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Nonlinear refraction of silver nanowires from nanosecond to femtosecond laser excitation

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Abstract In order to investigate the effect of pulse width and solvent on the nonlinear properties of metal nanostructures, silver nanowires were fabricated in a direct current electric field (DCEF) using a solid-state ionic method and characterized by transmission electron microscopy (TEM) and X-ray diffraction (XRD). The nonlinear refractive index (γ) of silver nanowires suspended in ethanol was measured using the Z-scan technique and laser radiation of various (femto-, pico-, and nanosecond) pulse durations. Experimental results indicated that silver nanowires have obvious positive refractive nonlinearities and γ (the Kerr-induced self-focusing) increases as the pulse duration increases from 7.4×10^{-8} cm^2/GW at 110 fs to 1.6×10^{-4} cm^2/GW at 8 ns, due to the additional influence of the atomic reorientational Kerr effect in the case of longer pulses. Due to the solvent dependence of the nonlinear behavior of the silver nanowires, the nonlinear absorption and refraction of silver nanowires suspended in de-ionized water are smaller than those of silver samples suspended in ethanol. The thermal nonlinearities are insignificant in our experimental conditions.

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1 Introduction

Motivated by the great potential applications of one-dimensional nanostructured metals in ultra-fast optical switching, high-density storage devices, etc. [1], much effort has been directed to the development of nanostructured noble metals with large third-order nonlinear optical susceptibility. Silver nanoparticles and nanowires have attracted much attention from the research community, because they exhibit the highest electrical conductivity among all metals and the surfaces of silver nanowires can significantly enhance the Raman scattering signal of molecules adsorbed on the surfaces [2]. Many experiments indicate that the studies of the nonlinear optical effects of nanomaterials are very important. People once used the large nonlinear effects of silver nanowires to realize upconversion using a two-photon fluorescence excited technique [3]. The nonlinear optical coefficients of ellipsoidal silver nanoparticles were measured in the longitudinal surface plasmon absorption range (800 nm) [4]. Much work has been done on the nonlinear optical properties of silver nanoparticles in various glass matrices and liquids in recent years [5–8]. The optical limiting performances of some metal nanowires are comparable to or better than that of carbon nanotubes [9].

In this paper, we present our studies of nonlinear refraction of silver nanowires prepared by a solid-state ionic method [10, 11] without any template at room temperature

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and in vacuum. We analyze nonlinear refraction of these media using the Z-scan technique [12] with radiation of different wavelengths, pulse-repetition rates, and pulse durations. The Z-scan technique, originally proposed by Sheik-Bahae et al., is based on the principles of the laser beam spatial distortion. As the sample is moved along the propagation path (z) of a focused Gaussian beam, the sign and magnitude of the third-order nonlinear refraction and absorption are easily deduced from the two transmittance curves (Z-scan) measured with or without a finite aperture in the far field, and the technique offers simplicity as well as very high sensitivity.

2 Experimental

Silver nanowires were fabricated in a direct current electric field (DCEF) using a solid-state ionic method, as shown in Fig. 1. The silver nanowires obtained were separated from the surface of the $RbAg_4I_5$ film by a needle point, and then ultrasonically suspended separately in de-ionized water and ethanol. The grown silver nanowires were characterized by transmission electron microscopy (TEM) and X-ray diffraction (XRD) [13].

The nonlinear refraction of the silver nanowires suspended in ethanol was measured using the Z-scan technique with three lasers operating at different lasing conditions. The first (L1) was a frequency-doubled, Q-switched, mode-locked Continuum ns/ps Nd:YAG laser, which produced 8-ns laser pulses at 532 nm with a repetition rate of 1 Hz. The second (L2) was an EKSPLA (PL2143A) ps laser, producing 30-ps laser pulses at 532 nm with a repetition rate of 2 Hz. Both the incident and transmitted laser pulses were monitored simultaneously using two energy detectors (818-09B, Newport Corp.). The lens had a focal length of 30.8 cm and the aperture had a linear transmittance S of 0.17.

The third laser (L3) was a Ti:sapphire laser (Spitfire regenerative amplifier, Spectra Physics), delivering femtosecond pulses ($t = 110$ fs, $\lambda = 795$ nm) with 1-kHz pulse-repetition rate. The lens had a focal length of 17.5 cm and the aperture had a linear transmittance S of 0.27. The Z-scan signal was detected with a photomultiplier tube (PMTH-S1-CR131, Hamamatsu) and displayed on the computer through an analog to digital converter.

Silver nanowires were suspended in ethanol and contained in a 2-mm-thick quartz cell for measurement. Although the volume fraction of silver nanowires in the tested solution could be different and very low (only about 10^{-5} to 10^{-6}), it could be adjusted in such a way that their linear transmittances in the three experiments were all 80%. The laser pulse energies used in our experiment were about 110, 6.2, and 4.0 μJ for L1, L2, and L3, respectively.

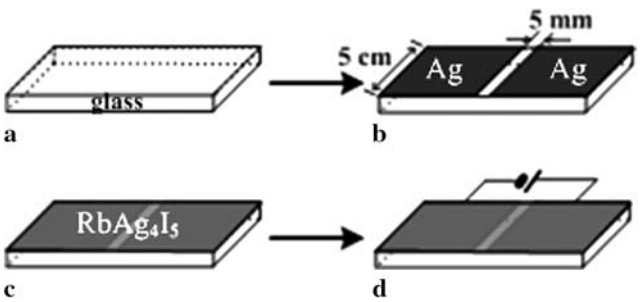

Fig. 1 Process diagram for fabrication of silver nanowires. (**a**) A clean glass substrate, (**b**) and (**c**) deposition of Ag film electrodes and $RbAg_4I_5$ film, respectively, (**d**) application of a DCEF between two Ag electrodes

3 Results and discussion

As shown in Fig. 2, silver nanowires are 0.8–1.0-μm long and 50–60 nm in diameter. It can be seen from the linear absorption spectrum of silver nanowires in ethanol shown in Fig. 3 that there is a specific surface plasmon resonance (SPR) absorption band around 410 nm.

To determine the nonlinear refraction of silver nanowires, the samples were scanned with a closed aperture and an open

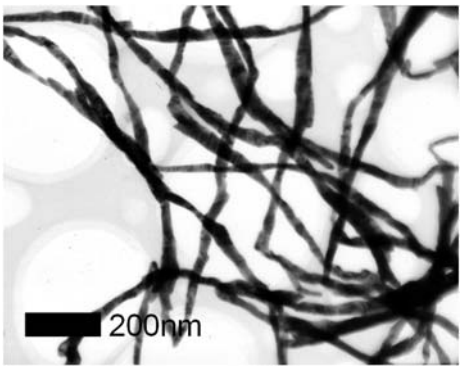

Fig. 2 TEM image of the ultrasonically dispersed silver nanowires

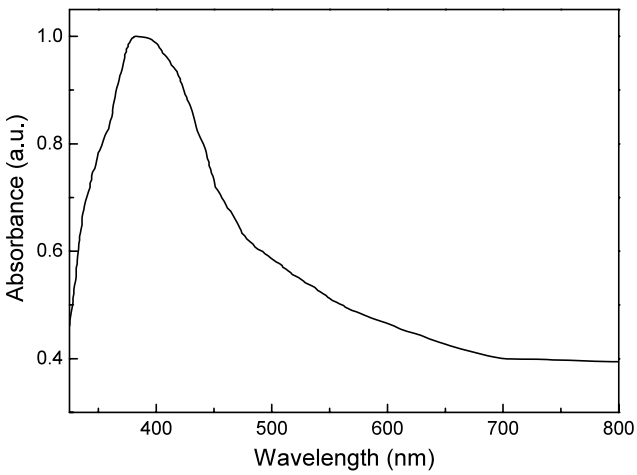

Fig. 3 The linear absorption spectrum of silver nanowires in ethanol

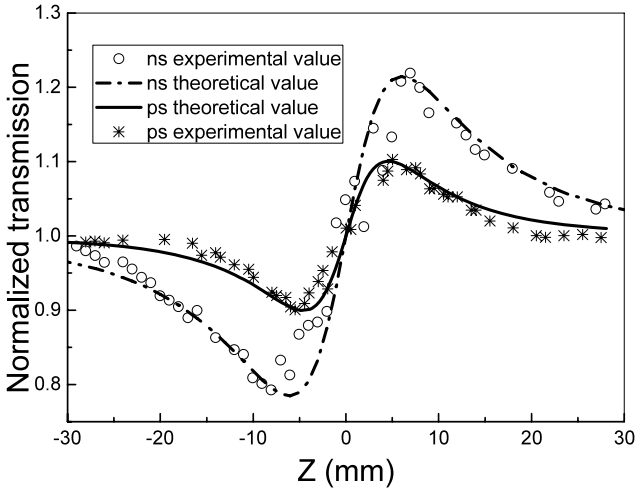

Fig. 4 The normalized transmittance of silver nanowires suspended in ethanol in the case of long pulses (8 ns) and short pulses (30 ps). Closed-aperture scheme, $\lambda = 532$ nm

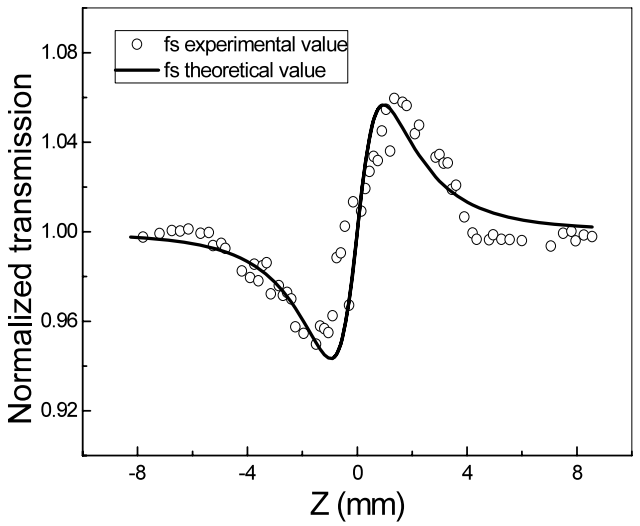

Fig. 5 The normalized transmittance of silver nanowires suspended in ethanol in the case of ultra-short pulses (110 fs). Closed-aperture scheme, $\lambda = 795$ nm

aperture ($S = 1$). In order to measure the nonlinear index of refraction, the closed-aperture data was divided by the open-aperture data to obtain the Z-scan transmission. The pure nonlinear index of refraction of the silver nanowires is shown in Figs. 4 and 5.

The prefocal valley and the postfocal peak of the curve indicate that the nonlinear refraction of the samples is positive and belongs to self-focusing nonlinearity.

The nonlinear refractive index, γ, of the silver nanowires can be evaluated by using the normalized transmittance difference between peak and valley, ΔT_{p-v}, as shown in Figs. 4 and 5. According to Z-scan theory [12], the nonlinear refractive index γ is related to ΔT_{p-v} as (1)–(3) below.

$$\Delta T_{p-v} = 0.406(1 - S)^{0.25}|\Delta\Phi_0|, \tag{1}$$

$$|\Delta\Phi_0| = (2\pi/\lambda)\gamma I_0 L_{\text{eff}}, \tag{2}$$

$$L_{\text{eff}} = \big(1 - \exp(\alpha L)\big)/\alpha, \tag{3}$$

where S is the aperture linear transmittance, $|\Delta\Phi_0|$ is the phase shift at the focus, I_0 is the on-axis intensity at the focus, λ is the wavelength of excitation light, α is the linear absorption coefficient, L is the thickness (2 mm) of the sample, and γ is the nonlinear refractive index expressed in SI units. According to (1)–(3), γ of silver is 1.6×10^{-4} cm^2/GW at 8 ns, 5.9×10^{-6} cm^2/GW at 30 ps, and 7.4×10^{-8} cm^2/GW at 110 fs.

We know from previous studies [5–8] that the nonlinear optical properties of Ag embedded in various glass matrices and Ag-containing liquids can be caused by the Kerr-induced self-focusing (or self-defocusing) and thermal-induced nonlinearity, etc. Therefore, we analyzed the influence of the thermal effect on observed nonlinear refraction of silver nanowires in the case of nanosecond pulses [13] and found that the thermal effect did not play an important role in our experimental conditions. The positive nonlinear refraction was due to the Kerr-induced self-focusing effect. Three contributions to the optical Kerr response are expected—an instantaneous electronic contribution arising from the interband contributions [14, 15], a rapid interaction-induced contribution, and a slower reorientational term (the nanowire adjusts its atomic arrangement so that the adopted orientation becomes parallel to the field). γ (the Kerr-induced self-focusing) increases as the pulse duration increases from 7.4×10^{-8} cm^2/GW at 110 fs to 1.6×10^{-4} cm^2/GW at 8 ns due to the additional influence of the atomic reorientational Kerr effect in the case of longer pulses.

We also found that, due to the solvent dependence of the nonlinear behavior of the silver nanowires, the nonlinear absorption and refraction of silver nanowires suspended in de-ionized water are smaller than those of the samples suspended in ethanol. The nonlinear refractive index for 8-ns pulses at 532 nm is larger than that reported in Ref. [13] for silver nanowires suspended in de-ionized water. As shown in Fig. 6, the nonlinear absorption of silver nanowires suspended in de-ionized water is also smaller than that of silver samples suspended in ethanol. The main reasons for these differences in the nonlinear absorption and refraction of silver nanowires between the two samples are due to the solvent effect. The solvent effect can be explained as follows.

According to the MGT (Maxwell–Garnett theory), the effective third-order nonlinear susceptibility of the composites can be expressed as [16]

$$\chi_{\text{eff}}^{(3)} = f\beta^2(\omega)\big|\beta(\omega)\big|^2 \cdot \chi_m^{(3)}, \tag{4}$$

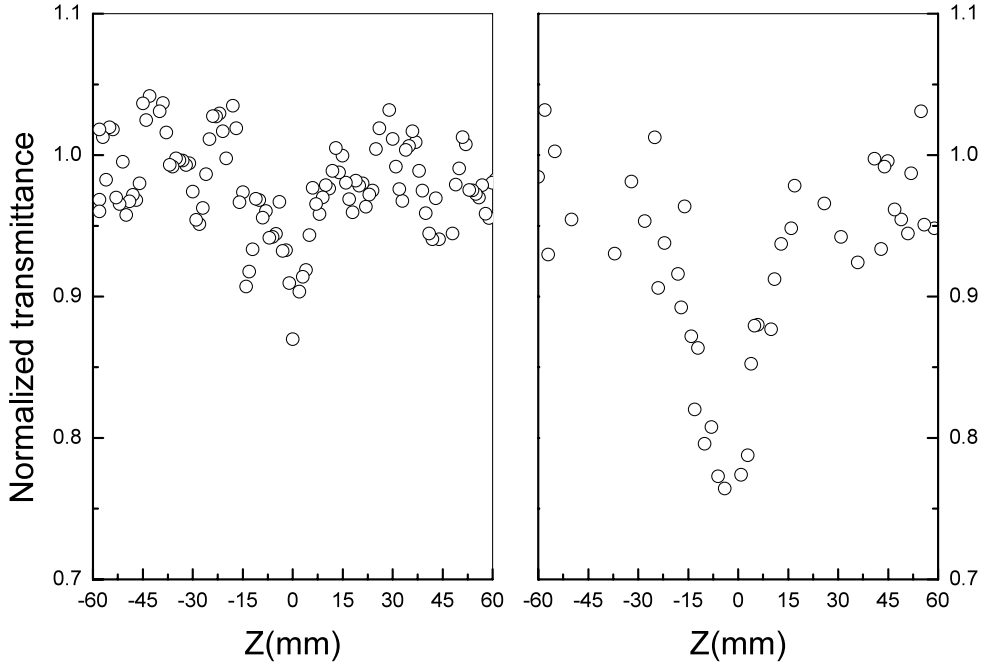

Fig. 6 The normalized transmittance of silver nanowires suspended in de-ionized water and ethanol, respectively, in the case of long pulses (8 ns). Open-aperture scheme, $\lambda = 532$ nm

where f is the volume fraction of silver, β is the local field factor, and $\chi_m^{(3)}$ is the third-order nonlinear susceptibility of the silver nanowire itself. The local field factor of nanorods can be expressed as [17]

$$\beta_{\text{nanorods}} = \frac{5\varepsilon_h + \varepsilon_m}{3(\varepsilon_h + \varepsilon_m)}, \tag{5}$$

where ε_m and ε_h are the dielectric constants of the silver nanorods and the surrounding dielectric, respectively.

It can be seen from (4) and (5) that different matrices have different effects on the same material when nanomaterials are of the same form. For Ag in the same form, the local field factor of Ag is different when it is dispersed in different matrices. For a fixed ε_m, β increases as ε_h increases, and so $\chi_{\text{eff}}^{(3)}$ is greater.

β of ethanol is greater than β of water, because ε_h of ethanol is greater than ε_h of water. Therefore, the nonlinear absorption and refraction of silver nanowires suspended in ethanol are greater than those of silver samples suspended in de-ionized water.

4 Conclusions

In summary, silver nanowires were fabricated in a direct current electric field using a solid-state ionic method and characterized by transmission electron microscopy (TEM) and X-ray diffraction (XRD). The nonlinear refractive index (γ) of silver nanowires suspended in ethanol was measured using the Z-scan technique and laser radiation of various (femto-, pico-, and nanosecond) pulse durations. Experimental results indicated that silver nanowires have positive refractive nonlinearities and γ (the Kerr-induced self-focusing) increases as the pulse duration increases from 7.4×10^{-8} cm^2/GW 110 fs to 1.6×10^{-4} cm^2/GW 8 ns, due to the additional influence of the atomic reorientational Kerr effect in the case of longer pulses. Due to the solvent dependence of the nonlinear behavior of the silver nanowires, the nonlinear absorption and refraction of silver nanowires suspended in de-ionized water are smaller than those of silver samples suspended in ethanol. The thermal nonlinearities are insignificant in our experimental conditions.

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