

Photochemical synthesis of bimetallic Au-Ag nanoparticles with “core-shell” type structure by seed mediated catalytic growth^①

DONG Shou-an(董守安), TANG Chun(唐 春)
(Institute of Precious Metals, Kunming 650221, China)

Abstract: The colloidal Au core/Ag shell structure composite nanoparticles were synthesized in PEG-acetone solution by photochemical route. The monodispersed Au nanoparticles with average diameter of 3.9 nm were used as growth seeds. The optical property of colloids and the sizes of composite nanoparticles were characterized when the molar ratio of Au to Ag ranges from 4:1 to 1:4. The results show that a composite nanoparticle structure similar to strawberry shape is formed at the molar ratio of Au to Ag from 4:1 to 1:1; the composite nanoparticles consisting of a core of Au and shell of Ag were generated at the 1:4 molar ratio, having a striking feature of forming interconnected network structure.

Key words: Au-Ag; photochemical synthesis; core-shell structure; seed

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1 INTRODUCTION

In recent years, the noble metal composite nanoparticles have attracted considerable attention from both the fundamental and applied research due to their potential applications in optics, electronics, catalysts and DNA biosensors^[1-6]. Consequently, a number of methods have been developed for fabricating bimetallic composite nanoparticle structures. In particular, Au-Ag composite nanoparticles from an alloy to core-shell structure have been synthesized in aqueous solution by co-reduction of HAuCl_4 and AgNO_3 or depositing Ag on Au particles with sodium citrate^[7-9] and by high-energy radiation^[10-12]. Treguer et al.^[10] reported a method by radiolysis of the mixed metal salt solutions, the composition of the composite clusters can be changed from a bilayered core-shell structure to an alloy with an increase of the radiolysis dose rate. However, the investigations on the preparation of core-shell particles by photochemical reduction are seldom reported^[13]. Herein, we report a photo-reduction method for generating core-shell particles consisting of a core of Au and a part or complete enveloped shell of Ag, based on the photo-reduction of both HAuCl_4 and AgNO_3 and the precipitation of Ag on the surfaces of the performed Au seed. Thus, the optical property of the colloids is easily tunable for optical applications requiring a certain absorption spectrum.

2 EXPERIMENTAL

HAuCl_4 and AgNO_3 were prepared from high pure gold and silver (the purity of 99.99%). The average molecular weight of Poly (ethylene glycol) (PEG) is 400. Double distilled water and analytical grade chemicals were used throughout experiment. The colloidal Au (or Ag) particles were prepared in Au (III) (or Ag^+)-PEG-acetone aqueous solution with UV irradiation of 300 nm^[14]. The final concentration of metallic ion, PEG and acetone is 2.44×10^{-4} , 5.64×10^{-2} and 0.5 mol/L, respectively. The composite nanoparticles with an Au core/Ag shell structure were synthesized photochemically under the same conditions, using pre-formed 3.9 nm Au particles as seeds (Fig. 1). The total concentration of Au^0 and Ag^+ ions remained 2.44×10^{-4} mol/L, and their molar ratio was changed in the ranges of 4:1 to 1:4.

The UV-Vis absorption spectra of the colloidal Au, Ag and composite nanoparticles were recorded on a Lambda 900 UV/VIS/NIR spectrometer with 1 mL quartz cuvette (Parker-Elmer). The images of nanoparticles were taken with a H800 TEM operated at 150 kV. TEM specimens were prepared by placing microdrops of colloid solution on a Formvar film supported by copper grids. The average diameter of the particles in different samples was determined by counting at least 200 particles from the TEM images.

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Correspondence: DONG Shou-an, Professor; Tel: + 86-871-5134163; E-mail: dsaw@xinhuanet.com

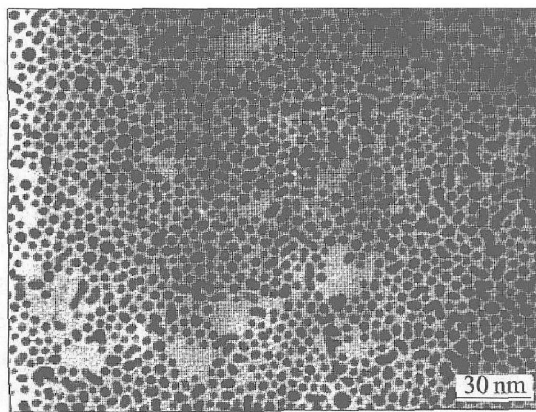


Fig. 1 TEM image of Au seed

3 RESULTS AND DISCUSSION

3.1 Photochemical preparation of colloidal Au and Ag particals

In photochemical preparation of the colloidal Au or Ag particals, PEG was mainly used as the protective agent and acetone can accelerate the photoreduction reaction. After 10 min irradiation, yellowy gold solution turned rose. A surface plasmon resonance (SPR) absorption band which did not change with further irradiation was at a maximum wavelength of 514 nm. TEM image characterized in Fig. 1 shows the monodispersed spherical Au particles with average diameter of 3.9 nm (Relative standard deviation(RSD)(%) = 16.0). These particles can be used as seeds for further formation of core-shell structure. For the preparation of Ag colloid, after 5 min irradiation, a SPR absorption band appears at 401 nm. However, the absorption intensity decreased with further irradiation, and transparent solution turned turbid. This can be attributed to the aggregation of Ag nanoparticles.

3.2 Optical property and TEM characterization

Based on photochemical formation of the colloidal Au and Ag particles, it is predictable to form Au-Ag composite nanoparticles in the above solution containing preformed Au seeds and Ag^+ ions. Therefore, the progressive evolution of SPR spectrum with time at different molar ratios of Au seed to Ag^+ is recorded in Fig. 2. After 5 min irradiation, SPR spectra gradually changed from the profile of pure Au colloid to that of pure Ag colloid at the molar ratio from 4:1 to 1:4. In the case of 4:1 molar ratio, the SPR spectra have an evident enlargement (see curves *a*, *b* and *c* in Fig. 2), because the Ag^+ ions are absorbed on the surface of Au seed particles and then catalytically reduce. After a long time (50 min) irradiation, the SPR peak has a slight red shift and its intensity decreases.

When the molar ratio of Au to Ag is changed to 1:1, after 2 min irradiation, two recognizable SPR peaks are observed as curve *b* in Fig. 2(b).

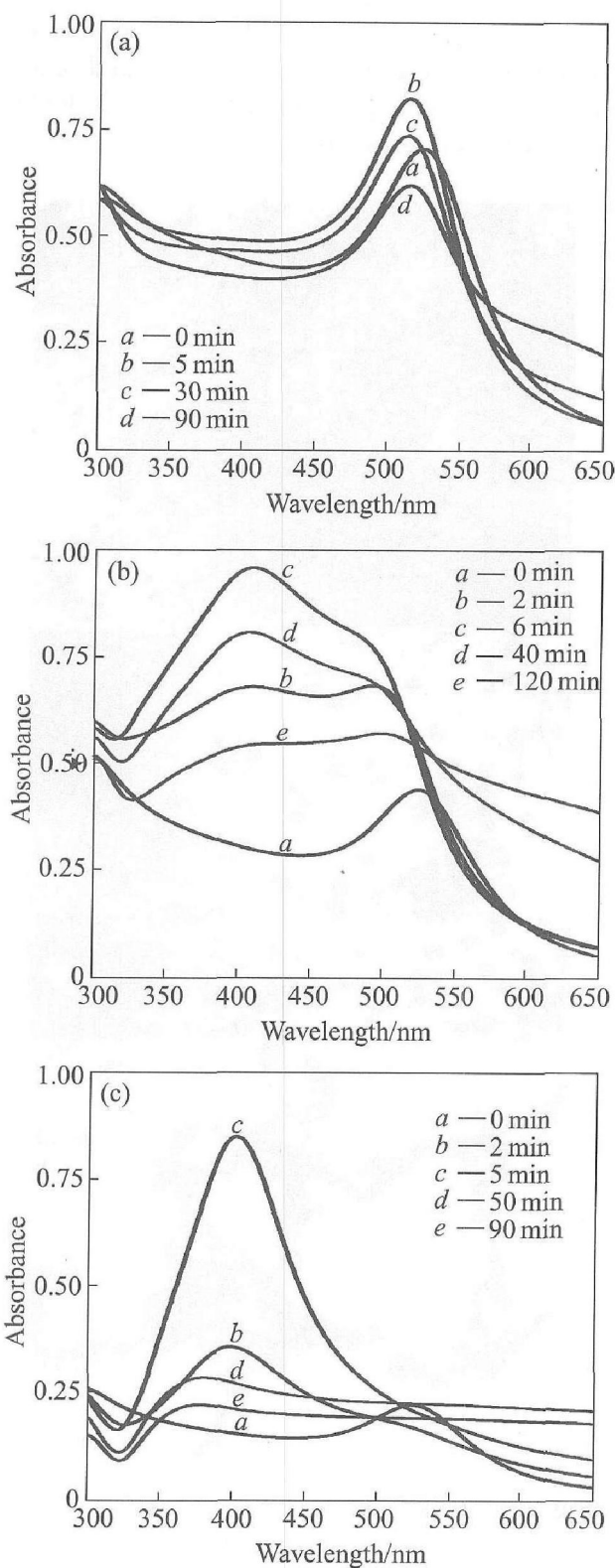


Fig. 2 Evolution of UV-vis SPR spectra of Au-Ag composite particles with time at different molar ratios of Au seed to Ag
(a) 4:1; (b) 1:1; (c) 1:4

After Ag^+ ions are completely reduced, the SPR spectrum presents a shoulder peak with Ag absorption feature (curve *c* in Fig. 2(b)), which disappears with further irradiation (curve *e* in Fig. 2(b)). For the above-mentioned molar ratio cases, the decrease of the SPR absorption intensity is probably due to photoinduced growth of composite

particles. TEM image characterized in Figs. 3(a) and (b) clearly shows that Au seed with average diameter of 3.9 nm is enlarged to 4.7 and 6.6 nm, corresponding relative standard deviation(RSD) is 24.9 and 17.4, respectively.

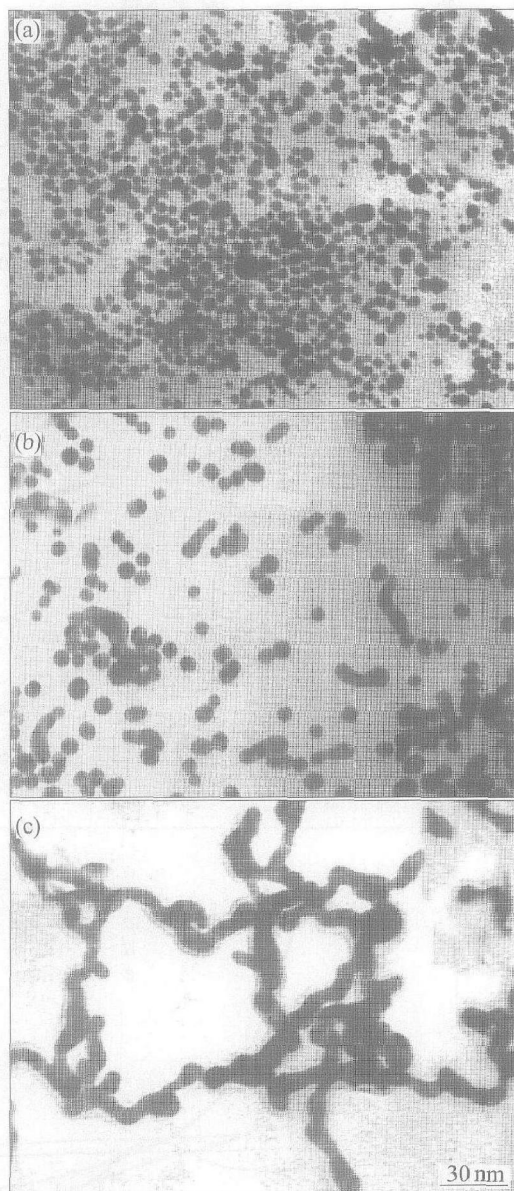


Fig. 3 TEM images at different molar ratios of Au to Ag
(a) $-4:1$, (b) $-1:1$; (c) $-1:4$

The SPR spectrum at the molar ratio of $1:4$ shows more Ag nanoparticle feature. The successive decrease of the absorption intensity with irradiation is probably concerned in gradual thickening of the Ag shell. After the composite particle colloid was placed for 24 h at room temperature, the tiny precipitate occurred. The most striking feature of TEM image at this molar ratio is the formation of an interconnected network structure, as shown in Fig. 3(c). Perhaps, that is the reason why the agglomerate easily appears in this colloidal solution of the composite nanoparticles.

3.3 Evidence for Au core/Ag shell composite nanoparticle structure

The previous studies^[7, 10, 12] have demonstrated that the alloyed Au-Ag nanoparticles have only one SPR peak. When both Au and Ag colloid prepared with photoreduction were mixed by a certain ratio, two plasmon peaks appeared in the absorption spectra. Obviously, the SPR spectra recorded here are completely different from the above two cases. Based on determining CN^- with Ag nanoparticles^[15] and CN^- dissolution rate for Au higher than that for Ag under ambient conditions, the Au core/Ag shell nanoparticle structure was confirmed again by the CN^- dissolution experiments. Fig. 4 (a) shows that the SPR peak contributed from Ag nanoparticles precipitated on the surface of Au seed appeared due to the dissolution of Au at the molar ratio of Au to Ag $4:1$, indicating the formation of the partially Ag covered gold particles, i. e., a strawberry-like conformation. However, Fig. 4(b) displays two SPR peaks to correspond to Ag and Au at the molar ratio of $1:4$ with the dissolution of Ag shell, revealing the formation of a shell layer on the surface of Au seed.

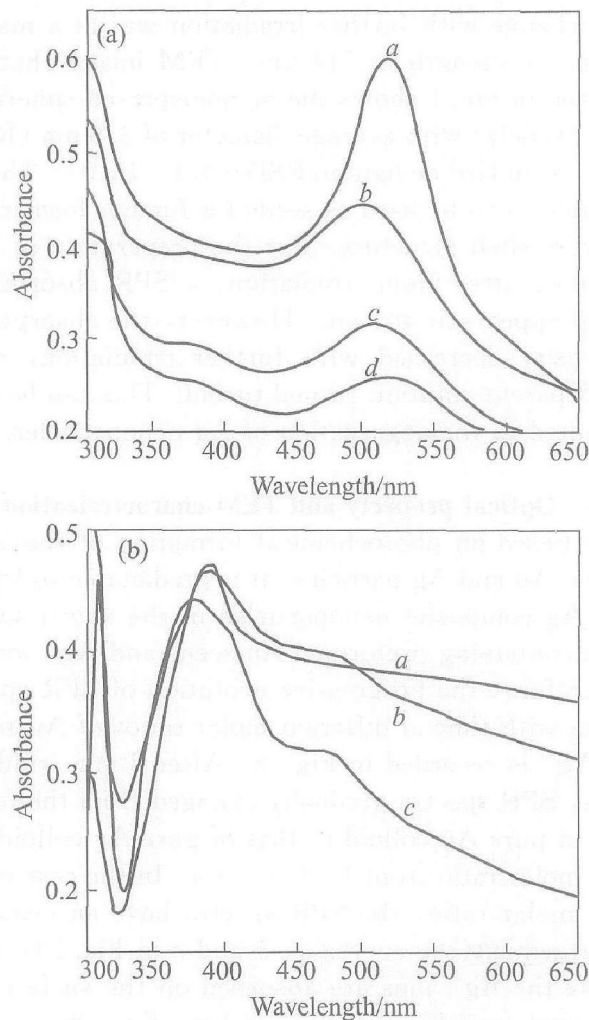


Fig. 4 Dissolution of composite particles at molar ratio of Au to Ag $4:1$ (a) and $1:4$ (b)
a—Without cyanide;
b—*d*—Increasing cyanide amount

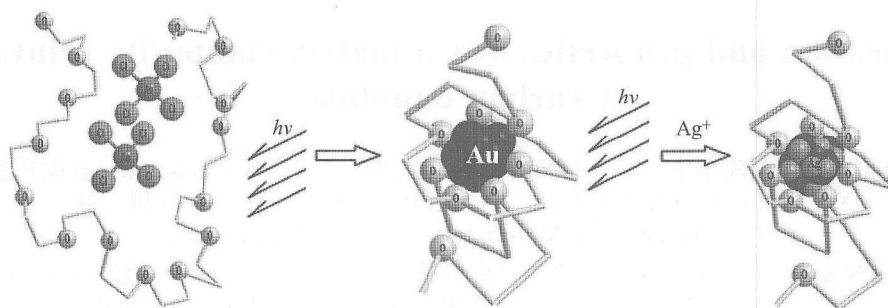


Fig. 5 Schematic illustration of mechanism of forming bimetallic core-shell structure protected by PEG

3.4 Mechanism of forming core/shell

The mechanisms on the autocatalytic growth of the Au seed particles and stabilization by the pseudo-crown ether in PEG-acetone solution under the condition of UV radiation have been illustrated in detail in Ref. [14]. Similarly, in the presence of Au seed particles, Ag^+ ions can be only catalytically reduced on the surface of Au particles in the UV irradiation process. More positive reduction potential of Au than Ag is an important factor, because the core-shell structure consisting of the Ag nucleus coated with Au particles can't be obtained in this reaction system due to the displacement reaction. In order to generalize the mechanism of forming bimetallic core-shell structure, a schematic illustration is given in Fig. 5.

4 CONCLUSIONS

The bimetallic Au-core/Ag-shell structure nanoparticles were synthesized in the PEG-acetone aqueous solution by photochemical route, using monodispersed colloidal Au particles as the mediated growing seeds. The size of Au core and thickness of Ag shell in the composite nanoparticles can be controlled to change the diameter of Au seed and Ag^+ concentration in the solution. Thereby, the optical property induced from the core-shell structure can be tailored through varying mole ratio of Au and Ag^+ . In addition, the evidence of core/shell structure and the model of mechanism of forming Au/Ag composite nanoparticles were also provided.

REFERENCES

- [1] Pan C, Dassenoy F, Casanove M, et al. A New synthetic method toward bimetallic ruthenium platinum nanoparticles; composition induced structural changes [J]. *J Phys Chem B*, 1999, 103(46): 10098 - 10101.
- [2] Mizukoshi Y, Okitsu K, Maeda Y, et al. Sonochemical preparation of bimetallic nanoparticles of gold/palladium in aqueous solution [J]. *J Phys Chem B*, 1997, 101(36): 7033 - 7037.
- [3] Wu M L, Chen D H, Huang T C. Synthesis of Au/Pd bimetallic nanoparticles in reverse micelles [J]. *Langmuir*, 2001, 17(13): 3877 - 3883.
- [4] Wang Y, Toshima N. Preparation of Pd/Pt bimetallic colloids with controllable core/shell structures [J]. *J Phys Chem B*, 1997, 101(27): 5301 - 5306.
- [5] Cao Y W, Jin R, Mirkin C A. DNA-modified core-shell Ag/Au nanoparticles [J]. *J Am Chem Soc*, 2001, 123(32): 7961 - 7962.
- [6] Wang J, Polsky R, Xu D. Silver-enhanced colloidal gold electrochemical stripping detection of DNA hybridization [J]. *Langmuir*, 2001, 17(19): 5739 - 5741.
- [7] Link S, Wang Z L, El-Sayed M A. Alloy formation of gold-silver nanoparticles and the dependence of the plasmon absorption on their composition [J]. *J Phys Chem B*, 1999, 103(18): 3529 - 3533.
- [8] Rivas L, Sanchez-Cortes S, García-Ramos J V, et al. Mixed silver/gold colloids: a study of their formation, morphology, and surface-enhanced raman activity [J]. *Langmuir*, 2000, 16(25): 9722 - 9728.
- [9] Ji X H, Wang L Y, Yuan H, et al. Formation mechanism of core-shell Au/Ag nanoparticles [J]. *Acta Chemica Sinica*, 2003, 61(10): 1556 - 1563. (in Chinese)
- [10] Treguer M, de Cointet C, Remita H, et al. Dose rate effects on radiolytic synthesis of gold-silver bimetallic clusters in solution [J]. *J Phys Chem B*, 1998, 102(22): 4310 - 4321.
- [11] Abid J P, Girault H H, Brevet P F. Selective structure changes of core-shell gold-silver nanoparticles by laser irradiation: homogenisation vs silver removal [J]. *Chem Commun*, 2001(9): 829 - 830.
- [12] Chen Y H, Yeh C S. A new approach for the formation of alloy nanoparticles: laser synthesis of gold-silver alloy from gold-silver colloidal mixtures [J]. *Chem Commun*, 2001(4): 371 - 372.
- [13] Mallik K, Mandal M, Pradhan N, et al. Seed mediated formation of bimetallic nanoparticles by UV irradiation: A photochemical approach for the preparation of "core-shell" type structures [J]. *Nano Letters*, 2001, 1(6): 319 - 322.
- [14] Dong S A, Tang C, Zhou H, et al. Photochemical synthesis of gold nanoparticles by the sunlight radiation using a seeding approach [J]. *Gold bulletin*, 2004, 37(3-4): 187 - 195.
- [15] Yang S C, Tang C, Dong S A, et al. Determination of cyanide on surface plasma resonance spectrum of silver nanoparticles [J]. *Chinese J Anal Labor*, 2005, 24(1): 55 - 58. (in Chinese)

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