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Abstract: Gold nanorods with different aspect ratios are prepared by a seeding growth approach in the presence of an aqueous miceller template. The aspect ratio of the nanorods is controlled by varying the ratio of AgNO3 in mixed solution. The nonlinear optical properties of gold nanorods are investigated by using the Open-aperture Z-scan technique with the nanosecond and picosecond pulse at a wavelength of 532 nm. It is identified that the nonlinear properties of gold nanoparticles are dependent on their aspect ratios and excitation of laser pulse duration. Moreover, the mechanism for the process of the nonlinear properties is also analyzed.

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**Highlights (for review)**

- Gold nanorods with controlled aspect ratios were prepared.
- The nonlinear optical properties of gold nanorods are investigated.
- Open-aperture Z-scan technique with nanosecond and picoseconds pulse was used.
- The mechanism of the nonlinear properties is analyzed.

# Nonlinear Optical Behaviors of Gold Nanorods with Different Aspect Ratios

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**Abstract**

Gold nanorods with different aspect ratios are prepared by a seeding growth approach in the presence of an aqueous miceller template. The aspect ratio of the nanorods is controlled by varying the ratio of $AgNO_3$ in mixed solution. The nonlinear optical properties of gold nanorods are investigated by using the Open-aperture Z-scan technique with the nanosecond and picosecond pulse at a wavelength of 532 nm. It is identified that the nonlinear properties of gold nanoparticles are dependent on their aspect ratios and excitation of laser pulse duration. Moreover, the mechanism for the process of the nonlinear properties is also analyzed.

*Keywords:* Gold nanorods; Nonlinear optical behaviors; Z-scan; Aspect ratio; Microstructure; Metal forming and shaping;

## 1. Introduction

Noble metal nanoparticles, especially Au and Ag, have received tremendous attention because of their interesting optical properties and potential applications. Nanostructured materials exhibit unique physical and chemical properties because of their small size. These properties differ largely from those of the corresponding single molecules and bulk materials [1-3]. Metal nanoparticles exhibit strong surface plasmon resonance(SPR) in visible region of electromagnetic spectrum, as a consequence of the electromagnetic field-induced collective oscillation of the free conduction electrons.[4] The plasmon resonance of these metal nanoparticles can cause enhancement of local electric field and lead to many interesting optical properties.[5] The SPR bands of these metal nanoparticles can be tuned from visible to near-IR range by varying the size and morphology of nanoparticles to be suitable for various applications.[6] The strong absorption, scattering, and considerable local-field enhancement occurring at the SPR results in a large optical polarization associated with the collective electron oscillations.[4] Because of this, there are many interesting nonlinear optical properties of metal nanoparticles or nanorods that give immense enthusiasm in applications, such as optical limiting device, plasmon waveguide, sensor protection, medicine, and nanoprobes.[7–10] What's more, gold nanorods will exhibit diverse nonlinear optical scattering properties when excited by different pulse widths laser. In this article, we report the nonlinear scattering behaviors of gold nanorods in nanosecond and picoseconds regimes and explain the mechanism for these behaviors.

In this paper, we have used a seeding growth method to make three kinds of gold nanorods(NRs) with different aspect ratios.[11-13] The aspect ratio of gold particles can be controlled by simply varying the ratio of $AgNO_3$ in the presence of a rodlike micellar template. The nonlinear optical properties of Au NRs are investigated at a wavelength of 532 nm with the pulses of 5 ns and 35 ps. The experimental results show that the nonlinear property of the Au NRs is dependent on their aspect ratios. These Au NRs are found to exhibit a nonlinear behavior transformation from reverse saturable absorption (RSA) (in nanosecond regime) to saturable absorption (SA) (in picoseconds regime). The strong RSA behavior is ascribed to the excited state absorption and nonlinear scattering of Au NRs and the RA behavior is caused by the bleaching of ground state plasmon band.

## 2. Experimental Section

The Au NRs were prepared by a modified synthesis method reported previously. The aspect ratio of nanorods is controlled by varying the ratio of silver nitrate to metal salt. First, a 10ml aqueous solution containing $2.5*10^{-4}$ M $HAuCl_4$ and 0.1 M cetyltrimethylammonium bromide (CTAB) was prepared in a conical flask. Next, 0.06 ml of 0.01 M $NaBH_4$ ice cold solution was added to the solution all at once while stirring. The color of solution changed immediately from yellow to brown after adding $NaBH_4$, which indicated that the gold nanoparticle seeds had been formed. The particles in this solution were used as seeds within 2–5 h after preparation.

For a typical preparation of Au NRs, the following solutions were added to a 100 mL conical flask in turn: 45 mL of 0.1 M CTAB solution, 0.200 mL of 10 mM $AgNO_3$ solution, and 2.5 mL of 10 mM $HAuCl_4$. Then the mixed liquor was added 0.275 mL of 0.1 M fresh ascorbic acid solution and the mixture was homogenized by shaking gently. Finally, 0.06 mL of seed solution was added and the entire mixed solution was left undisturbed overnight (14-16 h) in room temperature. The violet-brown colored gold nanorod solution was purified by centrifugation to remove excess CTAB (twice at 14 000 rpm, 10 min each time).

For preparation of Au NRs with other aspect ratios, the only difference was the amount of $AgNO_3$ addition in the last step. For sample a-c, 0.075mL, 0.150mL, and 0.400mL of 10 mM $AgNO_3$ solution was added in the mixed solution respectively.

**3. Results and discussion**

The morphologies of the obtained Au NRs were characterized by using a JSM- 6700F scan electron microscopy( SEM ). Figure 1 shows the SEM images of Au NRs with different aspect ratios. As the amount of $AgNO_3$ addition in the mixed solution increases, the aspect ratio of the Au NRs becomes larger.

The UV-visible absorption spectra of the obtained Au NRs were measured by using a Hitachi U-4100 spectrometer. Figure 2 shows the UV-Vis absorption spectra of Au NRs with different aspect ratio. It is evident that one peak appears in curve a and there are two SPR peaks in curve b and c. From Figure 1 we can see that the shape of sample a is almost nanosphere and the number of absorption peak should be only one theoretically. While for the two absorption peaks, the first small SPR peak at ~525 nm is due to the transverse mode perpendicular to the Au NRs; and the second strong SPR peak is due to the length of the Au NRs which gives rise to the longitudinal mode of SPR absorption. As nanorod aspect ratio increases, the longitudinal plasmon bands gradually red-shift and the SPR absorption peak increases, while the

transverse plasmon bands blue-shift a tiny little bit. The result is consistent with the theoretical calculations by Schatz et al. for gold and silver spheroids with aspect ratio from 1 to 6. [14, 15]

Nonlinear optical properties of the obtained Au nanorods were characterized by a open-aperture Z-scan experiment. To determine the nonlinear absorption of gold particles, a frequency-doubled Q-switched Nd:YAG laser (pulse duration: 5 ns and 35 ps, wavelength: 532 nm, repetition rate: 10 Hz) was used. The laser beam was focused onto the sample by a positive lens with 250 mm focal length. The sample was contained in a 5 mm thick quartz cell and the linear transmittance was adjusted to 75%. In the Z-scan measurement, the transmittance of the sample was measured when the sample moved near and away from the beam focus. The energy of the single pulse was 11.87 uJ with pulse duration of 5 ns and 1 uJ of 30 ps. The reflected and transmitted pulses energies were measured simultaneously by the energy detectors (Molectron J3S-10).

Fig.3 shows the open aperture Z-scan results of three kinds of Au NRs at 532nm with 5-ns pulses. All the curves exhibit a typical reverse saturable absorption (RSA) feature, and with the increasing of aspect ratio, Au NRs show stronger nonlinear optical absorption. Since the light at 532 nm which irradiated Au NRs could result in the strong transverse plasmon absorption followed by the excited-state absorption, the transmitted energy would decrease with increasing of laser intensity.

To describe the NLO property of the dispersions quantitatively, the curves were fitted and we get the effective nonlinear absorption coefficient $\beta_{eff}$ of the dispersions with the pulse width of 5 ns. Because the length of quartz cell used in our experiment is larger than the Rayleigh length of laser beam, we can fit the experimental results numerically by solving the propagation equation of the electric field intensity $E$ :

$$\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial E}{\partial r}\right)-2ik\frac{\partial E}{\partial z}-ik\alpha E+\frac{2k^2}{n_0}n_2\mid E\mid^2 E=0, \qquad (1)$$

$$\alpha=\alpha_0+\beta_{eff}I, \qquad (2)$$

where $\alpha_0$ is linear absorption coefficient, $I$ is laser radiation intensity, $n_0$ is linear refraction index, $n_2$ is nonlinear refraction coefficient, and $k$ is wave vector. The numerical simulation of Eq. (1) is processed with Crank–Nicholson finite difference method. The effective nonlinear absorption model and the effective nonlinear absorption coefficient $\beta_{eff}$ can be evaluated or compared with the nonlinear

optical properties of the dispersions quantitatively [16, 17]. The theoretical fitting curves (solid lines) deviate from the experimental data partly in Figure 3, which can be attributed to the difference between the effective nonlinear absorption model and the nonlinear scattering process of the dispersion. By fitting above result, we get the effective nonlinear absorption coefficient $\beta_{eff}$ =18 cm/GW, 26 cm/GW and 27 cm/GW for samples a-c, respectively.

In addition, the nonlinear scattering can exert an influence on the nonlinear optical absorptions for Au nanoparticles in solution [18, 19]. We have known that the micro-bubbles in solvent [20, 21] serving as scattering centers can result in the nonlinear scattering and accordingly enhance the NLO effect. Actually, nonlinear scattering depends on the size of particles and the bigger particles are, the stronger nonlinear scattering is. We can estimate that the nonlinear scattering is stronger than the plasmon and excited-state absorptions. In order to confirm the above viewpoint, we conduct the investigation on Au NRs at 532 nm with 30-ps pulses, and the result is shown in Fig. 4. All the curves exhibit a typical saturable absorption (SA) feature, although height of the peaks differs from one to another, indicating different SA abilities. The SA is a result of the ground-state plasmon bleaching at moderate intensities. Since the transverse SPR peak of Au NRs is near the excitation wavelength of 532 nm, the majority of electrons in the conduction band are pumped to the excited-state, and thus, resulting in the strong ground-state plasmon bleaching. Because the SPR peak of sample a and b is closer to 530nm than that of sample c, sample a and b exhibit stronger nonlinear saturable absorption. We fit the curves to get the effective nonlinear absorption coefficient $\beta_{eff}$ of the dispersions with the pulse width of 30 ps by solving the above propagation equation. We get $\beta_{eff}$ =1.28 cm/GW, 1.30 cm/GW, and 1.15 cm/GW for samples a-c, respectively

## 4. Conclusion

We have investigated the nonlinear optical properties of gold nanorods with different aspect ratios, with the excitation of nanosecond and picosecond pulses at 532 nm. We compare the optical nonlinearities of three gold nanorods and find the dependence on aspect ratio and excitation pulse duration. The optical nonlinearity is ascribed to the contributions of the plasmon absorption, nonlinear scattering resulting from micro-bubbles in solution with excitation of nanosecond pulses, and ground-state plasmon bleaching with picosecond pulses.

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**Figure Captions**

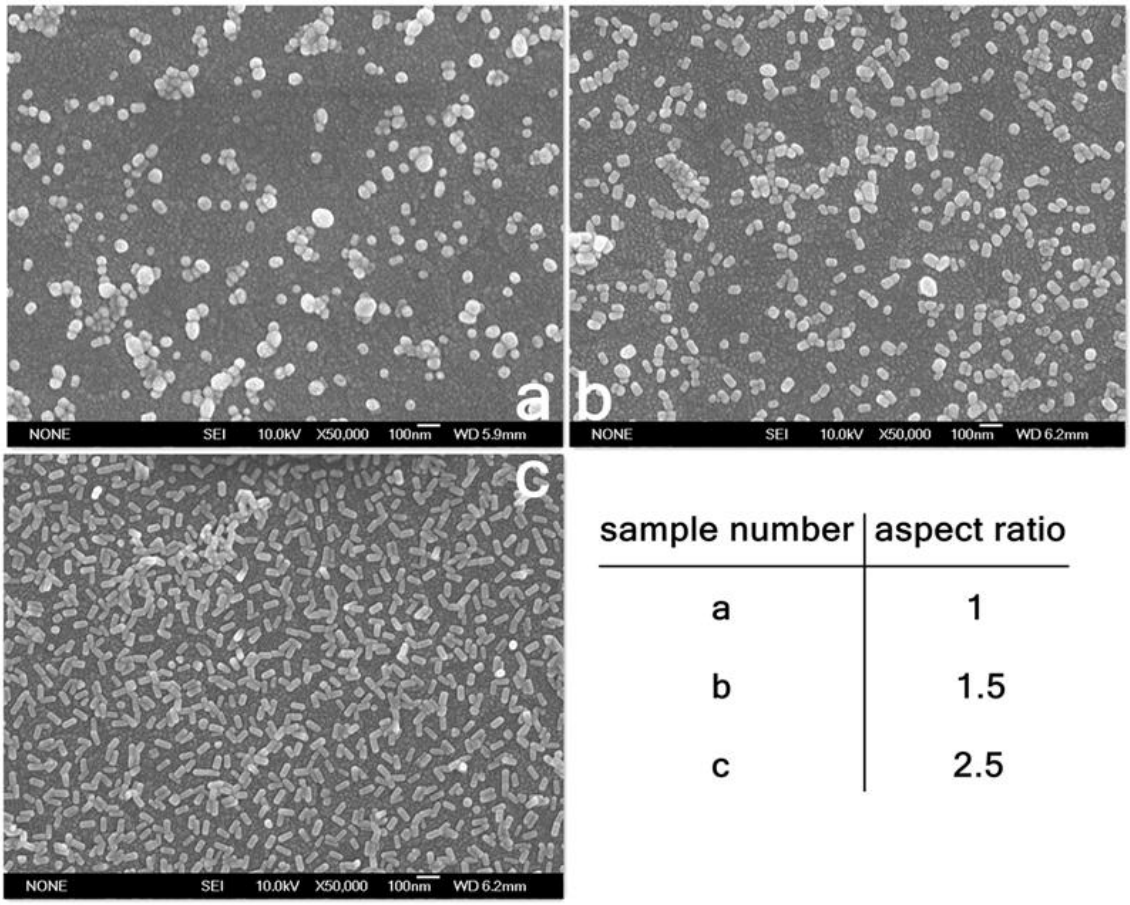
**Fig.1** SEM images of three gold nanorods (a-c) with different aspect ratios. Solution conditions are given in

the experimental section.

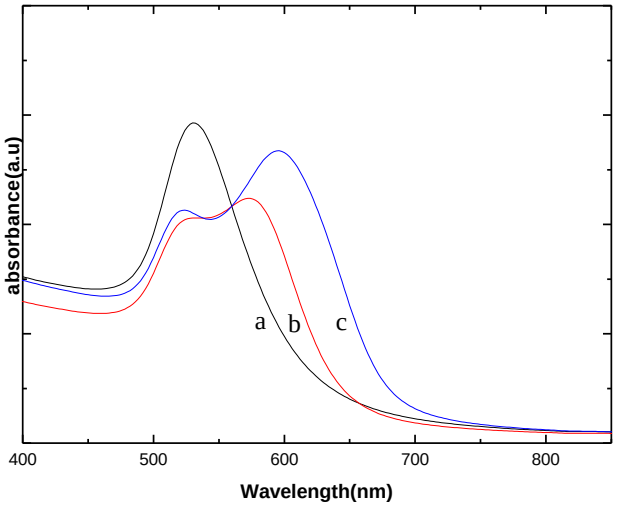
**Fig.2** UV-Vis absorption spectra of the gold nanorods corresponding to images a-c shown in Figure 1.

**Fig.3** Open aperture Z-scans of the three gold nanorods suspensions with the pulse-width of 5 ns. The solid lines represent the fitting results using the model described in the text.

**Fig.4** Open aperture Z-scans of the three gold nanorods suspensions with the pulse-width of 30 ps. The solid lines represent the fitting results using the model described in the text.




| sample number | aspect ratio |
|---|---|
| a | 1 |
| b | 1.5 |
| c | 2.5 |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b
c
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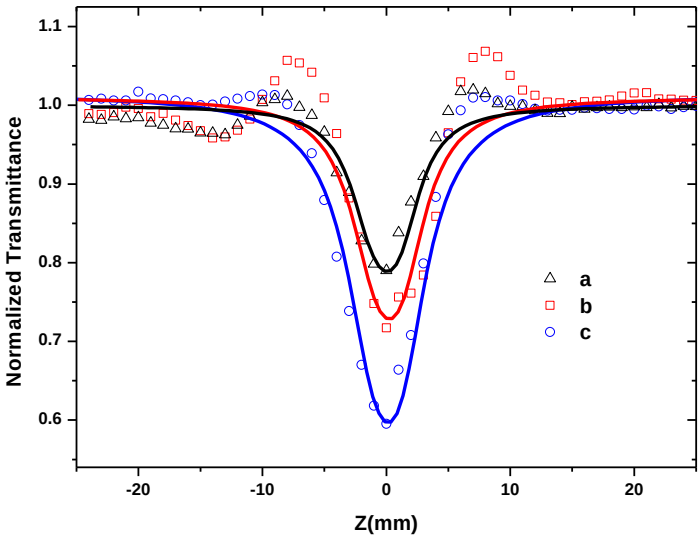
500
600
700
800
Wavelength(nm)


Normalized Transmittance
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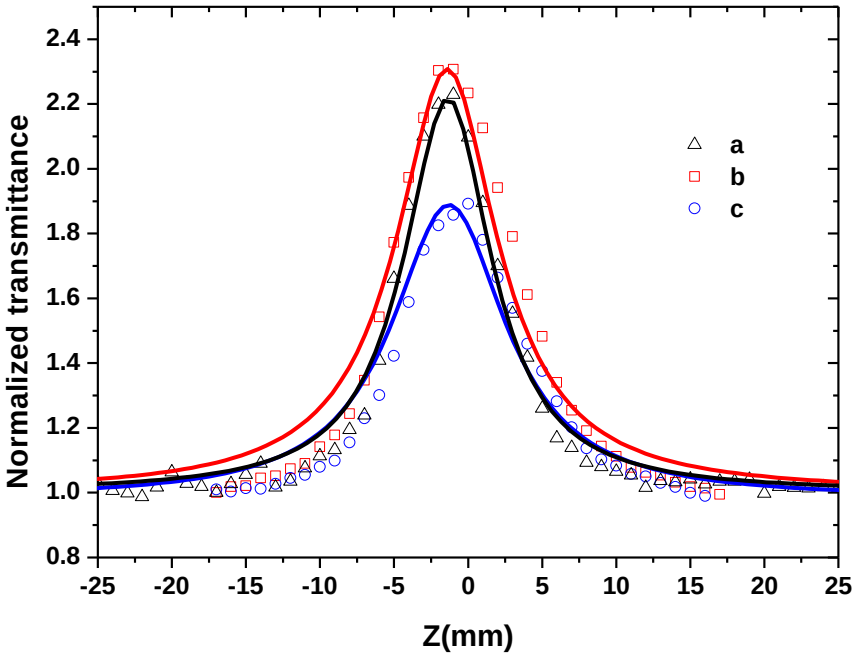
0.8
0.7
0.6
-20
-10
0
10
20
Z(mm)
a
b
c


Normalized transmittance
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2.0
1.8
1.6
1.4
1.2
1.0
0.8
-25
-20
-15
-10
-5
0
5
10
15
20
25
Z(mm)
a
b
c