*b*). The root-mean-square surface roughness within $10 \times 10\ \mu\mathrm{m}^2$, $5 \times 5\ \mu\mathrm{m}^2$, $2 \times 2\ \mu\mathrm{m}^2$ areas is 1.00 nm, 0.60 nm and 0.63 nm, respectively, indicating excellent smoothness and uniformity of the composite films. UV-visible absorption spectra of the composite films are shown in figure 2. As a reference, the absorption spectrum of undoped PVP thin films was also recorded (figure 2, curve (a)). Curve (b) displays two absorption peaks of Au/PVP composite films: the stronger one at 260 nm comes from the absorption of PVP and the weaker peak at 530 nm is due to the SPR of colloidal Au nanoparticles. The absorption properties of the composite film demonstrate that the colloidal gold nanoparticles were successfully mixed into and stabilized in the PVP films.

Typical Z-scan results of the Au/PVP composite film are shown in figure 3. The open circles indicate the measured data with each point corresponding to the average value of 15 measurements. The solid line represents a theoretical fit [12]. As the MgO substrate has a very weak nonlinear optical response at 532 nm, as measured by the same Z-scan setup, the large optical nonlinearities observed can be attributed to the Au/PVP composite films. The OA curve (*a*) in figure 3 exhibits a normalized transmittance valley, as a result of the presence of nonlinear absorption. The closed-aperture (CA) curve (*b*) exhibits the valley–peak curve, indicating a positive value for the nonlinear index $n_2$. The curve is asymmetric, the depth of the valley is enhanced and the peak is suppressed due to the presence of nonlinear absorption. The Z-scan data are analysed according to the Z-scan theory [12]. The solid



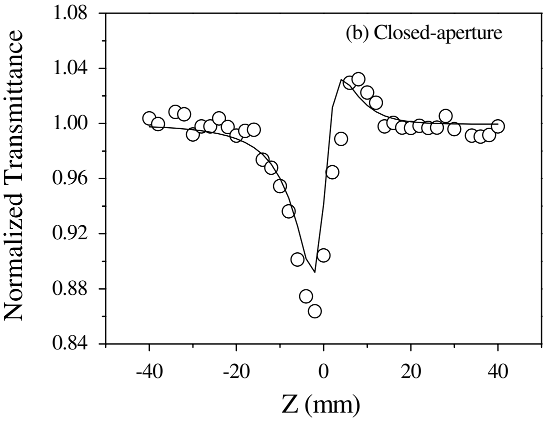


**Figure 3.** Z-scan results of the Au/PVP composite with 1 wt% Au: (*a*) data of open aperture, the solid line is the theoretical fit, (*b*) data of closed aperture, the solid line is the theoretical fit.

curve in figure 3(*a*) is obtained using the following equation, by adjusting $\beta = 1.0 \times 10^{-8}\,\mathrm{m\,W^{-1}}$:

$$T(z, S = 1) = 1 - \frac{\beta I_0 L_{\mathrm{eff}}}{2\sqrt{2}(1 + (z^2/z_0^2))}, \tag{1}$$

where $I_0 = 3 \times 10^{10}\,\mathrm{W\,cm^{-2}}$ is the on-axis irradiance of the laser beam at the focus, $z$ is the position of the sample, $L_{\mathrm{eff}} = [1 - \exp(-\alpha L)]/\alpha$ is the effective thickness of the film ($L = 107\,\mathrm{nm}$ is the film thickness) and $z_0 = k\omega_0^2/2$ is the diffraction length of the beam ($k = 2\pi/\lambda$ is the wave vector, $\omega_0$ is beam waist of the laser). The curve in figure 3(*b*) is obtained using the following equation [14], by setting $\beta = 1.0 \times 10^{-8}\,\mathrm{m\,W^{-1}}$ and adjusting $n_2$ to be $8.0 \times 10^{-16}\,\mathrm{m^2\,W^{-1}}$:

$$T(z) = 1 + \frac{4z/z_0}{(z^2/z_0^2 + 9)(z^2/z_0^2 + 1)}\Delta\Phi_0 - \frac{2(z^2/z_0^2 + 3)}{(z^2/z_0^2 + 9)(z^2/z_0^2 + 1)}\Delta\Psi_0, \quad (\Delta\Phi_0 \ll 1, \Delta\Psi_0 \ll 1), \tag{2}$$

where $\Delta\Phi_0 = kn_2 I_0 L_{\mathrm{eff}}$, $\Delta\Psi_0 = \beta I_0 L_{\mathrm{eff}}/2$. Considering the low laser radiation intensity used and the film thickness, $\Delta\Phi_0 \ll 1$, $\Delta\Psi_0 \ll 1$ should be satisfied in our Z-scan measurements. The real and imaginary parts of the third-order nonlinear optical susceptibility, $\mathrm{Re}\chi^{(3)}$ and $\mathrm{Im}\chi^{(3)}$ are calculated to be $4.7 \times 10^{-10}$ and $2.5 \times 10^{-10}$ esu, according to the following equations:

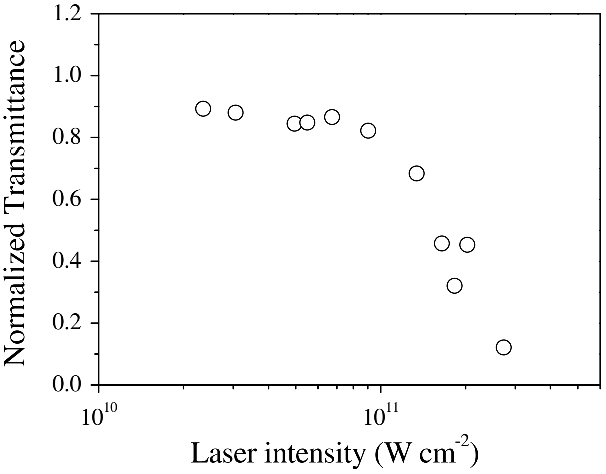


**Figure 4.** Transmittance dependence of Au/PVP composite film as a function of laser radiation intensity (λ = 532 nm).

$$\mathrm{Re}\chi^{(3)}(\mathrm{esu}) = cn_0^2 n_2\ (\mathrm{m^2\,W^{-1}})/120\pi^2, \tag{3}$$

$$\mathrm{Im}\chi^{(3)}(\mathrm{esu}) = c^2 n_0^2 \beta\ (\mathrm{mW^{-1}})/240\pi^2\omega. \tag{4}$$

Considering the elements involved in Z-scan measurements, such as the film thickness $L = 107 \pm 4$, linear refractive index $n_0 = 1.53 \pm 0.03$, the aperture linear transmittance $S = 0.25 \pm 0.02$, laser intensity $I$, etc, the total uncertainty of $\chi^{(3)}$ is estimated to be 25–30%. The measurements are repeated on different spots of the film in the same condition in order to check the uniformity of the film, as well as on different films to test the reproducibility of the results among different films. The relative uncertainty in $\chi^{(3)}$ results is within the limits of 30%. It is worth noting that the obtained third-order susceptibility $\chi^{(3)}$ of the Au/PVP film is comparable to or higher than that of the organometallic complexes reported as good nonlinear optical materials [15–17]. The large value of $\chi^{(3)}$ in the composite films could be attributed to both the large optical nonlinearities of colloidal Au nanoparticles and the nonlinear optical effect of PVP matrix. Furthermore, with short picosecond pulses and 1 Hz repetition rate, the thermal focusing effect can be negligible in our Z-scan measurements. Usually, for optical device applications, thermal-induced nonlinear effects are not useful.

In recent years, many considerations have been taken to investigate the effectiveness of nonlinear materials for practical use in ultra-fast all-optical switching devices [18, 19]. In order to evaluate the composite films for applications in such devices, two figures of merit have to be satisfied for a $2\pi$ phase shift [19]:

$$W = \frac{|n_2| I_{\max}}{\alpha_0 \lambda} > 1, \qquad T = \frac{\beta\lambda}{|n_2|} < 1, \tag{5}$$

where $I_{\max}$ is the maximum permitted value of the light intensity and $\alpha_0$ is the absorption coefficient ($600\,\mathrm{cm^{-1}}$). By supposing that $I_{\max}$ equals the maximal intensity used

($2 \times 10^{11}$ W cm$^{-2}$), we obtained $W = 50$, $T = 6.6$, indicating that the optical properties of the composite films are yet insufficient for applications in all-optical switching technology. However, the large value of $W$ made the composite films promising for use in optical switching devices.

The OL properties of the Au/PVP composite film were investigated in the OA Z-scan scheme. The results show that the composite film strongly limits picosecond laser pulses at 532 nm. Figure 4 presents the transmittance of the Au/PVP film as a function of the laser radiation intensity, and all the points are normalized by the linear transmittance. The transmittance value is nearly constant up to $I = 6 \times 10^{10}$ W cm$^{-2}$, but further increase of intensity leads to significant decrease in transmittance. The OL threshold of Au/PVP film is comparable to that of $C_{60}$ ($4 \times 10^{10}$ W cm$^{-2}$), a well-known optical limiter [20]. In our OL experiments, the OL behaviour of the composite film is attributed to nonlinear absorption that could be explained by the influence of two-photon absorption (TPA). As shown in figure 2, the linear absorption peak of PVP just located around 260 nm may lead to near resonance two-photon absorption (TPA) of the Au/PVP film at 532 nm with picosecond laser pulses. The strong OL effect in the visible region with short response time makes the composite film promising for applications such as laser switching system for protection of eyes or sensitive optical sensors from intense laser pulses.

## 4. Conclusions

In summary, colloidal Au/PVP composite films were prepared by spin coating. Z-scan measures showed that the composite films exhibit large optical nonlinearities with the real and imaginary parts of third-order nonlinear optical susceptibility $\chi^{(3)}$ to be $4.7 \times 10^{-10}$ esu and $2.5 \times 10^{-10}$ esu, respectively. OL experiments indicated that the composite film strongly limits picosecond laser pulses at 532 nm with OL threshold comparable to that of $C_{60}$. Large third-order optical nonlinearities and strong OL effect with ultra-fast response time, as well as simple fabrication process and relatively low cost, make the Au/PVP film a valid candidate for applications in optical devices.

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