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Shape dependence of nonlinear optical behaviors of nanostructured silver and their silica gel glass composites

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Nanostructured Ag in shapes of nanoplate, nanowire, and nanoparticle, as well as their silica gel glass composites have been prepared and characterized. Nonlinear optical (NLO) properties were measured at 532 and 1064 nm using open aperture *z*-scan technique and studied from the view of shape effect. NLO behaviors of the nanostructured Ag are found to be shape dependent in suspensions at both the investigated wavelengths, although they originate differently. Comparing to the mother suspensions, the Ag/silica gel glass nanocomposites present rather dissimilar NLO behaviors, which is quite interesting for further studies. © *2008 American Institute of Physics.*
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The linear and nonlinear optical (NLO) properties of nanostructured noble metals, which are supposed to be drastically influenced by quantum confinement effect and therefore different from bulks, are among the highlighted researches in years due to their promising applications in optoelectronic field. The understanding of size/shape dependence of their linear and NLO behaviors is crucial for designing of an effective component and device, and hence, intensive efforts have been made toward this end, from both theoretical and experimental aspects.[1–6]

Meanwhile, most of these studies were conducted in liquid matrices. Despite the significant fundamental importance for the formulation of size/shape design strategy, from the viewpoint of practical use, it is of the same importance to homogeneously disperse the nanostructured metals in solid-state matrices to avoid their easy agglomeration and instability in suspensions. In this case, investigation of their NLO behaviors and possible mechanisms in solid matrices becomes the most significant step toward the development of practical optoelectronic components and devices.

In this letter, we describe the synthesis and NLO properties of three different shapes of nanostructured Ag (nanoplates, nanowires, and nanoparticles), as well as the fabrication of optically transparent composites consisting of such nanostructures in silica gel glass matrix under room temperature and atmospheric bench top conditions. Our emphasis in this letter is on the NLO properties originated from nonlinear scattering (NLS)/absorption (NLA). In particular, we observed quite complicated open aperture (OA) *z*-scan profiles of the nanostructured Ag in solid-state silica gel glass matrix at both 532 and 1064 nm, which are very different from their mother suspensions.

We respectively synthesized Ag nanoplates, nanowires, and nanoparticles, using procedures reported by other groups.[7–9] Briefly, for the synthesis of Ag nanowires, 6 ml of an ethylene glycol (EG) solution of 0.1*M* AgNO₃ and 6 ml of an EG solution of Poly(vinyl pyrrolidone) (PVP) [0.6*M* in repeating unit, molecular weight (MW) 55 000] were mixed uniformly under stirring at room temperature. The mixture was then injected dropwise into 10 ml of EG, which had been previously refluxed at 170 °C for about 1 h. The reac-

tion was continued at 170 °C for 60 min under vigorous magnetic stirring. Finally, resultant Ag nanowires were separated by centrifugation at 2000 rpm for 20 min and followed by washing for four to five times with alcohol and acetone. Ag nanoparticles were made similarly by changing the molar ratio of PVP to AgNO₃ to 10:1 and using lower molecular weight PVP (MW 40 000). For the synthesis of Ag nanoplates, 20 ml of a N,N-dimethylformamide (DMF) solution of 0.1*M* AgNO₃ was added dropwise into 20 ml of a DMF solution of 0.5*M* PVP (MW 40 000). The mixture was subsequently refluxed at 140 °C for 90 min. Ag nanoplates were then obtained by centrifugation at 6000–8000 rpm and following washing.

The optically transparent Ag/Silica gel glass nanocomposites were fabricated by the hydrolysis and polycondensation of 3-aminopropyltrie-thoxysilane [NH₂(CH₂)₃Si(OC₂H₅)₃, APTES] and 3-glycidoxy-propltrimethoxysilane [CH₂OCHCH₂O(CH₂)₃Si(OCH₃)₃, GPTMS] in the presence of nanostructured Ag. Specifically, 3.6 ml APTES, 10 ml GPTMS, 16 ml ethanol, and 10 ml DMF were mixed under magnetic stirring for 15 min. Then 2.4 ml nanostructured Ag containing water suspension was added gradually and stirred continuously for 4 h. After that, the mixture was divided into several equal volume divisions, cast into polystyrene cells individually, sealed and left aging and drying for several weeks. The finally obtained nanocomposite samples are transparent gel glasses with optical quality and a uniform thickness of 1.3 mm, which are sufficient to meet the requirements of optical measurements without further processing.

To confirm the geometry of the obtained nanostructured Ag, scanning electron microscopy (SEM) measurements were performed (Fig. 1). Figures 1(a)–1(c) show the dominant and uniform shapes of Ag nanoplate, nanowire, and nanoparticle, respectively, in the samples. Meanwhile, the extinction spectra of the nanostructured Ag suspended in water, together with that of the gel glass composites, were characterized with a ultraviolet (UV)-visible spectrophometer (Fig. 2). All the absorption spectra were normalized for clear presentation. From Fig. 2(a), we can see that the extinction spectra of nanostructured Ag are strongly shape dependent in suspensions, which have be theoretically predicted and experimentally confirmed. For Ag nanoplates, the spectrum
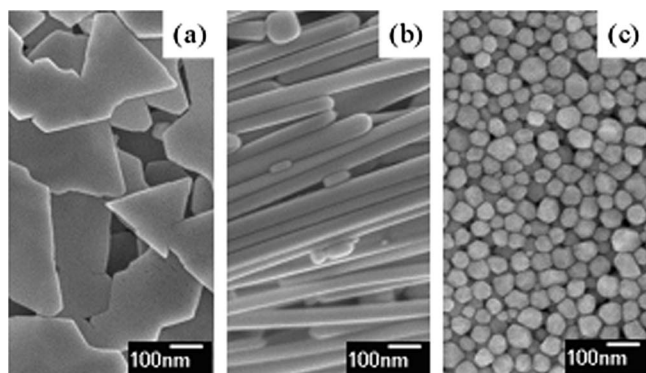
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FIG. 1. SEM images of the investigated Ag nanoplates (a), nanowires, (b) and nanoparticles (c).

FIG. 3. (Color online) OA *z*-scan curves of the investigated nanostructured Ag suspensions at 532 (a) and 1064 nm (b). The dots correspond to experimental results; the solid lines are just guides to the eye. Inset: scattering curves.

mainly consists of three peaks, a shallow peak around 730 nm, a strong one around 510 nm, and a small but sharp one at 350 nm. The former one is due to out-of-plane polarization, while the latter two belong to in-plane polarization.[10] For Ag nanowires, the spectrum has two peaks, a strong one around 420 nm, and a shallow and broad one around 570 nm, which could be attributed to transverse and longitudinal modes of surface plasmon resonance (SPR) of Ag nanowires, respectively.[11] Last, for Ag nanoparticles, it has only one peak around 450 nm, which is obviously the extinction peak of Ag nanospheres according to the Mie theory.[12] On the other hand, Fig. 2(b) shows the broadening of the absorption peaks after the nanostructured Ag was introduced into solid-state matrix, which is not unpredictable because of the easy agglomeration of these nanostructures.

The NLO properties of the water suspended nanostructured Ag and their silica gel glass nanocomposites were investigated with 8 ns laser pulses, at a repetition rate of 1 Hz, from a Nd: YAG (yttrium aluminum garnet) laser at wavelengths of 532 and 1064 nm. The bean waists were ~14.5 μm (532 nm) and ~29.0 μm (1064 nm). The energy of single pulse was 0.25 mJ. Liquid samples were contained in 1 mm thick quartz cuvettes, while solid samples were fixed vertically using a clamp. Linear transmittance of all the tested samples, including suspensions and gel glasses, was adjusted to ~70% at both the investigated wavelengths.
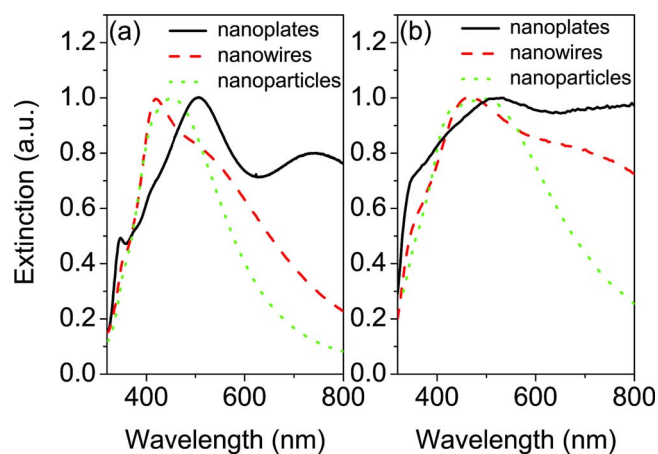

FIG. 2. (Color online) UV-vis extinction spectra of the investigated nanostructured Ag water suspension (a) and Ag/silica gel glass nanocomposites (b).
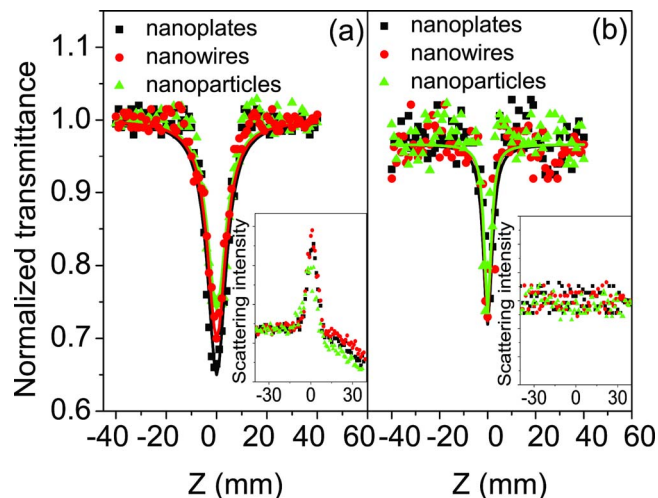
Figure 3 shows the OA *z*-scan response of the nanostructured Ag in water suspensions at 532 and 1064 nm. All the curves present a typical reverse-saturable absorption (RSA) feature, although deepness of the valleys differs from one to another, indicating different RSA abilities. Among these *z*-scans, Ag nanoplates always show the best NLO properties. To further investigate the origin of the RSA, we carried out scattering measurements at an angle of 45° (Fig. 3, inset), which clearly shows that there is strong scattering at 532 nm, but none at 1064 nm. Based on this, we attribute the RSA at 532 nm to NLO scattering, similar to that of carbon nanotubes. The key mechanisms are the photon-induced ionization and excitation of the Ag atoms, which lead to the formation of rapidly expanding microplasmas and microbubbles, strongly scatter the incident light and finally results in RSA.[13,14] In this case, the larger the scattering center, the more efficient the NLO scattering, and this can well explain the RSA sequence of the nanostructured Ag at 532 nm. On the other hand, due to none scattering at 1064 nm, the RSA at this wavelength may originate from free carrier absorption, which is a common phenomenon at infrared wavelength region. Nanoplates have the largest absorption cross section, and therefore, the largest RSA effect.

NLO behaviors of the Ag/silica gel glass nanocomposites were also investigated (Fig. 4). In contrast to their mother suspensions, the composites demonstrate quite complicated OA *z*-scan traces and the traces are not sensitive to the nanostructured shapes. It is worth noting that to a different extent, all the traces share a same feature, two symmetrical humps (increase in transmittance) flanking the valley around the focus. While hump indicates saturable absorption (SA) and valley represents RSA, this result is indeed in very good agreement with the NLO behaviors observed in gold-precipitated Na–Ca–Si–O glasses made by reduction in gold ions under femtosecond laser irradiation.[15] For the case of solid-state matrix, it is impossible that the NLO behaviors of the nanocomposite stem from the scattering of microbubbles due to the rigid solid-state environment of surrounding silica network. Therefore, it is reasonable to attribute the NLO behaviors to NLA of the embedded nanostructured Ag, which may originate from transitions from ground state to excited
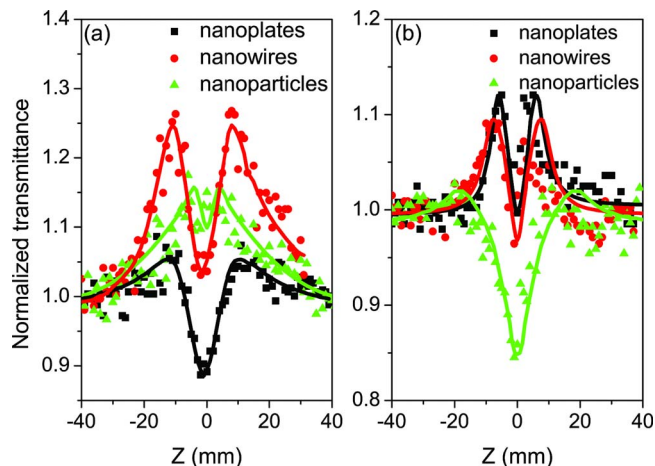
FIG. 4. (Color online) OA z-scan curves of the investigated Ag/silica gel glass nanocomposites at 532 (a) and 1064 nm (b). The dots correspond to experimental results; the solid lines are just guides to the eye.

state in the conduction band (intraband transition), as well as transitions from the valence band to the conduction band (interband transition). Under relatively lower radiation, most of the ground-state electrons are pumped to the excited state, and left behind many empty states which are unlikely filled up by electrons from the valence band due to the weak interband transition. The combination of these two factors directly leads to the reduction in electronic population of ground-state, and therefore the bleach of ground-state absorption, which ultimately leads to the decrease in the light absorption and the increase in the transmittance (hump). However, under high irradiation near the focus, the electrons in the excited state are excited further by laser pulses. Free carrier absorption appears and dominates. As the result, transmittance reduces and valley appears in the OA z-scan curves.

Interestingly, the very similar behaviors were observed in gold nanorod suspensions under femtosecond laser irradiation around the longitudinal SPR peak of 800 nm.[16] In this work, the NLA signals transfered from SA to RSA when the input irradiance was increased from 0.62 to 24 GW/cm.[2] The same behavior also appeared in our own experiments when we carried out OA z-scan measurements on 5 nm gold nanospheres at 532 nm wavelength. When we gradually increased the input energy from 0.6 to 1.5 mJ, we found the NLA signals changed from SA to RSA.

In conclusion, we have investigated the shape dependent NLO behaviors of nanostructured Ag (nanoplates, nanowires, and nanoparticles) suspensions, and their silica gel glass composites at both 532 and 1064 nm. NLO abilities of the nanostructured suspensions are found to be shape dependent at both the wavelengths, although they may have different origins. The nanocomposites present rather dissimilar NLO behaviors in comparison to their mother suspensions, which is quite interesting for further studies.

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