

## Enhanced Third-order Optical Nonlinearities of Au-CdS Core-Shell Nanoparticles Embedded in BaTiO<sub>3</sub> Thin Films

Yong Yang, Jianlin Shi,\* Hangrong Chen, Shugang Dai, and Ye Liu†

*State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, P. R. China*

*†Physics Department, National Key Laboratory of Applied Surface Physics, Fudan University, Shanghai, P. R. China*

(Received March 11, 2002; CL-020234)

Au-CdS core-shell nanoparticles (CSNs) are synthesized by a simple method based on directly self-assembling process and successfully integrated into BaTiO<sub>3</sub> films. The significant enhancement of third-order nonlinear optical nonlinearities of Au-CdS CSNs were reported for the first time.

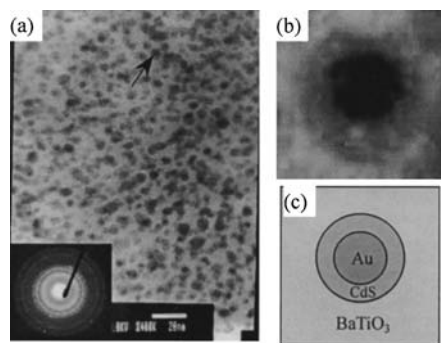
Nonlinear optical materials have attracted increasing interest over the past twenty years, due to the numerous applications in various fields such as telecommunications, optical data storage and information processing.<sup>1</sup> Semiconductor and metal nanoparticles have been studied extensively because of their larger third-order nonlinear susceptibilities and ultra-fast nonlinear optical response.<sup>2</sup> Especially, the semiconductor-metal CSNs suspended in a nonlinear medium should exhibit strongly enhanced nonlinear response by several orders of magnitude higher than that of their single component proposed by Neeves from theoretical calculations.<sup>3</sup> Recently, Honma et al.<sup>4</sup> claimed to have synthesized silver colloidal particles surrounded by the CdS shell. Kimura et al.<sup>5</sup> also reported to have prepared Au-CdS CSNs by assembling the pre-formed monodisperse CdS and gold nanoparticles into hybrid particles, based on the electrostatic interaction between the amine-covered CdS and thiolcarboxylate-covered gold nanoparticles. However, to the best of our knowledge, there were seldom related reports<sup>6</sup> about their nonlinear properties reasonably available to verify Neeves' theoretical predictions. In addition, the nonlinear materials had better be integrated into existing structures such as optical fibers and films to meet the optical needs such as optical switching and amplification. BaTiO<sub>3</sub> thin films have good optical transparency and high dielectric constant, which can influence the local fields around the composite particles. In the present paper, we present a simple method to directly self-assemble the Au-CdS CSNs and successfully integrate the composite nanoparticles into BaTiO<sub>3</sub> thin films. The enhanced optical nonlinear response of Au-CdS CSNs were reported for the first time.

Several methods have been employed to prepare core-shell structural materials, including surface precipitation reaction,<sup>7</sup> surface reaction,<sup>8</sup> self-assembly,<sup>9,10</sup> some problems associated with their preparation have limited the application of the final particles. A major requirement pertaining to the procedures used to coat particles is that they do not aggregate with each other, thus rendering the particles usable for many purposes. However, in those reported papers, when coupling agents (such as alkanethiols) coupled between two kinds of metal ions (such as Cd<sup>2+</sup>, Pb<sup>2+</sup>) or metal nanoparticles (such as Au, Ag) in the solution, these composite nanoparticles usually came a rapid agglomeration and precipitation out of solution. It is difficult to control this

procedure and integrate the aggregated particles into films. To overcome these problems, here we employed a new coupling agent to directly self-assemble the Au-CdS core-shell colloid solution. Thiourea, as a double-function reagent used to be the weak linkage agent between Cd<sup>2+</sup> ions and gold nanoparticles, provides thioketone group which can form fairly stable Cd<sup>2+</sup>-thiourea complexes with Cd<sup>2+</sup> ions in acidic solutions, and amine group which can combine with gold atom. Thiourea can link with Cd<sup>2+</sup> ions and gold particles by weak coordination bonding and keep considerably stable in acidic solutions (not precipitate for long time).<sup>11</sup> Then the composite colloids can be easily integrated into BaTiO<sub>3</sub> precursor solution.

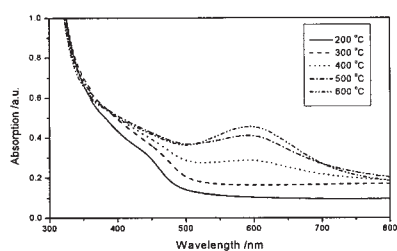
In this study, gold nanoparticles were prepared firstly according to the literature method.<sup>12</sup> Four ml (24.3 mM) HAuCl<sub>4</sub> ethanol solution was added into a boiling solution of tri-sodium citrate (100 ml of 1.0 mM) with rapid stirring. After the solution turning purple red within 30 seconds, the solution was cooled quickly in the ice-bath and concentrated to 20 ml in vacuum. CdS colloids were prepared with Cd(CH<sub>3</sub>COO)<sub>2</sub> and CS(NH<sub>2</sub>)<sub>2</sub>, Cd(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O (1.0 mmol) was dissolved in acetic acid (20 ml), and equivalent molar CS(NH<sub>2</sub>)<sub>2</sub> was dissolved in 2-methoxyethanol (20 ml). Then two solutions were mixed and stirred for 60 min at 40 °C at an pH = 3. Gold colloid was injected into CdS sol with the molar ratio of Au/Cd = 1 : 10. Soon gold colloid turned brown from purple red. To make BaTiO<sub>3</sub> precursor solution,<sup>13</sup> Ba(CH<sub>3</sub>COO)<sub>2</sub> (10 mm) was dissolved in a mixed solution of acetic acid (10 ml) and 2-methoxyethanol (10 ml). After stirring the solution for 30 min, appropriate amount of acetylacetone was added to stabilize the solution. Then titanium butoxide (3.4 ml) was added and stirred for another 30 min, aged for one week, the solution turned light yellow. Au-CdS core-shell colloid solution was injected into BaTiO<sub>3</sub> precursor solution slowly. Thin films were dip-coated on glass slides at withdrawal speed 75 mm/min. Each film was dried at 60 °C for 10 min and heated to 200–600 °C for 20 min in N<sub>2</sub> atmosphere.

The size distribution and shape of composite nanoparticles were characterized by transmission electron microscopic (TEM) and selected area electron diffraction (SAED). Figure 1(a) displays the TEM image of the composite film annealed at 500 °C and Figure 1(b) clearly displays the typical Au-CdS core-shell structure of composite nanoparticle marked by arrow in Figure 1(a). The SAED pattern of composite nanoparticle marked by arrow shows polycrystalline diffraction fringes, which include two kinds of space lattice of Au fcc and CdS cubic zinc blende structure. The diffraction spots/rings are indexed to CdS(200), Au(111), CdS(220) or Au(200), Au(220) and CdS(420) planes, respectively. This result is also consistent with the analytical results from X-ray diffraction (XRD).<sup>14</sup>



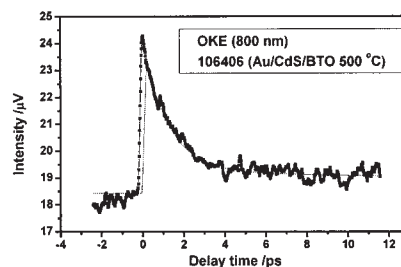
**Figure 1.** (a) TEM micrograph of Au-CdS CSNs incorporated in BaTiO<sub>3</sub> film, the inset shows the SAED pattern of composite particle marked by arrow. (b) An enlarged view of Au-CdS CSN marked by arrow. (c) The simulated image of Au-CdS CSN.

Figure 2 shows the UV-vis absorption optical spectra of composite films annealed at different temperatures. These curves have onsets in the 480–500 nm wavelength range, which are contributed to the absorption edge of CdS nanocrystals ( $R = 2\text{--}3\text{ nm}$ ). With the increase of annealing temperature, the absorption edges shift towards longer wavelength due to the quantum confinement. These absorption peaks at about 590 nm are contributed to the surface plasmon resonance (SPR) of gold nanoparticles. Films annealed at 200 °C and 300 °C show no SPR peaks of gold nanoparticles, but films annealed at 400 °C, 500 °C and 600 °C exhibit SPR peaks of gold particles. Because the SPR of metal nanoparticle is very sensitive to the absorbed ions, chemisorbed  $\text{I}^-$ ,  $\text{SH}^-$ ,  $\text{NH}_2^-$  agents often result in damping of the SPR of metal nanoparticle.<sup>10</sup> This result implies that gold particles were completely capped by  $\text{Cd}^{2+}$ -SC( $\text{NH}_2$ )<sub>2</sub> shell at relatively low annealing temperature. While at elevated temperature, some  $-\text{NH}_2$ - and  $-\text{CS}$ -groups would vaporize or be oxidized and CdS came into being and crystallized, so films began to exhibit the enhanced SPR peak.



**Figure 2.** The UV-vis absorption spectra of Au-CdS CSNs embedded in BaTiO<sub>3</sub> films heat-treated at different temperatures.

The off-resonance third-order nonlinear susceptibilities  $\chi^{(3)}$  of composite films were estimated in accordance with OKE (Optical Kerr effect). 800 nm pulse laser with a width of 100 fs was generated by Ti:sapphire femtosecond laser (Coherent Mira 900F), 800 nm pulse was used as pump pulse and probe beam.  $\text{CS}_2$  was used as a standard sample, with its model of  $\chi^{(3)}$  being  $1.0 \times 10^{-13}$  esu. Figure 3 shows the OKE signal of Au-CdS nanoparticles embedded in BaTiO<sub>3</sub> films. The calculated  $\chi^{(3)}$  values (model)<sup>15</sup> of the film annealed at 500 °C is  $(7.2 \pm 1.4) \times 10^{-11}$  esu, which is several times larger than the summation of



**Figure 3.** OKE signal of Au-CdS CSNs embedded in BaTiO<sub>3</sub> film heat-treated at 500 °C.

equal molar single gold and CdS nanoparticles embedded in BaTiO<sub>3</sub> films prepared at the same condition (Those are  $(0.66 \pm 0.12) \times 10^{-11}$  esu and  $(1.58 \pm 0.30) \times 10^{-11}$  esu, respectively). It also implies that CdS and gold nanoparticles were not simply co-doped into films but formed core-shell structure. The enhancement of third-order nonlinear susceptibilities  $\chi^{(3)}$  of the films should be attributed to the inter-nanoparticle interactions or the coherent coupling between CdS and Au nanoparticles under laser excitation.<sup>16</sup> The local field can be concentrated in both the interior and the exterior neighborhoods of the CSNs at the surface-mediated plasmon resonance.<sup>3</sup> The increased field is then utilized for self-enhancements of the optical nonlinearity from each component of the composite films including Au-core, CdS-shell and BaTiO<sub>3</sub> medium. To our knowledge, this is the first report for the enhancement of nonlinear optical susceptibility in the Au-CdS core-shell nanoparticle.

In summary, we have applied a directly self-assembling process to synthesize Au-CdS CSNs and successively incorporated into BaTiO<sub>3</sub> films. The core-shell structure of Au-CdS is proved by optical absorption spectra, XRD and TEM. The enhancement of nonlinear optical susceptibility in the composite nanoparticle with core-shell structure support the theoretical model<sup>3</sup> raised by Neeves from the experiment.

#### References and Notes

- 1 Y. Shi, C. Zhang, H. Zhang, J. H. Bechtel, L. R. Dalton, B. H. Robinson, and W. H. Steier, *Science*, **288**, 119 (2000).
- 2 Y. Wang, *Acc. Chem. Res.*, **24**, 133 (1991).
- 3 A. E. Neeves and M. H. Birnboim, *J. Opt. Soc. Am. B*, **6**, 787 (1989).
- 4 I. Honma, T. Sano, and H. Komiyama, *J. Phys. Chem.*, **97**, 6692 (1993).
- 5 S. Chen and K. Kimura, *Chem. Lett.*, **1999**, 233.
- 6 W. Nie, *Adv. Mater.*, **5**, 520 (1993).
- 7 a) H. S. Zhou, I. Honma, H. Komiyama, and J. W. Haus, *Phys. Rev. B: Solid State*, **50**, 12052 (1994). b) L. M. Liz-Marzan, M. Giersig, and P. Mulvaney, *Chem. Commun.*, **1996**, 731.
- 8 A. Dokoutchaev, J. T. James, S. C. Koene, S. Pathak, G. K. S. Pralash, and M. E. Thompson, *Chem. Mater.*, **11**, 2389 (1999).
- 9 F. Caruso, R. Caruso, and H. Möhwald, *Science*, **282**, 1111 (1998).
- 10 P. V. Kamat and B. Shanghavi, *J. Phys. Chem. B*, **101**, 7675 (1997).
- 11 K. Yamaguchi, P. Mukherjee, T. Yoshida, and H. Minoura, *Chem. Lett.*, **2001**, 864.
- 12 X. Zhan, Y. Liu, D. Zhu, W. Huang, Q. Gong, *Chem. Mater.*, **13**, 1540 (2001).
- 13 a) P. Duran, F. Capel, D. Gutierrez, J. Tartaj, M. Banares, and C. Moure, *J. Mater. Chem.*, **11**, 1828 (2001). b) H. Tian, W. Luo, X. Pu, P. Qiu, X. He, and A. Ding, *Thermochim. Acta*, **360**, 57 (2000).
- 14 The XRD data shows two peaks at  $d = 2.36 \text{ \AA}$  and  $2.04 \text{ \AA}$ , respectively corresponding to (111) and (200) plane of Au fcc structure (JCPDS, 4-784); and two peaks at  $d = 2.90 \text{ \AA}$  and  $2.06 \text{ \AA}$ , corresponding to (200) and (220) planes of CdS cubic zinc blende structure (JCPDS, 10-454).
- 15 B. Liu, C. Chew, L. Gan, and G. Xu, *J. Mater. Res.*, **16**, 1644 (2001).
- 16 B. V. Enüstün and J. Turkevich, *J. Am. Chem. Soc.*, **85**, 3317 (1963).