

# Tunable surface plasma resonance frequency in Ag core/Au shell nanoparticles system prepared by laser ablation

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A method for preparation of Ag core/Au shell nanoparticles with tunable surface plasma resonance (SPR) band was presented and studied. It was found that the tunable SPR band could be significantly conducted and achieved by laser ablation to Au plate in Ag colloidal solution, leading to the formation of Ag core/Au shell structure by the deposition of Au atoms on the surface of Ag nanoparticles. Dependence of the tunable shift of SPR bands on Ag core/Au shell structure was further illustrated by simulation of absorption spectra based on Mie theory, and consistent with the experimental results. © 2008 American Institute of Physics. [DOI: 10.1063/1.2829588]

The application potential of composite noble metallic nanoparticles due to the unique optical properties has currently aroused the great interest. Study to the preparation of such nanoparticles has become a significant subject.<sup>1-4</sup> There are several methods of preparing Ag/Au composite nanoparticles reported.<sup>4-8</sup> Recently, the technique of ablating the metal plates with pulsed laser in different excitation wavelengths has been employed to prepare the metal nanoparticles in different sizes and shapes in various solvents.<sup>9</sup> The dynamic mechanism of forming the metal nanoparticles was studied,<sup>9,10</sup> and Ag/Au alloy nanoparticles have been obtained by laser ablating Ag/Au bulk alloys in solution.<sup>11</sup> Moreover, compared with the chemical methods,<sup>2</sup> laser ablation can produce alloy nanoparticles with advantages as follows: (1) the preparation is relatively simple and convenient. (2) The obtained nanoparticles have regular spherical shape. (3) The nanoparticles system is pure without other remnants from the chemical reactions.

In this paper, we prepared Ag core/Au shell nanoparticles by ablating golden plate in silver nanoparticle colloid with a neodymium-doped yttrium aluminum garnet (Nd:YAG) pulsed laser at 1064 nm wavelength. It was found that the surface plasma resonance (SPR) frequency of this Ag core/Au shell colloid system could be dramatically and continuously tuned depending on the thickness of Au coverage layer shell induced by laser ablation. Calculation based on Mie theory was consistent well with the experimental results.

A pure Ag plate (99.99%) was placed at the bottom of quartz cell with 10 ml redistilled de-ionized water. A Nd:YAG pulsed laser (Quanta Ray QBY-200) with the excitation wavelength at 1064 nm (the repetition of 5 Hz, pulse duration between 6 and 9 ns, and pulse energy of 300 mJ), was focused on the Ag plate at 90° incidence angle for ablation. Ag nanoparticles were obtained (product I) 30 min, and then Ag plate was replaced by Au plate in the quartz cell. Finally, the products II, III, IV, V, and VI were obtained by

ablating Au plate in product I for 30, 60, 90, 120, and 150 min respectively. The absorption spectra were performed with a UV-visible spectrophotometer (Shimadzu UV-2401PC). The patterns of all the above products were measured and investigated by transmission electron microscope (TEM) (JEOL JEM-2010) and scanning electron microscope (SEM) (HITACHI S-4800).

Figure 1 shows the UV-visible absorption spectra of products I–VI. Curve I describes the surface plasma resonance (SPR) absorption spectrum of pure Ag colloid obtained by ablating Ag plate for 30 min (product I). The SPR band is centered at 388 nm. After then, Ag plate was replaced by Au plate in quartz cell. The products II, III, IV, V, and VI were obtained by ablating Au plate in product I for 30, 60, 90, 120, and 150 min, respectively. Curves I–VI describe the corresponding absorption spectra, indicating that

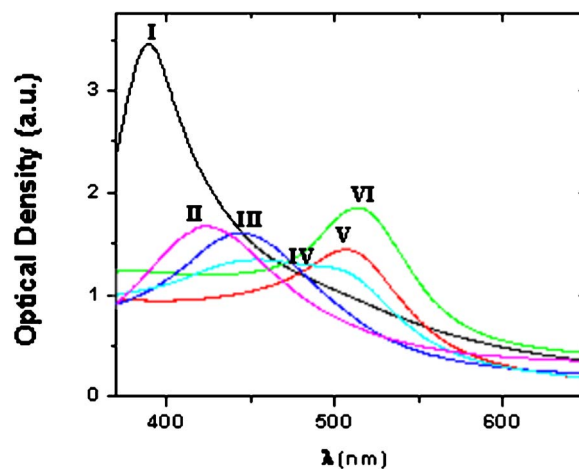


FIG. 1. (Color online) Absorption spectra of colloidal nanoparticles. Curve I shows the Ag colloid formed after laser ablation of the Ag plate for 30 min. Curves II–VI, the laser ablation to the Au plates in product I for 30, 60, 90, 120, and 150 min, respectively.

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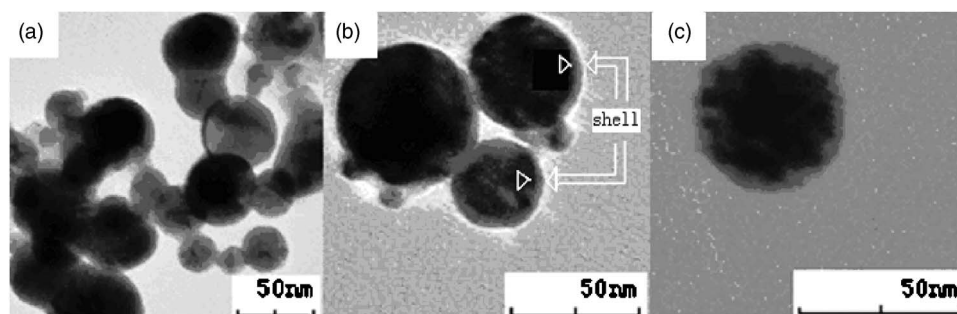


FIG. 2. Ultrahigh-resolution TEM images of colloid III.

the SPR band gradually redshifts from 388 to 513 nm with the ablation duration extending. When the ablation duration to the Au is longer than 120 min, there is no further redshift observed. The fact that the SPR band could redshift continuously in the wavelength region from 388 to 513 nm, implies that tunable SPR band could be significantly conducted and achieved under the control of ablation duration.

The pattern of Ag/Au colloidal nanoparticles was observed and investigated by TEM. Figure 2 shows the TEM images of nanoparticles in product III. The sizes of the nanoparticles range from 15 to 50 nm in diameter [Fig. 2(a)]. The Ag core/Au shell nanostructures can be clearly observed in Figs. 2(b) and 2(c). Statistically, the thickness of Au shell was about 5 nm. For further study of the Ag core/Au shell structure, electron energy spectrum of the nanoparticles was also measured (Fig. 3). For area i in the SEM image of Fig. 3(a), the ratio of gold and silver atoms calculated from the electron energy spectrum in Fig. 3(b) is 32:1. The electron beam size is about 1  $\mu\text{m}$ . For areas ii and iii, the ratios are 30:1 and 25:1, respectively. Usually the penetration depth of the electron beam to the Ag core/Au shell particle surface is less than 6 nm, the ratios mainly reflect the atoms distribution on the Ag particle interface, indicating that the coverage layer on the surface of Ag nanoparticles mainly consists of gold atoms. It is evident that Au shells are formed on the Ag nanoparticles by ablating Au plate in Ag colloidal solution, i.e., Au atoms were deposited on the surface of Ag nanoparticles by laser ablation in water.

We believe that the tunable characteristics of SPR band results from the formation of the Ag core/Au shell structure. As an evidence, the pure Ag colloid and Au colloid were prepared by laser ablation, respectively, and then both colloids were mixed with concentration ratio 1:1. Figure 4(a) shows absorption spectrum of the mixed colloid. Two distinct SPR bands separately appeared at 406 and 518 nm corresponding to the SPR bands of conventional Ag nanoparticles (at 400 nm)<sup>12</sup> and Au nanoparticles (at 520 nm),<sup>13</sup> respectively, because Ag and Au nanoparticles were independently suspended in this mixed colloid. Furthermore, there is

no observable shift in both bands with the time. This indicated that the SPR bands of this Ag/Au mixed colloid were not tunable due to the lack of the shell structure, compared with the case in products II–VI (Fig. 1). It is also notable that SPR band of pure Ag colloid (product I) is not redshifted with the ablation duration [Figs. 4(c) and 4(d)] if no Au atoms were ablated to deposit on the Ag nanoparticles surface. This demonstrated that continuous laser irradiation to Ag colloid could not move the SPR band to the red, same as the case of pure Au colloid produced by laser ablation.

Dependence of the tunable effect of SPR bands on Ag core/Au shell structure and the shift of SPR bands on the thickness of Au shell, were further illustrated by simulation of absorption spectra based on Mie theory.<sup>14</sup> Figure 5 shows the calculated absorption spectra of the Ag core/Au shell nanoparticles with different thickness of the Au shell. The diameter of Ag core (bare Ag particle) is fixed at 40 nm. When the thickness of Au shell is in the region of 1–2 nm, the SPR band of Ag bare particles is significantly affected by the Au shell. When the thickness is more than 10 nm, the SPR band of Ag core/Au shell nanoparticles further shifts to the red and becomes strong in intensity with increase in the thickness of Au shell. The calculated results are well consistent with the experimental spectra in Fig. 1. This indicates that the SPR band of Ag core/Au shell colloid is dependent on the formation of Au shell. The SPR band can be continuously moved to the red when the thickness of Au shell is increased, which could be controlled by laser power and ablation time.

The formation of the Ag core/Au shell particles could be understood as follows: when the Au plate is ablated in Ag colloidal solution, the Au plate absorbs most of the laser energy. As a result, Au atoms escaping from the Au surface can be deposited on the spherical surface of Ag particles to form an Au shell in such a rich-Au-atoms environment. With the ablation time increased, the Au shell could be formed due

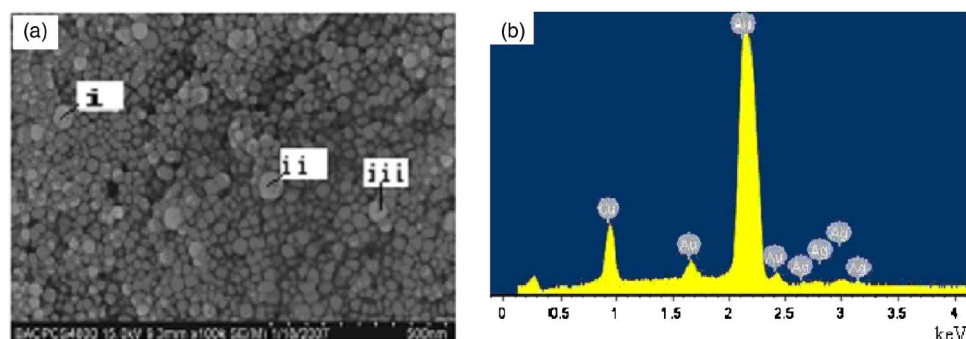


FIG. 3. (Color online) (a) SEM images of the nanoparticles in the product III. (b) Electron energy spectrum for the area i in (a).

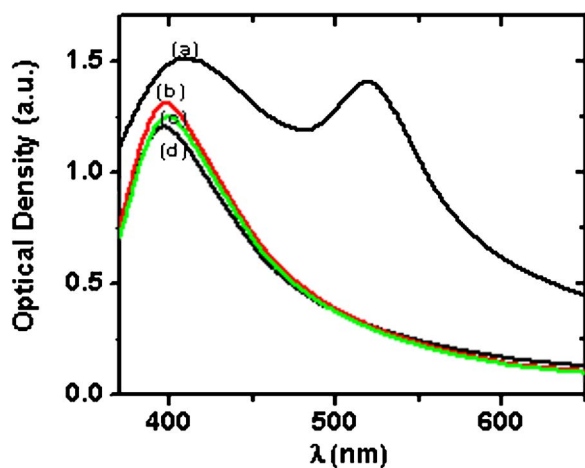


FIG. 4. (Color online) Absorption spectra of nanoparticle colloids of (a) the mixed Ag and Au colloid; (b) the Ag colloid the same as I in Fig. 1; (c) further laser irradiated for 30 min and (d) for 60 min.

to the rich-Au-atoms environment and the thickness of Au shell increases gradually as well.

As a summary, the Ag core/Au shell colloid was prepared and studied. The tunable SPR band could be significantly conducted and achieved under the control of ablation duration. It was further demonstrated that Au shells are formed on the Ag nanoparticles by ablating Au plate in Ag colloidal solution, i.e., Au atoms were deposited on the surface of Ag nanoparticles by laser ablation in water. Dependence of the tunable effect of SPR bands on Ag core/Au shell structure and the shift of SPR bands on the thickness of Au shell were further illustrated by simulation of absorption spectra based on Mie theory, and are consistent with the experimental results. This method could also be extended to produce other core/shell nanoparticles, such as transition metals that is a subject of future studies. This implies a significant method of preparing nanoparticle materials.

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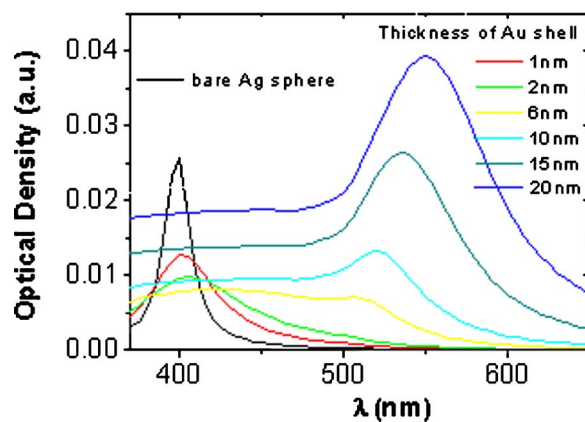


FIG. 5. (Color online) Absorption spectra of Ag core/Au shell nanoparticles calculated by computer simulation based on Mie theory. The diameter of Ag core is 40 nm. The thicknesses of the Au shell are 1, 2, 6, 10, 25, and 40 nm, respectively.

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