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Surface-plasmon enhanced ultrafast third-order optical nonlinearities in ellipsoidal gold nanoparticles embedded bismuthate glasses

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ABSTRACT

Ellipsoidal gold nanoparticles embedded bismuthate glasses have been prepared via a facile melt-annealing approach. Femtosecond *Z*-scan measurement shows that the nanocomposites exhibit a maximum third-order nonlinear susceptibility $\chi^{(3)}$ of 4.88×10^{-10} esu at 800 nm, which is two orders higher than that of the host glass. Optical Kerr shutter measurement demonstrates ultrafast response time (in scale of sub-picosecond) of the intraband transition enhanced third-order nonlinearities.

1. Introduction

In the past decades, great progress has been made in nanomaterials for nonlinear optics [1]. In particular, metal nanoparticles signified by surface plasmon resonance (SPR) are of considerable attentions [2–4] due to the enhanced optical nonlinear processes within their SPR region. For spherical metal particles that most previous studies focused on, the SPR-assist nonlinearities were unfortunately limited in a narrow range because such particle geometry results in a single SPR band [5], usually in visible region. Alternatively, for prolate spheroid particles, electronic oscillations parallel (longitudinal mode) and perpendicular (transverse mode) to their particles principle axes could give rise to wide SPR coverage spanning from visible to near-infrared [6]. However, controlled synthesis of such special particles has been found difficult in solid state matrix with high chemical stability and mechanical strength, which hindered their practical applications in optical devices.

Very recently, by taking advantage of the reduction capacity of defect structures in bismuthate glasses (e.g. Bi^0, Bi^+ and Bi^{2+}) [7], precipitation of silver atom (Ag^0) clusters from Ag^+ ions was discovered during a single-step melting process [8], which is considered as an new strategy for fabrication of bismuth oxide based glasses containing metallic nanostructures.

In this Letter, we report the preparation of ellipsoid shaped gold clusters in bismuthate glass $60Bi_2O_3$–$30B_2O_3$–$10SiO_2$ (mol%) using such facile technology, and third-order nonlinearities (TON) of the nanocomposites were characterized by femtosecond *Z*-scan and optical Kerr shutter (OKS) measurements at wavelength of 800 nm.

2. Experimental

High purity chemicals of bismuth oxide (Bi_2O_3, 99.999%), boric acid (H_3BO_3, 99.9%), silica (SiO_2, 99.9%) and gold chloride (AuCl, 99.9%) were used as starting materials. Nominal glass composition used was $60Bi_2O_3$–$30B_2O_3$–$10SiO_2$ in molar fraction (abbreviated as BBS, hereafter). The nanocomposite glasses were made with additional 0.1 wt.% (abbreviated as BBS-Au1) and 0.2 wt.% (BBS-Au2) AuCl. Approximate 15 g raw materials were carefully grinded and melted in high purity alumina crucibles at 1200 °C for 30 min, and then annealed at 390 °C for 2 h. The sample plates of 1.5 mm thickness were cut and polished for optical measurements.

Morphology images of the nanoparticles were taken using transmission electron microscopes (TEM, FEI, Tecnai F20, 200 kV). Optical absorption spectra were measured by a Perkin-Elmer Lambda 950UV/VIS/NIR spectrophotometer. In the TON measurements, a Ti:sapphire laser (Coherent Mira 900-D) with pulse duration of 200 fs at 76 MHz repetition rate was used as excitation source, and the operating wavelength λ was set at 800 nm. In the section of *Z*-scan, the incident laser power was ~60 mW low enough to avoid thermal effect, and the beam profile is GAUSSIAN type (TEM_{00} mode) with waist ω_0 of 24 μm at focus detected by a beam propagation analyzer-M^2 (Spiricon, M2-200s-FW), corresponding to laser density I_0 of ~1.42 GW/cm^2. For OKS measurements, the probe and pump pulses power were set at ~3 and ~28 mW, respectively.

3. Results and discussion

Figure 1a shows a typical TEM image taken from BBS-Au2. It is of interest to note that Au^0 clusters formed in the glass exhibit an elliptical configuration and align in a common direction, and their diameters are from 3 to 9 nm in major axis with aspect ratio of

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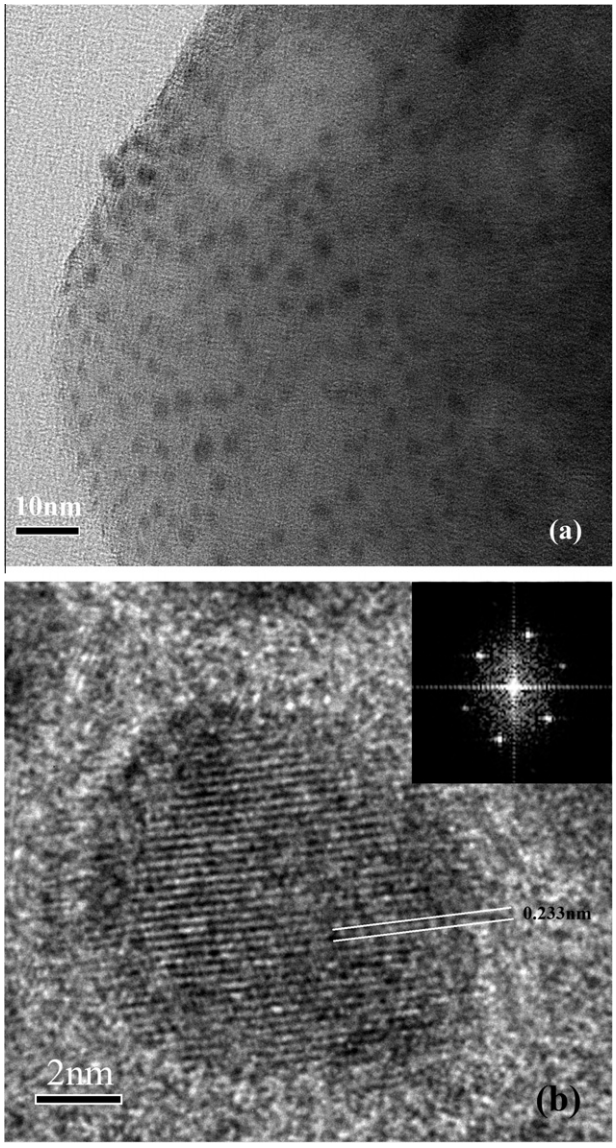

Figure 1. (a) TEM image taken from BBS-Au2; (b) high resolution TEM image taken from an elliptical gold particle together with its lattice space and electron diffraction pattern.

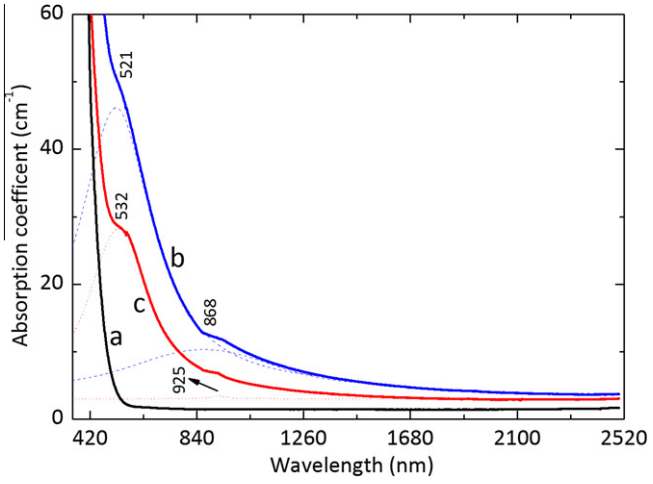

Figure 2. Optical absorption spectra of the samples (a, the host; b, BBS-Au1; c, BBS-Au2), and GAUSSIAN decompositions for BBS-Au1 (dashes) and BBS-Au2 (dots).

about 1.2, which is in good agreement with the morphous of gold nanoparticles in antimony glasses [9] prepared by similar method. Figure 1b shows the high resolution TEM image taken from an elliptical Au particle (EAP), it is clear to observe that the EAP is consisted of crystal lattice with *d*-spacing of 0.233 nm from which the electron diffraction pattern (as seen in the inset) can be obtained by fast Fourier transform illustrating the presence of (1 1 1) crystallographic plane of Au^0 clusters. This assignment was also confirmed by the absorption spectra as depicted in Figure 2: when these uniformly aligned EAPs were present in the glasses, the overlapped transverse and longitudinal SPRs [10] can be clearly observed in the spectra, and the maxima of these two SPR components were found at ~530 and ~900 nm by applying GAUSSIAN decomposition. Notably, the SPR intensities of BBS-Au1 are much stronger than those of BBS-Au2 consistent with the tendency in AgCl doped Bi_2O_3–B_2O_3–SiO_2 glasses [8], and the explanation of this behavior can be: when small amount of AuCl was introduced to the Bi_2O_3-based glass matrix, the Bi^x ($x = 0$, +1, and +2) defect atoms or ions [7,11] as reducing agents could reject part of gold ions from entering the glass network during the annealing process and cause the formation of EAPs in their structural sites; for higher AuCl doping level (BBS-Au2), the aggregation of adjacent Au^0 clusters leaded to larger volume of the gold particles which would weaken the size confinement effects, i.e. longer electron mean free path as manifested from its weak and red-shifted SPRs, meanwhile, more Au^+ and Au^{3+} ions would join in the glass matrix as network terminals and disorders which enhanced verification and further resulted in decreasing number of EAPs; finally, it can be concluded that BBS-Au2 contains larger but fewer gold particles as compared to BBS-Au1. On the other hand, the steep absorption edge near 420 nm of the host glass originated from electronic transitions between 6*s* and 6*p* levels of Bi^{3+} ions [12], and it is slightly red-shifted in the composites due to SPR as well as UV absorption of gold ions. By definition of optical band gap E_{opg} at absorption coefficient of 1000 cm^{-1} [13], E_{opg}s of the host glass, BBS-Au1 and BBS-Au2 were estimated to be 2.25, 2.21 and 2.18 eV, respectively.

Figure 3 displayed the closed-aperture (CA) *Z*-scans which were used to determine nonlinear refraction γ, signifying the intensity of Kerr effect from the normalized transmittance distance between peak and valley ΔT_{p-v} [14], and the configuration (peak following valley) of each curve suggests positive sign of γ, namely self-defocusing. In Figure 3b, it is of interest to note that the composites samples exhibit asymmetric CA *Z*-scans, which were found originating from their strong beam-focusing effect at the later half of *Z*-scan ($Z > 0$). By fitting the CA curves with the well-established procedures [15,16], γ values were estimated from ΔT_{p-v} and listed in Table 1: BBS-Au1 possesses higher γ than BBS-Au2, agrees with its higher Kerr intensity, i.e. larger ΔT_{p-v} as indicated in Figure 3b. The stronger SPR of BBS-Au1 at 800 nm gives a reasonable explanation for above results. Accordingly, amplification of γ magnitude could be expected by exciting the composites at short wavelength region where intense transverse SPR occurs.

Nonlinear absorption coefficient β was deduced by open-aperture (OA) *Z*-scan measurements. As shown in Figure 4, all OA *Z*-scans exhibit normalized transmittance valley, illustrating reverse saturated absorption, i.e. positive sign of β. Since no optical damage occurred during the measurements and E_{opg}s of the samples studied are between $h\nu$ and $2h\nu$ (where $h\nu = 1.55$ eV is incident photon energy at 800 nm), the RSA can be assigned to two-photon absorption (TPA) [17]. By fitting the OA curves with TPA process model, βs were calculated and summarized in Table 1. Notably, the higher β of BBS-Au1 deviates from its weaker normalized valley as illustrated in Figure 4; its stronger SPR absorption at 800 nm which