Preparation and Raman enhancement properties of gold nanostars

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Abstract. Gold nanostars (GNSs) have a series of sharp tips structures, which will produce strong hot spots and have great application potential in Raman enhancement. In this paper, muti-tip GNSs have been prepared experimentally, and the control techniques of their tip and size have been mastered. For the first time, a fast and efficient self-assembly technique without additives has been developed, and a series of Surface Enhanced Raman Scattering (SERS) substrates have been successfully prepared by using this technique. The effect of different GNSs density of substrates on SERS signal is further studied experimentally. The results show that the SERS signal is closely related to the density of particles in the substrate. The higher density of GNSs in the substrate, the more hot spots covered by the incident light plate, and the greater contribution to the SERS signal.

1. Introduction
In recent years, metal nanomaterials, such as gold and silver, have become the focus of research in nanophotonics and related fields because of their unique surface plasmon optical properties such as local field enhancement, strong scattering and so on [1,2]. Surface Plasmon is an optical phenomenon of metal nanomaterials. Their essence is the electromagnetic mode formed by the interaction of free electrons in the metal surface region and excited electromagnetic waves. The optical properties of surface Plasmon of metal nanomaterials are closely related to the size, shape and structure of the materials. Controlling the shape of nanomaterials and adjusting the optical properties of surface Plasmon was one of the important research directions in the field of nano-optics at that time. Due to the novel optical properties of surface Plasmon, metal nanomaterials have been widely used in Surface Enhanced Raman Scattering (SERS), optical sensing, solar cells and other fields [3-7].

Metal nanomaterials have important prospects especially in SERS field. At present, researchers have tried a variety of methods to prepare ultra-high SERS substrates with hot spots effect [8-13]. High enhancement factor and large area substrate can be prepared by electrochemical etching,
chemical etching and vapor deposition [8-12]. This substrate can facilitate the probe molecule to reach the hot spot. However, these methods can not accurately control the shape, density, location of hot spots, so the substrate uniformity is poor, and the substrate developed in different batches cannot achieve high reproducibility. Nano-printing technology with SiO$_2$ particles assembled honeycomb compact arrangement of two-dimensional template evaporation plating, and then removes the template to obtain the rest of the substrate [13]. By adjusting the parameters of the particles, the size and spacing of the substrate and the coupling effect between the triangular plate nanostructures can be controlled. However, this method is complex in process, high in cost and dependent on precise instruments and equipment. Self-assembly based on metal nanoparticles is an efficient method for preparing SERS substrates, which is not only low-cost, but also can be carried out in conventional laboratories. The focus of preparation by this method is usually the aggregation metal nanoparticles. The process is simple and the electromagnetic enhancement effect is obvious. However, the hot spots formed by the aggregated metal nanoparticles are random and cannot be controlled, it can be said that there is no repeatability. In order to solve this problem, we can control the shape of the synthesized metal nanoparticles, and synthesize the particles which have a lot of sharp tips structures to produce hot spots. Rather than the hot spots produced by the aggregation of metal nanoparticles.

In this paper, GNSs with multi-tip structure were synthesized by multi-step method. The GNSs synthesized by this method are fast, simple and very high yield. On the basis of this, we prepared GNS SERS substrate by using the method of self-assembly without auxiliary for the first time. By adjusting the self-assembly time, the substrate samples with different density were realized. The R6G molecules were tested by Raman spectroscopy using these substrates. The results show that for the same R6G molecular concentration, the higher the density of GNSs, the stronger the SERS signal. This is because there are more hot spots for high-density GNSs per unit area distribution.

2. Results and Discussions
The schematic diagram of our multi-step process for the preparation of GNSs is shown in Figure. 1. In the process of preparation, the formation of the tip structure of GNSs is closely related to the amount of Ag$^+$ in the reaction solution. The inhibitory effect of AgNO$_3$ and HCl reactions on the growth of GNSs is the essential reason for the formation of the tips. The specific mechanism is that the AgNO$_3$ and HCl reaction will produce AgCl precipitation, and AgCl precipitation will be adsorbed on the surface of the GNSs. In the reaction process, the coverage effect of AgCl precipitation plays a decisive role in the morphology of GNSs. AgCl adsorbed on the surface of the seed, preventing the gold atom from growing at the precipitate, so the seed grows anisotropic. As the gold atoms grow on the surface of the particles, they form multi-tip GNSs.

![Figure 1. Schematic diagram of multi-step process for the preparation of GNSs.](image)

2.1. Preparation and characterization of gold seeds
First of all we use deionized water to clean the necessary experimental equipment to prevent the residual impurities from affecting the experimental results.

(1) Solution with synthetic gold seeds. 100 ml HAuCl$_4$·3H$_2$O solution with concentration 1 mM of and 15 ml trisodium citrate solution with mass fraction of 1% were prepared and stirred for 30 min to ensure their complete dissolution.
(2) Gold seed preparation. Quickly add trisodium citrate solution to boiling HAuCl$_4$$\cdot$3H$_2$O solution, stir it violently, heat it for 15 min, and then stop heating. The solution is naturally cooled to room temperature and stored in the refrigerator for long-term use. In general, seeds must be filtered with 22 μm filter to remove large particles before use. Before the experimental reaction, the color of the HAuCl$_4$$\cdot$3H$_2$O solution is bright yellow. After adding the trisodium citrate solution, the color of the solution changes rapidly from bright yellow to dark red, and finally to wine red.

In order to determine the morphology and size of the synthesized gold seeds, transmission electron microscopy (TEM) and optical fiber spectrometer were used to characterize them, as shown in Figure 2. As can be seen from figure 2a, the morphology of the gold seeds prepared by us is uniform and the dispersity is very good. In order to determine the grain size of the gold seed, a statistical analysis of the size of the TEM image was carried out, as illustrated in the inset of figure 2a. The results show that the size of the synthesized gold seeds was mainly between 10 and 20 nm and was very uniform. Figure 2b is the absorption spectrum of gold seed. The absorption peak of gold seed solution is about 520 nm, which is consistent with the results reported in the literature [14].

![Figure 2](image_url)

**Figure 2.** (a) TEM image of gold seeds, inset: gold seeds statistical analysis image, (b) Normalized absorption spectra of gold seed solution.

2.2. Preparation and characterization of GNSs
First, mix a HAuCl$_4$$\cdot$3H$_2$O solution of 100 ml with a concentration of 10 mM and HCl solution of 100 μl with a concentration of 1 M and stir violently. And then add 1 ml of gold seed solution filtered by 22 μm filters. Then, at the same time, quickly add the AgNO$_3$ solution of 1 ml with a concentration of
30 mM and an ascorbic acid solution of 500 μl with a concentration of 100 mM. After 30 s stop stirring, the solution quickly changed from bright yellow to ink blue, and then the reaction is over. According to the whole experiment process, the synthesis process of GNSs is very fast, it can be completed within 30 s, and the operation flow is relatively simple.

In order to evaluate the morphology of the prepared GNSs, we use TEM to characterize them, as shown in figure 3. It can be seen from figure 3a that the GNSs we synthesized have multiple tips and are very dispersive, which indicates that this method can be used to synthesize very high-yield GNSs. Then we measured the solution absorption spectrum of the particles by optical fiber spectrometer. Before measuring, the above GNSs solution was treated by centrifugation (4500 rpm, 45 min). The aim is to remove unreacted AgNO₃ and ascorbic acid from solution. After centrifugation, the supernatant is taken out, the precipitate is diluted in 5 ml deionized water, the ultrasonic is dispersed for 10 min, and the resulting clean GNSs solution is used for spectral analysis. Figure 3b shows the extinction spectrum of the GNSs solution, the extinction peak of which is about 820 nm.

![Figure 3](image.png)

**Figure 3.** (a) The TEM image of GNSs, (b) Normalized extinction spectra of GNSs solution.

2.3. The preparation of SERS substrate

Put the prepared GNSs solution into a 50 ml beaker. Then, the ITO glass substrate treated with detergent, acetone and deionized water in turn are placed in the solution, half of which are exposed to the solution. 8 h later, we took out the ITO glass substrate and found that the color of the glass in the solution changed and was basically the same as the color of the solution. It can therefore be determined that a GNSs film, that is SERS substrate, is successfully assembled on ITO glass substrate without any auxiliary agent.

Through further experiments, we found that this self-assembly method without additives is selective. In this experiment, only the ITO glass substrate will be assembled, but the ordinary glass will not be assembled. In order to fully demonstrate the advantages of this non-auxiliary self-assembly technique, we designed the patterned ITO glass substrate, and then further verified the selective assembly of
GNSs, hoping that it could be used in some special fields. As shown in figure 4, we designed the abbreviations of southeast university ‘SEU’ and ‘NANO’. The size of the glass substrate is 20X40 mm, the lower left figure is the reference sample before assembly, and the middle and right side are the substrates behind the deposited GNSs, respectively. The effect of assembly can be clearly seen from the figure 4, which verifies the technology of self-assembly without additives.

![Figure 4. Effect diagram of patterned ‘SEU’ and ‘NANO’ substrates self-assembly without auxiliaries.](image)

The time of assembly has a great effect on the density of GNSs on the substrate. Figure 5 shows the effect of assembly time on GNSs deposition density. The assembling time of sample S1, S2 and S3 are 2, 4 and 8 h, respectively. It can be seen that with the increase of assembly time, the density of GNSs on the substrate increases gradually. The GNSs density on the surface of S2 (figure 5b) is gradually increasing; while the GNSs density on the surface of sample S1 (figure 5b) is basically discrete. When the assembly time was up to 8 h, the GNSs density on the surface of sample S3 (figure 5c) was relatively thick and even superposed. When the density of GNSs is high, then there will be more GNSs in the area of incident laser, which will produce more hot spots.

![Figure 5. The SEM images of GNSs film with different assembly time. (a) 2 h (S1), (b) 4 h (S2), (c) 8 h (S3).](image)

3. SERS measurements of GNSs SERS substrates
   
   In order to verify the SERS enhancement properties of the GNSs substrate prepared by the self-assembly method, we selected 30 μl R6G methanol solution with a concentration of $10^{-6}$ M and dripped on the surface of S1, S2 and S3, respectively. The corresponding SERS spectra were measured (figure 6). As shown in figure 6, we find that the SERS characteristic peak of R6G on S1 is are very weak, while the S2 shows a strong SERS signal at 615 cm$^{-1}$ and 776 cm$^{-1}$ position. For sample S3, the SERS signal of R6G is greatly enhanced. Among them, the Raman peak of 615 cm$^{-1}$ corresponds to the deformation in the C-C-C ring plane of the R6G molecule. The Raman peak of 776 cm$^{-1}$ corresponds to the vibrational of in-plane deformed C-H bond. By comparing the GNSs density of the three samples in figure 5, we can see that the strong SERS enhancement of sample S3 substrate is mainly attributed to the larger GNSs distribution per unit area. In addition to producing a large number
of hot spots themselves, these GNSs will also produce a great number of hot spots from the coupling effect between the GNSs. These two actions increase the electric field intensity around the R6G molecule at the same time, thus realizing the remarkable enhancement of SERS signal.

**Figure 6.** SERS signal of R6G with a concentration $10^{-6}$ M on the S1, S2 and S3 substrates.

In order to further verify the sensitivity of the GNSs SERS substrate prepared by the self-assembly method to the detection of SERS signal, we continue to reduce the concentration of the R6G molecules and re-test their SERS signal. In the process of the test, 30 μl of the R6G solution with a concentration of $10^{-6}$ M, $10^{-7}$ M, $10^{-8}$ M were added to the three identical S3 substrates. Figure 7 shows a SERS signal obtained on S3 substrate by a R6G molecule with a concentration of $10^{-6}$ M, $10^{-7}$ M, $10^{-8}$ M, respectively. It can be seen that there are a lot of hot spots on the surface of S3 substrate, even if the concentration of the R6G solution drops to $10^{-8}$ M, we can still see a very strong Raman peak of R6G molecule. The results show that the fine SERS enhancement effect can be obtained with the appropriate assembling time. This method provides a simple and practical approach for high sensitivity SERS substrates.

**Figure 7.** SERS signal of R6G with a concentration $10^{-6}$ M, $10^{-7}$ M, $10^{-8}$ M on the S3 substrates.
4. Conclusion

We have prepared GNSs with multi-tip structure quickly and efficiently by multi-step method. It is the first time to find a non-auxiliary self-assembly technology for the preparation of GNSs SERS substrates. The micromorphology of GNSs and the effect of GNSs density on SERS signal were studied systematically. This assembly method has the advantages of simple preparation process and high speed. The coupling effect between high density GNSs has a stronger electric field. And the number of hot spots on the substrate can be controlled by adjusting the assembly time and other parameters. Therefore, the substrate prepared by this method provides support for the development of high sensitivity enhancement techniques.

Acknowledgments

This work is supported by Scientific Research Foundation of Graduate School of Southeast University YBJJ1513 and YBJJ1613.

References

[1] K. L. Kelly, E. Coronado, L. L. Zhao, The optical properties of metal nanoparticles: the influence of size, shape, and dielectric environment, J. Phys. Chem. B 107 (2003) 668-677.
[2] G. Mie, Beiträge zur Optik trüber Medien, speziell kolloidaler Metallösungen, Ann. Phys. 25 (1908) 377-445.
[3] X. Zhang, Y. L. Chen, R. S. Liu. Plasmonic photocatalysis, Rep. Prog. Phys. 76 (2013) 046401.
[4] Y. Liu, C. Rui, L. Lei, Plasmon resonance enhanced multicolour photodetection by graphene, Nat. Commun. 2 (2011) 1-7.
[5] J. N. Anker, W. P. Hall, O. Lyandres, Biosensing with plasmonic nanosensors, Nat. Mater. 7 (2008) 442-453.
[6] K. M. Mayer, J. H. Hafner. Localized surface plamon resonance sensors, Chemical Reviews 111 (2011) 3828-3857.
[7] R. Gordon, D. Sinton, K. L. Kavanagh, A new generation of sensors based on extraordinary optical transmission, Accounts of Chemical Research 41 (2008) 1049-1057.
[8] Z. Q. Tian, B. Ren, D. Y. Wu, Surface-enhanced Raman scattering: from noble to transition metals and from rough surfaces to ordered nanostructures, J. Phys. Chem. B 106 (2002) 9463-9483.
[9] B. Ren, G. K. Liu, X. B. Lian, Raman spectroscopy on transition metals, Anal Bioanal Chem 388 (2007) 29-45.
[10] P. Gao, M. J. Weaver. Surface-enhanced Raman spectroscopy as a probe of adsorbate-surface bonding: benzene and monosubstituted benzenes adsorbed at gold electrodes, J. Phys. Chem. 89 (1985) 5040-5046.
[11] J. A. Dieringer, A. D. Farland, N. C. Shah, Introductory lecture: surface enhanced Raman spectroscopy: new materials, concepts, characterization tools, and applications, Faraday Discuss. 132 (2006) 9-26.
[12] J. C. Hulteen, D. A. Treichel, M. T. Smith, Nanosphere Lithography: Size-Tunable Silver Nanoparticle and Surface Cluster Arrays, J. Phys. Chem. B 103 (1999) 3854-3863.
[13] S. Link, M. A. El-Sayed. Spectral properties and relaxation dynamics of surface plasmon electronic oscillations in gold and silver nanodots and nanorods, J. Phys. Chem. B 1999,103 (1999) 8410-8426.