

Large third-order optical nonlinearity of periodic gold nanoparticle arrays coated with ZnO

Tingyin Ning, Yueliang Zhou, Hong Shen, Heng Lu, Zhihui Sun, Lingzhu Cao, Dongyi Guan, Dongxiang Zhang and Guozhen Yang

Institute of Physics, Chinese Academy of Sciences, PO Box 603, Beijing 100080, People's Republic of China

E-mail: ylzhou@aphy.iphy.ac.cn

Received 16 July 2007, in final form 19 September 2007

Published 19 October 2007

Online at stacks.iop.org/JPhysD/40/6705

Abstract

The third-order optical nonlinearity of a composite film consisting of periodic triangular gold nanoparticle arrays coated with ZnO was investigated by the z -scan technique. The third-order nonlinear susceptibility, $\chi^{(3)}$, measured at a wavelength of 532 nm with a pulse duration of 10 ns, was up to 1.3×10^{-5} esu. The figure of merit, $\chi^{(3)}/\alpha$ (where α is the absorption coefficient) was about 1.1×10^{-9} esu cm. The large optical nonlinearity is likely due to the strong local electromagnetic field near the triangular gold particles and ZnO matrix. The results show that the composite film has great potential for nonlinear optical devices.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Materials with large third-order nonlinear optical susceptibility are of great importance for future optical device applications, such as ultrafast optical switches, optical phase conjugation, optical computation and information processing [1, 2]. Composite films consisting of metal clusters embedded in dielectric matrices have been widely investigated due to their large third-order susceptibility and ultrafast response time [3–5]. The enhancement of the third-order nonlinear optical response comes from the strong local electromagnetic field of the metal nanoparticles near the surface plasmon resonance (SPR) [1]. However, the resonance absorption is so large that it could lead to exponential damping of optical intensity and the caused thermal effect may damage the materials. For practical application, materials with a large off-resonance value of $\chi^{(3)}$ are very important. Theoretical studies indicated that the anisotropy of both the shape and geometric distribution of the metal nanoparticles in dielectric composite films could cause a separation of the absorption peak and the enhancement of the optical nonlinearity [6, 7]. Experimental investigations also confirmed the improvement of $\chi^{(3)}$ and $\chi^{(3)}/\alpha$ via geometric anisotropy for Au/SiO₂ and Ag/BaTiO₃ composite films [8, 9]. Additionally, nanosphere

lithography (NSL) as an inexpensive and high-throughput nanofabrication was widely used to produce anisotropic nanostructures [10]. The optical nonlinearity of pure Au nanoparticle arrays fabricated using NSL has been reported recently, and pronounced enhancements of $\chi^{(3)}$ and $\chi^{(3)}/\alpha$ were observed compared with that of ultra thin Au film consisting of randomly distributed spheroidal clusters [11, 12]. In this paper, we report the large optical nonlinear susceptibility $\chi^{(3)}$ and figure of merit (FOM) of Au/ZnO composite film consisting of ordered triangular gold nanoparticles coated with ZnO matrix fabricated using NSL.

2. Experimental

The composite film comprising Au nanoparticle arrays embedded in ZnO was prepared on the glass substrate ($18 \times 18 \times 0.2$ mm³). Firstly, the periodic pure gold nanoparticle arrays were fabricated using NSL. The procedures have been described in detail elsewhere [11]. Here the diameters of polystyrene nanospheres were 360 nm. Then, the gold nanoparticle arrays were coated with ZnO film using PLD technique. During the deposition process, a XeCl excimer laser beam (308 nm, 17 ns full width at half maximum, 2 Hz repetition rate) was focused on the sintered ZnO

(99.999%) target, which was prepared using the conventional ceramic technique, 40 mm from the substrate. The ZnO film was deposited for 10 min at room temperature in pure O₂ atmosphere at a pressure of 10 Pa. The thickness of the ZnO was about 45 nm determined by the growth rate, about 0.07–0.08 nm s⁻¹.

The nanostructure of the film was investigated by atomic force microscopy (AFM) in contact model. Optical absorption spectra were measured for the Au nanoparticle arrays and Au/ZnO composite film in the range from 330 to 800 nm using a Spectrapro500i spectrophotometer (Acton Research Corporation) at room temperature. The absorption spectra were corrected automatically by the spectrophotometer, taking into account the absorbance from the glass substrates.

The nonlinear optical properties of the sample were characterized by the single beam *z*-scan technique [13]. The *z*-scan technique is an effective tool for determining the nonlinear optical effect. It is widely used in the characterization of optical nonlinearity because it provides not only the magnitudes but also the signs of the real and imaginary parts of the third-order nonlinear susceptibility $\chi^{(3)}$. When the measurement is performed without the aperture (open-aperture), the *z*-scan profile reveals the nonlinear absorption β alone. While for the small aperture (closed-aperture), the transmittance is affected by both the nonlinear refraction and the nonlinear absorption. Therefore, in order to obtain nonlinear refraction information, an approximate method was used so that the closed-aperture transmittance was divided by the corresponding open-aperture data.

A Nd:YAG *Q*-switched laser with a frequency doubled at 532 nm and a pulse width of 10 ns was used as the light source. The laser beam was focused on the sample with a 150 mm focal length lens, leading to a measured beam waist (ω_0) of 30 μm , and a pulse energy of 8.0 μJ at the focus. The Rayleigh length was calculated to be 5.3 mm, which was much longer than the film plus substrate thickness. The on-axis transmitted beam energy, the reference beam energy, and the ratios of them were measured using an energy ratiometer (Rm 6600, Laser Probe Corp.) simultaneously. In order to reduce the possible thermal accumulative effect, the laser repetition rate was set to 1 Hz.

3. Results and discussion

Figure 1 shows 2D and 3D AFM images of $2 \times 2 \mu\text{m}^2$ area of pure gold nanoparticle arrays. The images exhibit typical hexagonal patterned periodic nanoparticle arrays consisting of almost homogenous triangular-shaped gold nanoparticles. The out-of-plane height of the nanoparticle arrays is about 16 nm, which can be varied depending on the deposition time. The in-plane particle diameter, defined as the perpendicular bisector of the equilateral triangle, is estimated to be about 84 nm. The tip-to-tip interparticle spacing is about 100 nm, which is in agreement with the geometric analysis.

Figure 2 gives the corresponding AFM images of $2 \times 2 \mu\text{m}^2$ area of gold nanoparticle arrays coated with ZnO. The ZnO nanoparticles were deposited homogeneously on both the bare glass and the top of Au nanoparticle arrays so the hexagonal patterned 2D structure is still clear. The Au concentration was calculated to be about 0.5 at.%, and the volume fraction was about 8%.

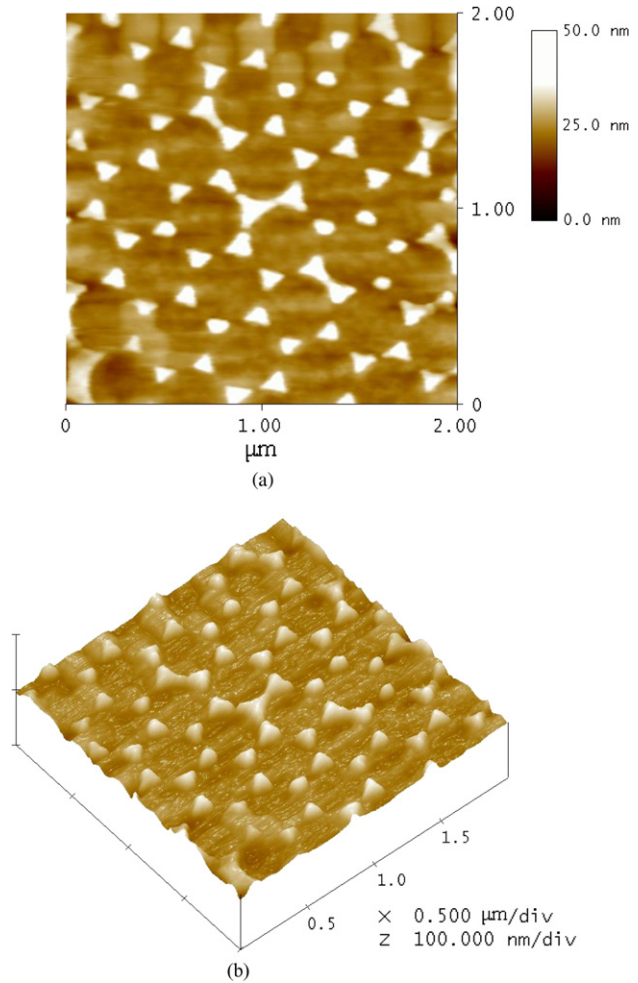


Figure 1. (a) 2D and (b) 3D AFM images of pure gold nanoparticle arrays.

Figure 3 shows the linear optical absorption spectra measured at room temperature for the Au nanoparticle arrays and Au/ZnO composite film in the range from 330 to 800 nm. An obvious SPR peak near 630 nm of the Au nanoparticle arrays was observed (curve (a)). The broad peak was due to the large Au particles. After coated with ZnO film (curve (b)), the SPR peak redshifted slightly because of the change of local dielectric environments. The absorption peak at wavelength 356 nm arose from the exciton absorption of ZnO nanocrystallites. The absorption coefficient was calculated to be $1.2 \times 10^4 \text{ cm}^{-1}$ at 532 nm, which is smaller than some representative metal/dielectric composite films ever investigated [3, 4, 8, 9]. The reasons may be the low concentration of the Au nanoparticles and the off-resonance absorption.

Typical open-aperture (OA) and closed-aperture (CA) *z*-scan curves of the sample are shown in figure 4. The filled black squares indicate the measured data, with each point corresponding to the average value of 10 pulses. The solid line represents a theoretical fit [13]. As the glass substrate has a very weak nonlinear optical response, the observed large optical nonlinearities resulted from the composite film. The OA curve shows a normalized transmittance peak, indicating the presence of nonlinear absorption saturation. The CA curve

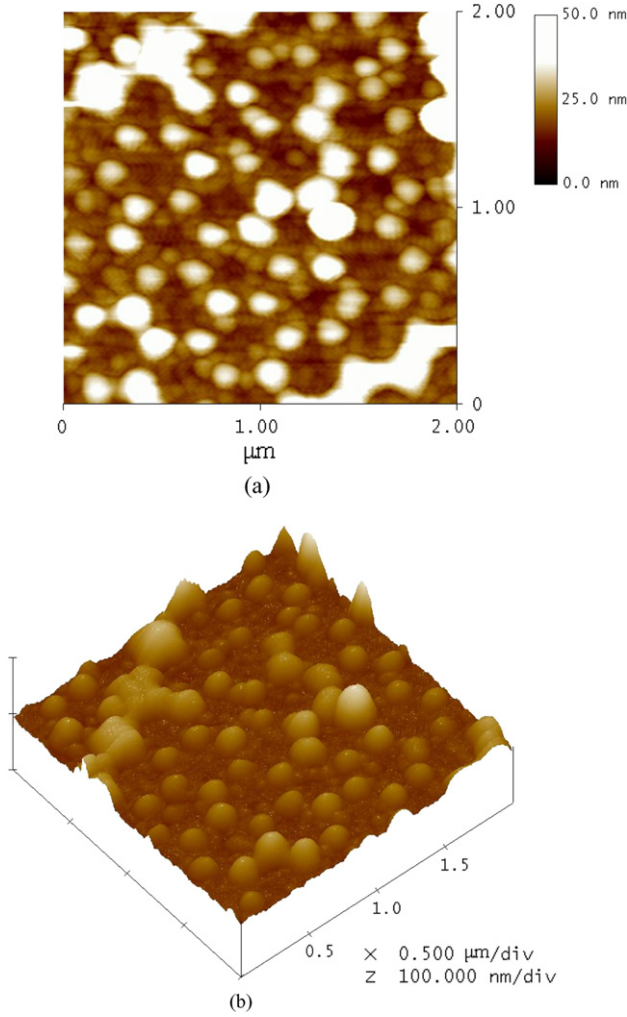


Figure 2. AFM images of Au nanoparticle arrays coated with ZnO nanoparticles, (a) 2D and (b) 3D.

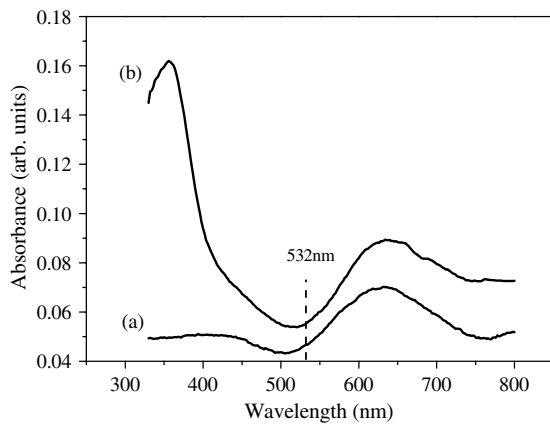


Figure 3. The optical absorption properties of (a) Au nanoparticle arrays and (b) Au/ZnO composite film. The measurement wavelength 532 nm is clearly off the SPR frequency.

has the peak-valley configuration, corresponding to a negative nonlinear refractive index.

The data were analysed using the procedures described by Sheik-Bahae *et al* [13]. The nonlinear refractive index n_2 (esu), and real part of the third-order nonlinear

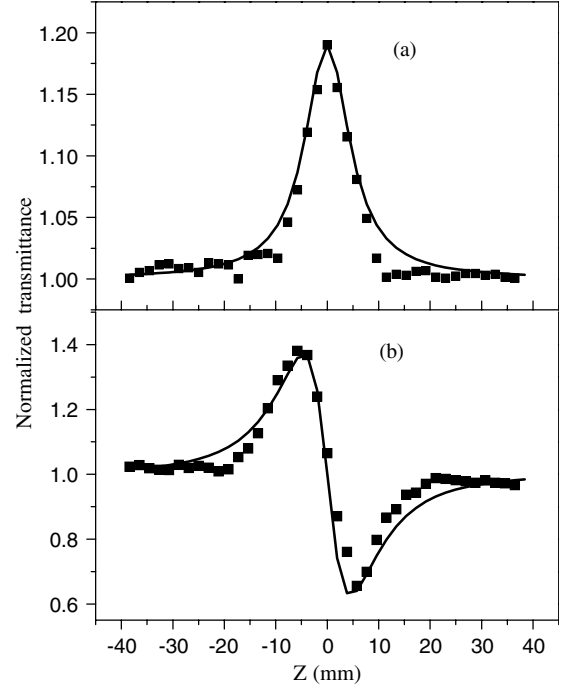


Figure 4. The z -scan data of sample with (a) an open-aperture and (b) a closed-aperture. The solid lines indicate the theoretical fit.

susceptibility, $\text{Re}\chi^{(3)}$ (esu), are given by the following equations:

$$n_2(\text{esu}) = \frac{cn_0}{40\pi^2} \frac{\lambda \Delta T_{p-v}}{0.812(1-S)^{0.25} L_{\text{eff}} I_0}, \quad (1)$$

$$\text{Re}\chi^{(3)}(\text{esu}) = \frac{n_0 n_2(\text{esu})}{3\pi}, \quad (2)$$

where c is the velocity of light, n_0 is the linear refractive index of the sample, λ is the wavelength of light, ΔT_{p-v} is the difference between the normalized peak and valley transmittance, which can be obtained through the best theoretical fit of z -scan curve as shown in figure 4(b). The linear transmittance, S , of the far-field aperture, defined as the ratio of the pulse energy passing the aperture to the total pulse energy, was measured to be 0.2. And $L_{\text{eff}} = 1 - \exp(-\alpha L)/\alpha$ is the effective thickness of the sample (L is the sample thickness, α is the linear optical absorption coefficient), and I_0 is the laser intensity at the focal point. The nonlinear absorption coefficient β (mW^{-1}) of the sample can be calculated from the normalized transmittance for the OA by the relation

$$T(z, S = 1) = \sum_{m=0}^{\infty} \frac{[-q_0(z)]^m}{(m+1)^{3/2}}, \quad (3)$$

where $q_0(z) = \beta I_0 L_{\text{eff}} / (1 + z^2/z_0^2)$, z_0 is the diffraction length of the beam. The relation between β (mW^{-1}) and $\text{Im}\chi^{(3)}$ (esu) is shown as follows:

$$\text{Im}\chi^{(3)}(\text{esu}) = \frac{n_0^2 c^2}{240\pi^2 \omega} \beta (\text{mW}^{-1}), \quad (4)$$

where ω is the angular frequency of light field.

The calculated nonlinear refractive index n_2 and absorption coefficient β are $-1.3 \times 10^{-11} \text{ m}^2 \text{ W}^{-1}$ and $-4.2 \times 10^{-5} \text{ m W}^{-1}$, respectively. The real and imaginary part of the third-order nonlinear susceptibility, $\text{Re}\chi^{(3)}$ and $\text{Im}\chi^{(3)}$, were calculated to be $-1.3 \times 10^{-5} \text{ esu}$ and $-1.8 \times 10^{-6} \text{ esu}$, respectively. The absolute value of $\chi^{(3)}$ is about $1.3 \times 10^{-5} \text{ esu}$, which is about one or two orders of magnitude larger than that of some representative nanocomposite materials with high metal concentrations at absorption resonance wavelength excited by nanosecond laser pulse [3, 9, 14]. The measurements were repeated on different spots of the film in the same condition to check the uniformity of the film, as well as at different energies for many times to test the reproducibility of the results. The relative uncertainty in the results was within the limits of 20–30%. The large optical nonlinearity could be mainly due to the microstructure of the Au nanoparticles of the composite film. Both the theoretical and experimental studies demonstrated that the local electric field near the particle surface is more intense for nonspherical particles, especially in the spots with the high-curvature radius, which tends to concentrate the electromagnetic field, and $|E|^2$ is as much as 10^4 times the incident field near the tips [15, 16]. On the other hand, the matrix of ZnO semiconductor nanoparticles that has been widely investigated also plays an important role [17–19]. First, ZnO nanoparticles has large third-order optical nonlinearity as a result of the quantum confinement effect and second, the large dielectric constant of ZnO results in the large local-field factor, which influence the enhancement of $\chi^{(3)}$ following a fourth-power law [20].

The FOM was calculated to be $1.1 \times 10^{-9} \text{ esu cm}$. Compared with some representative nonlinear optical materials [9, 14, 21], the FOM is greatly enhanced for the Au/ZnO composite film with rather low metal concentration due to the large off-resonance $\chi^{(3)}$. The results indicate that the composite film has a great potential for nonlinear optical devices.

4. Conclusions

In summary, periodic triangular gold nanoparticle arrays coated with ZnO composite film were fabricated using NSL. The third-order nonlinear optical properties were investigated by the z-scan technique at a wavelength 532 nm with laser pulse duration of 10 ns. The large third-order nonlinear optical susceptibility $\chi^{(3)}$ and FOM $\chi^{(3)}/\alpha$ reached $1.3 \times 10^{-5} \text{ esu}$ and $1.1 \times 10^{-9} \text{ esu cm}$, respectively, which are both about one or two orders of magnitude larger than some representative metal/dielectric composite materials. The large optical nonlinearity could be due to the giant local

electromagnetic field near the tips of triangular gold nanoparticle arrays. The matrix of ZnO nanoparticles also plays an important role in the enhancement of optical nonlinearity. The large optical nonlinearity and FOM indicate that the material has great potential application in future optical devices.

Acknowledgments

This work is supported by the National Nature Science Foundation of China, Grant 10574157, and the National Basic Research Program of China, No 2006cb302900.

References

- [1] Ricard D, Roussignol P and Flytzanis C 1985 *Opt. Lett.* **10** 511
- [2] Cotter D, Manning R J, Blow K J, Ellis A D, Kelly A E, Nesses D, Phillips I D, Poustie A J and Rogers D C 1999 *Science* **286** 1523
- [3] Tanahashi I, Manabe Y, Tohda T, Sasaki S and Nakamura A 1996 *J. Appl. Phys.* **79** 1244
- [4] Liao H, Wen W, Wong G K L and Yang G 2003 *Opt. Lett.* **28** 1790
- [5] Hamanaka Y, Kuwabata J, Tanahashi I, Omi S and Nakamura A 2001 *Phys. Rev. B* **63** 104302
- [6] Yuen K P, Law M F, Yu K W and Sheng P 1997 *Phys. Rev. E* **56** R1322
- [7] Gao L, Yu K W, Li Z Y and Hu B 2001 *Phys. Rev. E* **64** 036615
- [8] Liao H B, Wen W and Wong G K L 2005 *Appl. Phys. A* **80** 861
- [9] Guan D Y, Chen Z H, Wang W T, Lu H B, Zhou Y L, Jin K-J and Yang G Z 2005 *J. Opt. Soc. Am. B* **22** 1949
- [10] Haynes C L and Van Duyne R P 2001 *J. Phys. Chem. B* **105** 5599
- [11] Shen H, Cheng B, Lu G W, Ning T Y, Guan D Y, Zhou Y L and Chen Z G 2006 *Nanotechnology* **17** 4274
- [12] Wang W T, Wang Y M, Dai Z H, Sun Y M and Sun Y P 2007 *Appl. Surf. Sci.* **253** 4673
- [13] Sheik-Bahae M, Said A A, Wei T H, Hagan D J and Van Stryland W 1990 *IEEE J. Quantum Electron.* **26** 760
- [14] Yang G, Wang W T, Zhou Y L, Lu H B, Yang G Z and Chen Z G 2002 *Appl. Phys. Lett.* **81** 3969
- [15] Jensen T, Kelly L, Lazarides A and Schatz G C 1999 *J. Clust. Sci.* **10** 295
- [16] Haes A J, Zou S, Schatz G C and Van Duyne R P 2004 *J. Phys. Chem. B* **108** 6961
- [17] Guo L, Yang S, Yang C L, Yu P, Wang J N, Ge W K and Wong G K L 2000 *Appl. Phys. Lett.* **76** 2901
- [18] Petrov G I, shcheslavskiy V, Yakovlev V V, Ozerov I, Chelnokov E and Marine W 2003 *Appl. Phys. Lett.* **83** 3993
- [19] Lamrani M A, Addou M, Sofiani Z, Sahraoui B, Ebothe J, El Hichou A, Fellahi N, Berne'de J C and Dounia R 2007 *Opt. Commun.* **277** 196
- [20] Smith D D, Fischer G, Boyd R W and Gregory D A 1997 *J. Opt. Soc. Am. B* **14** 1625
- [21] Wang W T, Chen Z H, Yang G, Guan D Y, Yang G Z, Zhou Y L and Lu H B 2003 *Appl. Phys. Lett.* **83** 1983