Frabrication of Au Nanoparticles in Various Shapes and Their Application in Surface-enhanced Raman Scattering

Chen-yang XUE(薛晨阳)，Hui-juan WANG(王慧娟)，Yong-feng LIANG(梁永峰)，
Rong CHEN(陈　容)，Jun LIU(刘　俊)

(*National Key Laboratory for Electronic Measurement Technology*, *North University of China*, *Taiyuan* 030051, *China*)

Abstract － Anisotropic metallic Nanoparticles (NPs) have unique optical properties, such as Surface Enhanced Raman Scattering (SERS) spectroscopy. In this paper, star-shaped and sphere gold NPs were prepared by seed-mediated growth and France methods respectively. The reaction process and the effect of reagent in seed-mediated growth of gold nanostar particles were systematically described. After fabricating NPs the authors test their Raman enhancement using Crystal Violet (CV) molecules apart. The experimental results indicated that star-shaped Au NPs had stronger Raman enhancement spectrum than that of sphere Au NPs.

Key words － gold nanoparticles; seed-mediated growth method; SERS

1　Introduction

　　Recently, the noble metal nanoparticles, especially of gold and silver, have received a great deal of attention for their distinctive optical properties and their unique size-dependent properties. It is well known that as the size of the particle decreases to the $1 \sim 100$ nm range, electronic, optical and thermodynamic properties deviate from bulk properties[1-3]. Surface-enhanced Raman scattering (SERS) is one of the most important optical properties dependent on size and shape effect, which have received extensive attention. This property can be tailored by properly controlling the size and shape of the nanoparticles. Accordingly, much work has been devoted to control particles size, shape, composition, and also surface properties of the noble metal NPs for their optimum application in SERS.

　　The phenomenon that intensity of Raman signal was enhanced markedly because of molecules or something else adsorbed is closed to the surface of nanostructure[4].

Chemical and electromagnetic are two effects pervasive considered as the origin of the enhanced Raman signal. An increased local field resulted from surface plasmaon resonance (SPR) is the main factor for the electromagnetic component of the enhancement. It has been reported that aggregates of metallic NPs generate very intense enhanced Raman signals at the junction between two NPs called "hot spots"[5-6]. Similar phenomenon is also found at the tips of NPs with sharp feature. Therefore, anisotropic, metallic NPs are great candidates for SERS substrates and an active area of research[7].

　　This work demonstrates a method synthesis of gold nonspherical NPs and gold nanostars. To achieve the gold spherical NPs, we adopted the classical France formation. The chemical method of the seed-mediated growth was introduced for nanostars. In order to control fabrication of nanostars, we need to investigate fundamental aspects of synthetic conditions, such as the amount of growth solution, the amount of reagent and the influence of temperature. We also present a SERS study between gold nanosphere and gold star-shaped NPs in aqueous solution to compare their SERS.

2　Experimental section

　　Chemicals and Materials：$HAuCl_4 \cdot 4H_2O$ (99%), trisodium citrate (99%), silver nitrate (99%), ascorbic acid (AA, 99%), cetyl trimethyl ammonium bromide (CTAB, 99%), deiomized water (18 MΩ).

2.1　Preparation of gold nano-sphere

　　100 mL of 0.01% $HAuCl_4 \cdot 4H_2O$ was added to a round flask and boiled, with rapidly stirring 3.5 mL of 1% trisodium citrate which was added in quickly and then boiled for 15 min. The solution was gradually cooled to room temperature[8]. This method fabricates gold nano-

particles of size about 10 nm. Fig. 1 was its Transmission Electro Microscopy (TEM) image.
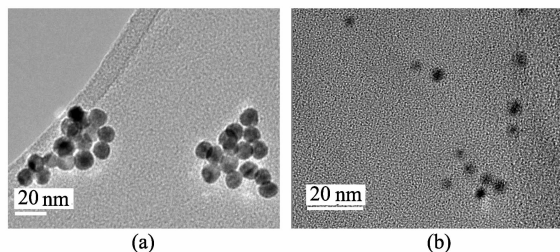

Fig. 1　TEM image of gold nano-sphere: (a) trisodium citrate was employed as reduced agent at the temperature of 100 ℃, (b) NaBH₄ act as reduced agent, reaction occured at room temperature, and trisodium citrate was used as capping agent

2.2　Preparation of gold nano-star

Preparation of gold seed solution[9]: Aqueous 1% trisodium citrate 3.5 mL was added to 10 mL of 0.1% aqueous $HAuCl_4 \cdot 4H_2O$. After being stired for 3 min, 0.3 mL of 0.01 M freshly ice-cold NaBH₄ solution was added all at once, followed by further stirring for 5 min. The solution takes on wine red, indicating nano-sphere particles formation, and the size of particles is about 8 nm. This seed solution was maintained at room temperature for about 2 h before use. But it cannot excess 24 h, for the seed solution surface will form a thin film, which suggests Au particles aggregation and can't be used as seed.

Preparation of growth solution[10-11]: Weigh CTAB 7.28 g, AgNO₃ 1.36 mg, $HAuCl_4 \cdot 4H_2O$ 20.6 mg, and dissolve them in 200 mL DI water. The solution was heated to 40 ℃ while melting CTAB. After being mixed, the color of this solution becomes bright yellow. Cool the solution to room temperature and store it at 27 ℃. Then 10 mM freshly prepared AA solution was divided into 0.06 mL, 0.6 mL, and 6 mL. Three volumes (1, 10, and 100 mL) of bright yellow growth solution were mixed with the above three AA solutions, respectively. Solutions changed into colorless immediately.

These three solutions were added to the 0.1 mL gold seed solution stepwise at intervals of 45 s. The whole experiment was kept in temperature 27 ℃. Through the whole process, solution experienced three color transition, starting with colorless, and then slight blue, finally, to purple/fuscous blue indicating nanostars formation.

2.3　Preparation of testing samples

Before preparing testing samples, the solution should be dealt with the following method. First, the surfactant was separated from the metal particles by centrifugation. 2 mL of sample was centrifuged for 10 min at speed of 14 000 r/min. The upper part of colorless solution was removed and the particles at the bottom was redispersed in DI water, reaped for 2~3 times. Then the solution was redispersed with DI water and sonicated for 3 min.

Preparation of TEM Grid: Some of the above redis-

persed particle suspension was dropped on the carbon coated copper grid and dried at room temperature.

Preparation of SERS samples: Mixing 1 mL of pretreatment gold sphere and star-shaped colloid solutions with 0.1 mL of 10^{-5} g/L aqueous probe molecule Crystal Violet (CV) solution, respectively. The samples were sonicated for 10 min prior to the measurements. Testing samples were put in glass capillary, and then the solution can be used to test SERS[12].

3　Results and discussion

3.1　Process analysis of fabricating nana-star shaped particles

In the experiment of preparing gold nano-stars, seed solution takes on wine red. In this process, NaBH₄ was employed as the reducing agent to reduce Au salts in the solution, and trisodium citrate as capping agents, which can be used to restrict particle growth. After adding NaBH₄ and stirring for about 5 min, the color of solution became wine red tardily, indicating that Au^{3+} in solution was reduced to Au and the size about 8 nm nanoparticles have been formed(see Fig. 1(a)). If NaBH₄ was replaced with trisodium citrate, the color of solution will not change, the reason for this phenomenon was trisodium citrate which can't act as reduced agent in room temperature, so there is no gold NPs formation. In the absence of seed, particle formation rate is very slow, with no solution color change, and a gray deposition forms after approximately 24 h.
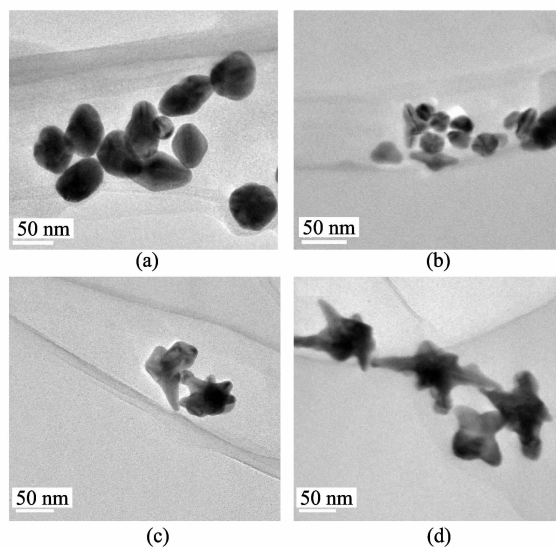

Fig. 2　TEM images of gold products synthesized under varying volume growth solution: (a) 100 mL growth solution, (b) adding 1 mL, 100 mL of growth solution stepwise at intervals 45 s, (c-d) adding 1 mL, 10 mL, 100 mL of growth solution stepwise at intervals 45 s, (c) products of reacting 15 min, the color of solution was light blue, (d) products of reacting 5 h, the color of solution was navy blue

When mixing growth solution and adding react reagent, the order of CTAB, HAuCl₄ and AgNO₃ is not

strict, but AA must be put in before seed solution. Overturn of this order reduces the speed of reaction greatly. $AgNO_3$ is indispensable in producing anomalistic shape particles. Some experiments have been made to investigate whether it is Ag^+, or NO_3^- which plays the important role in controlling the morphology of the products. Some results indicate that Ag^+ and CTAB act as the template to control the shape of nanoparticles. The blocking effect of silver on certain facets may suppress the growth of rods, further facilitating the change in the growth produced from anisotropic to isotropic[13]. Varying the volume of template, especially the amount of Ag^+, can make rods/star-shaped/bipyramid/sphere nanoparticles.

Murphy and co-workers[14] have found that the amount and the properties of seed particles also critically determine the product. This investigation develops a method that keeps the [growth solution]/[seed] ratio constant through the whole reaction. The volume of the growth solution is 10 times that of seed every time. Fig. 2 shows the TEM graphs of gold nanoparticles which growing in varying volume growth solution. We can observe that figure A contains bipyramid and sphere, while the color of solution corresponding to this image was amaranth. When growth solution was increased, the shape of particles contains bipyramid, sphere and irregularly tips (Fig. 2(b)), and the color of solution became amethyst. Growth solution continually being increased, star-shaped nanoparticles have formed (Fig. 2(c) and (d)), and the ultimate color of solution take on navy blue. Comparing with Fig. 2(c) and (d), we also obtained that this process need longer time. In Fig. 2(c), it's clearly observed that both shape and yield were not very well. In order to explain the above-mentioned results, we explore from the mechanism of this synthesis process, it conventional includes successive nucleation and growth steps. We propose that for the volume of growth solution is not enough, cluster Au in growth solution used to deposit on seeds was ill too.

3.2 Comparison of the effect of SERS between varying shaped nanoparticles

The enhanced Raman signal of colloidal Au NPs is dependant upon varying factors including NPs concentration, shape, and its concentration in the sample solution. Throughout our comparison of SERS activity, we only discuss the fact of shape influencing Raman enhanced signal. All other parameters in this experiment are the same.

From Fig. 3, we can detect that when the concentration of CV is lower enough (10^{-4} g/L), the Raman spectrum nearly has no wave crest. But after mixing with NPs, signals were inspected, and have different degrees enhancement. The star-shaped NPs SERS enhancement is stronger than that of nanorods obviously. By further increasing the nanoparticle concentration and improving on the condition of testing method, which will increase the

"hot spots", we can also achieve better Raman enhancement.
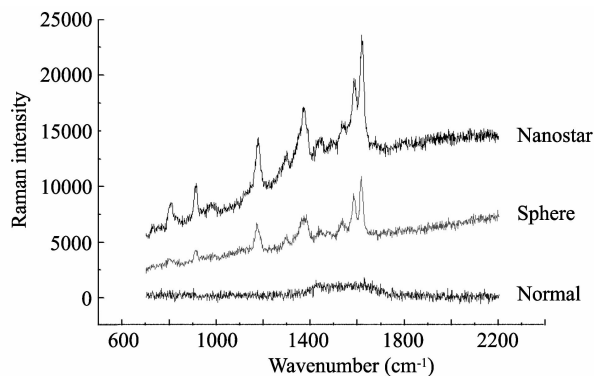

Fig. 3 SERS spectra comparison of CV adsorbed on varying shape Au NPs. The bottom Spectrum is the ordinary Raman Spectrum of CV, and the concentration is 10^{-4} g/L

Compared with the Raman spectrum enhancement of nanospheres and nanostars, the latter has stronger enhancement. The discrepancy between nanostars and nanospheres is likely due to the obvious structural differences of NPs. Nanostars are suspicious of their more SERS-active sites because of their anisotropic shapes compared to nanospheres. These tips on nanoparticles may preferentially adsorb molecules CV to be made detection easily even though at the lower adsorbate concentrations. Kudelski[15] reported preferential adsorption of the CV molecules at highly SERS-active sites on electrochemically roughened silver surfaces. Our observed differences in the relative activity of these distinctive NPs shapes at low CV concentrations also suggest the preference of CV molecules toward highly SERS-active sites.

4 Conclusion

In this paper, two methods of fabricating gold nanosphere and gold nanostar were proposed. The reaction process in the seed-mediated growth of gold nanostar NPs had been systematically described with effect of reaction reagent on the growth of NPs studied in detail.

After NPs being fabricated, their optical character of surface enhanced Raman scattering was tested. It can be seen that nano-stars have stronger SERS than nano-spheres while the optical properties of Au NPs mainly depends on their shapes. More facts on their SERS which should be investigated have influences like concentration of NPs, type of testing solution. Moreover, optimum conditions of NPs formation are necessary. For example reaction temperature, dosage of each reaction reagent and so on, are very useful to enhance NPs' Raman signal.

Reference

[1] Clemens Burda, Xiao-bo Chen, Radha Narayanan, Mostafa A. El-Sayed, 2005. Chemistry and properties of nanocrystals of different shapes. *Chem. ReV*, 105: 1025-1102.

［2］ S. Nie, S. R. Emory, 1997. Probing single molecules and single nanoparticles by surface-enhanced Raman scattering. *Science*, 275(5303): 1102-1106.

［3］ P. M. Tessier, O. D. Velev, A. T. Kalambur, J. F. Rabolt, A. M. Lenhoff, E. W. Kaler, 2000. Self-assembly of Resorcinarene-stabilized Gold Nanoparticles: Influence of the Macrocyclic Headgroup. *Am. Chem. Soc*, 122: 9554.

［4］ M. Grzelczak, J. Pérez-Juste, P. Mulvaney, L. M. Liz-Marzán, 2008. Formation of gold and gold sulfide nanoparticles and mesoscale intermediate structures in the reactions of aqueous $HAuCl_4$ with sulfide and citrate ions. *Chem. Soc. ReV*. 37: 1783-1791.

［5］ S. M. Nie, S. R. Emory, 1997. Single-molecule and single-nanoparticle SERS: from fundamental mechanisms to biomedical applications. *Science*, 275: 1102.

［6］ J. Jiang, K. Bosnick, M. Maillard, L. Brus, 2003. Single molecule Raman spectroscopy at the junctions of large Ag nanocrystals. *Phys. Chem. B*, 107: 9964.

［7］ P. S. Kumar, I. Pastoriza-Santoz, B. Rodriguez-Gonzalez, F. Javier Garcia de Abajo, L. M. Liz-Marzan, 2008. Spatial Nonlocality in the Optical Response of Metal Nanoparticles. *Nanotechnology*, 19: 1.

［8］ J. E. Martin, J. P. Wilcoxon, J. Odinek, P. Provencio, 2000. Control of the interparticle spacing in gold nanoparticle superlattices. *Phys. Chem. B*, 104: 9475.

［9］ Chen, H. M. Liu, R. S. Asakura, K. Jang, L. Y. Lee, J. F, 2007. Controlling the Length and Shape of Gold Nanorods. *Phys. Chem. C*, 111: 18550.

［10］ Hao-ming Chen, Ru-shi Liu, Din-ping Tsai, 2009. A Versatile Route to the Controlled Synthesis of Gold Nanostructures. *Crystal Growth & Design*, 9(5): 2079-2087.

［11］ T. K. Sau, C. J. Murphy, 2004. Room temperature, high-yield synthesis of multiple shapes of gold nanoparticles in aqueous solution. *Langmuir*, 20: 6414.

［12］ D. Cialla, H. Uwe, H. Schneidewind, J. Popp, 2008. Microfabricated SERS-arrays with sharp-edged metallic nanostructures. *Chem Phys Chem*, 9: 758.

［13］ M. Liu, P. Guyot-Sionnest, 2005. Ultrafast resonant optical scattering from single gold nanorods: Large nonlinearities and plasmon saturation. *J. Phys. Chem. B*, 109: 22192.

［14］ T. K. Sau, C. Murphy, 2004. Seeded high yield synthesis of short Au nanorods in aqueous solution. *Langnuir*, 20: 6414.

［15］ A. Kudelski, 2005. Raman studies of rhodamine 6G and crystal violet sub-monolayers on electrochemically roughened silver substrates: Do dye molecules adsorb preferentially on highly SERS-active sites? *Chem. Phys. Lett*, 414: 271.