Preparation and SERS Study of Triangular Silver Nanoplates

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Abstract: Metal nanostructures have unique properties that differ from their bulk structures. Of the metals, silver has probably play the most important role in the development of plasmonics, and its unique properties make it well-suited for most of the next-generation plasmonic technologies. Among the various silver nanostructures, silver nanoplates have attracted considerable attention because of their shape-dependent optical properties, which have been applied in surface enhanced Raman spectroscopy (SERS). In this study, the direct chemical reduction route was used to prepare silver nanoplates. Then the influence of experimental conditions on the morphologies of silver nanoplates has been studied. The results have been proved by the UV-vis spectrum and the transmission electron microscope images of the triangular silver nanoparticle. Finally, the silver nanoplates have been applied in SERS properties with Rhodamine 6G as the probe molecules. It was found that the SERS enhancement ability of the silver nanoplates is remarkable. By comparing the advantages and disadvantages of solid Raman and liquid Raman tests, Liquid Raman test is considered to be simpler and more convenient, with high performance price ratio and extremely high application value in the future.

1. Introduction

Raman spectroscopy can give the information about the vibrational energy level or rotational energy level of a molecule. It is widely used in the detection of substances because it can give the information of complex structures in a fast and non-destructive way, and the peaks of the spectroscopy are sharp and easy to distinguish. However, due to the small cross sections of the Raman spectroscopy, its practical applications are severely limited [1,2]. In 1974, Fleischmann [3] has discovered the Raman enhancement spectrum, which can greatly enhance the light intensity of the Raman spectroscopy. With the continuing research, the biggest obstacle to the application of Raman spectroscopy has been overcome [4-6]. There are two main mechanisms [1] that contribute to surface enhanced Raman spectroscopy (SERS): (1) electromagnetic enhancement mechanism; (2) chemical enhancement mechanism. The excitation of the surface plasmons of noble metal nanostructures plays a major role on electromagnetic enhancement. When a Raman scattering molecule is subjected to intense electromagnetic fields generated on metal surfaces, the higher electric field intensity results in stronger polarization of the molecule and thus the higher induced dipole moment is acquired. This enhancement is proportional to Raman scattered light intensity and considered as the major component of the enhancement mechanism. On the other hand, chemical enhancement is based on charge transfer between metal and adsorbed molecules on plasmonic nanostructures. However, the chemical enhancement contribution is limited and its contribution is dependent on the chemical structure of the molecule.

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In 2001, Jin and Mirkin et al synthesized triangular silver nanoplates [8] for the first time. Due to the excellent characteristics of the nanoplates, they have been widely studied by scientific researchers since then. Triangular silver nanosheets have outstanding features with adjustable LSPR peaks. In the early research, researchers changed the shape and size of silver nanoparticles by changing the temperature, chemicals (oxidants, reducing agents, surface adsorbents, stabilizers, etc.). The LSPR peak can be adjusted from the visible to the near-infrared region [9]. With the development of nano-preparation technology, the peak can be adjusted to 2000 nm finally [10, 11]. It is the anisotropy of triangular silver nanoplates that make LSPR adjustability become wide. And the large side-to-thickness ratio can promote their local surface plasma (LSPR) resonance. The maximum electromagnetic field is enhanced. According to the calculation of the Kelly et al. [12], the tip has a stronger field enhancement factor at the dipole LSPR peak (excitation wavelength 770 nm). When the quadrupole resonance is excited (excitation wavelength 460 nm), the position where the field strength is the largest is on the side edge. Dipole LSPR excitation produces stronger field enhancement than quadrupole LSPR excitation, resulting in the strongest enhancement that appears at the tip. Moreover, the electric field attenuation distance generated by the dipole SPR is longer than the electric field of the quadrupole LSPR, that is, it can enhance the surrounding electric field in a larger range. Guedje et al. obtained more consistent results with experiments through the finite difference time domain (FDTD) [13]. Their results show that the maximum electric field enhancement (E2) is at the tip, which is 3.7 x 10^4 times larger than the applied electric field under dipole LSPR excitation. It can be seen that triangular silver nanoplates have great application potential in surface-enhanced Raman spectroscopy. Compared with the current extensive solid Raman test, liquid Raman has also begun to attract the attention of researchers. Liquid Raman can obtain a surface-enhanced Raman spectrum of the tested substance with a simpler operation while consuming less raw materials, while its detection intensity gradually approaches solid Raman detection. And it can also effectively solve the agglomeration problem of the tested substance. It will be one of the most effective testing methods for surface Raman enhanced spectroscopy.

In this paper, the triangular silver nanoplates were successfully synthesized, and then the triangular silver nanoplates were characterized by UV-Vis spectroscopy and TEM. The influence of relevant experimental factors on their morphology was studied. Finally, it was applied to the surface-enhanced Raman spectroscopy with R6G as the probe molecule and silver nanoplates as the reinforcing substrate. The results show that the silver nanoplates are both have very good enhancements in these two environments.

2. Materials and methods

2.1. Materials
Silver nitrate (AgNO₃, Shanghai Chemical Co.), trisodium citrate dihydrate (C₆H₅Na₃O₇, Shanghai Chemical Co.), sodium borohydride (NaBH₄, Sinopharm Chemical Reagent Co.) and H₂O₂ (30 wt%, Sinopharm Chemical Reagent Co.) poly(vinyl pyrrolidone) (PVP, MW z 29,000)

2.2. Structural Characterizations
Vacuum drying oven (Gongyi City Yuhua Instrument Co., Ltd., DZF-6020), Electronic Balance (Shanghai Yueping Scientific Instrument Co., Ltd., FA2104B), High-speed centrifuge (Changsha Yingtai Instrument Co., Ltd., TG20, MAX20000r/min.), Transmission Electron Microscope (TEM) (JEM.21 00 200KV manufactured by JEOL Ltd.), UV-visible absorption spectroscopy measurement (Shimadzu, Japan, UV210011PC), Liquid Raman spectroscopy (OCEANOPTICS INC. MAYA2000PRO-NIR), Solid Raman spectroscopy (HJY HR800 manufactured by Jobin-Yvon Co.)

2.3. Preparation and characterization of silver nanoplates
Direct chemical reduction route was used to prepare silver nanoplates. In the first step, Silver-nitrate solution (70μL, 50mM), sodium citrate solution (300μL, 75mM) and H₂O₂ solution (80μL, 80mM)
were injected into 24.25ml of deionized water under magnetic stirring. The mixed solution was stirred for five minutes to make it evenly distributed. In the second step, sodium borohydride solution (250 μL, 0.1 M) was added to the mixed solution under magnetic stirring and the solution turned pale yellow immediately. Then, after stirring for 5 minutes, it was allowed to stand for about 30 minutes to drive the reaction to completion. When the solution turns dark blue, the triangular silver nanoplate stock solution can be preliminarily prepared. The prepared silver nanoplate solution will be centrifuged at 8000rpm for 10min.and the bottom precipitate was redispersed to 25 ml with deionized water for secondary centrifugation. The bottom precipitate was finally redispersed to 3 ml with deionized water and stored in a low temperature environment for testing. The sample was analyzed for its peak value by ultraviolet-visible spectroscopy, and its morphology and size were observed by TEM. By changing the amount of H2O2 added into the solution, experiments on the effects of experimental materials on the morphology of silver nanoplates were carried out.

2.4. SERS sample preparation and testing
R6G molecules were used as probe molecules, and they were subjected to solid and liquid surface-enhanced Raman scattering effects. Solid and liquid Raman samples were prepared with the triangular silver nanoplate solutions that has been prepared before. Liquid Raman samples was prepared firstly, 2ml R6G concentration gradient 10^{-4}-10^{-5} solution was directly prepared by mixing 200μl silver plate solution and certain concentration of R6G solution in a beaker, then The mixed solution was ultrasonically oscillated for 2h to fully polymerize silver nano solution and R6G solution. Surface enhanced Raman effect Spectral measurements were configured with Liquid Raman spectroscopy, which is excited at 785 nm.

The steps of solid Raman preparation are more complicated. In the first step, similar to liquid Raman, a 2 ml R6G concentration gradient 10^{-4}-10^{-6} solution containing 200 ml of a silver nanoplate solution was prepared. In the second step, after sonication for 2 h, the solution was dropped onto a single polished silicon wafer and placed in a dry box for drying. Finally, it was stored in the dark and then subjected to Raman test. Surface enhanced Raman effect Spectral measurements are configured with CCDHR800 Raman microscope with a detector at 633 nm excitation wavelength. The objective lens used in the Raman microscope is a 50x focal length mirror head. The cumulative time of one acquisition is 5 s. the samples were taken multiple different bits and the end result is the average of all the values.

3. Results and discussion

3.1. Synthesis of the Ag nanoplates
The UV-Vis spectra of the prepared triangular silver nanoplates are shown in Figure 1. It can be seen from Figure 1(a) that the curve has no absorption peak at 420 nm, indicating that there are fewer spherical particles in the system [14]. Moreover, the three main absorption peaks of triangular silver nanoplates are shown in the Figure 1(a): the small peak at 330 nm is the out-of-plane dipole peak of the silver nanoplate; the shoulder at 440 nm is the in-plane quadrupole of the silver nanoplate; the strong peak at 880 nm is the in-plane dipole peak of the silver nanoplate. And the successfully prepared solution was in dark blue, mainly due to the in-plane dipole peak of the triangular silver nanoplate at 880 nm.

Then we use H2O2 as a variable to explore the effect of specific experimental variables on the size and morphology of triangular silver nanoplates. While keeping other experimental conditions unchanged, the amount of H2O2 added was changed to synthesize triangular silver nanoplates.20, 60, and 80 ml of H2O2 were added to synthesize silver nanoplates. As shown in Figure 1(b), as the H2O2 increases, the dipole extinction peak of the nanoparticle at 400 nm gradually weakened while the in-plane quadrupole peak of the silver nanoplates at 420 nm gradually appeared, indicating that the silver nanoparticle gradually disappeared and the anisotropic structure of the silver nanoplate gradually formed. Moreover, the in-plane dipole peak of the silver nanoplate gradually red-shifted, and the
triangular silver nanoplate gradually became larger in size. According to the analysis, the product will be silver nanoparticle when the concentration of H$_2$O$_2$ becomes very low. With the increase of H$_2$O$_2$ concentration, the nanoparticles can be re-eroded into an ionic form and then redeposited by the reducing agent to redeposit on the surface of the seed crystal with defects to form a sheet-like structure. However, the experimental results also show that when the concentration of H$_2$O$_2$ is too high, all of the silver appears in an ionic form, and silver nanoplates cannot be synthesized. Therefore, we can conclude that silver nanoplates can be obtained by rationally regulating the concentration of H$_2$O$_2$.

![Graph](image1.png)

**Figure 1.** (a) UV-Vis spectrum of silver nanoplates. (b) UV-Vis spectra of silver nanoplates with different H$_2$O$_2$ additions.

![Graph](image2.png)

**Figure 2.** (a) and (b) are TEM images of triangular silver nanoplates, the inset in (a) is the particle size statistics, and the inset in (b) is the thickness size statistics.

Silver nanoplate solution can produce the peak that we need when 60ml H$_2$O$_2$ added with repeated experiments, Figure 2(a) (b) is the TEM image of silver nanoplates with composition of 60 ml of H$_2$O$_2$. 
It can be seen from the figure that most of the prepared silver nanoplates have a triangular shape, and some triangular tips have a certain truncation. Triangular structure of silver nanoplates prepared have sharp edges, high symmetry so that it can produce more "hot spots". The particle size (triangle side length) inset in Figure 2(a) shows that the side length is mainly concentrated at about 45 nm, and the thickness statistics inset in Figure 2(b) show that the synthesized triangular silver nanoplate has a thickness of about 4.5 nm. So that we can draw a conclusion that the silver nanoplates prepared have relatively uniform morphology and low dispersibility.

Therefore, we have successfully prepared a uniform triangular silver nanoplate containing a tip that can be used as a substrate for surface Raman enhancement experiments.

Figure 3. (a) the solid Raman test of different rhodamine 6G concentrations enhanced by triangular silver nanoplates. (b) the liquid Raman test of different rhodamine 6G concentrations enhanced by triangular silver nanoplates.

3.2. Solid and liquid surface Raman enhanced scattering
Using R6G molecule as the probe molecule, the results of SERS effect of solid substrate and liquid substrate are shown in Figure 3. It can be found that the characteristic peaks of R6G near 1182, 1312, 1362, 1510 and 1654 cm⁻¹ are obviously displayed. It can be seen from Figure 3(a) that the minimum test concentration of solid SERS reaches 10⁻⁶ M. And as the concentration of the R6G increasing, the Raman enhancement intensity also increases. The prepared triangular silver nanoplates have good
detection ability for \textit{R6G} and have significant Raman enhancement effect. And it can be seen from Figure 3(b) that liquid \textit{SERS} has a minimum detection limit of only $10^{-5}$M. But the peaks it shows are very clear and easy to distinguish, and have the potential to continue to improve. Moreover, its operation is simple and the peak is more prominent, and the materials using for test are also relatively less, which can reduce environmental pollution, so that it is easier to promote in practical applications.

\textbf{Summary}

In this study, we successfully prepared triangular silver nanoplates by direct reduction method. The results show that with the increase of H$_2$O$_2$ concentration, the silver nanoparticles gradually decrease, and the sheet structure gradually forms. Further, the in-plane dipole peak of the silver nanoplates gradually red shifts, and the triangular silver nanoparticles gradually become larger. Using \textit{R6G} molecule as the probe molecule, the results of \textit{SERS} effect of solid substract and liquid substract of synthesized triangular silver nanoplate were studied. The results show that \textit{R6G} has a significant Raman enhancement effect in both environments.

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