Surface enhanced Raman spectroscopy of Rhodamine 6G on different-sized silver truncated nanotriangles formed agglomerates

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Abstract

This reported study investigated the use of agglomerates fabricated from different-sized Ag truncated nanotriangles in highly sensitive surface enhanced Raman scattering (SERS) by employing Rhodamine 6G dye as the probe molecule. It was found that the SERS intensity of R6G was enhanced as the size of the Ag truncated nanotriangles increased. It was postulated that this phenomenon resulted from the generated hot spots and the roughness of the surface of the agglomerates. In addition, the results exhibited an independent feature on the surface plasmon resonance position. The experimental results showed that the prepared SERS substrate was able to detect R6G over a wide concentration range of 10^{-5} - 10^{-11} M and could be used as an effective SERS substrate in trace detection.

1. Introduction

Surface-enhanced Raman scattering (SERS) technique is a powerful analytical method for obtaining chemical information about molecules adsorbed on the surface of certain metallic substrates. The mechanisms of SERS can be attributed to two main forms. One is the chemical (CM) mechanism [1] and the other is electromagnetic (EM) mechanism [2]. It is

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widely accepted that the CM enhancement is due to the charge transfer between the metallic substrates and the adsorbed molecules. And the EM mechanism is considered to contribute the most for SERS test. The EM enhancement generally originates from the enhanced local electric field in the vicinity of the metal's surface, which results in a significant increase in the cross section of the Raman scattering [3, 4]. The EM enhancement is depended on many factors, such as the shape of the nanoparticles, dielectric environment, metal type and aggregation state [5, 6]. The enormous enhancement of the SERS is commonly believed to be derived from "hot spots" at the junction of two or more aggregated metal nanoparticles [7-9]. Therefore, the SERS properties on substrate rich with hot spots have become one of the important subjects. Since the EM enhancement of SERS originates from the localization and amplification of incident light fields by a surface plasmon resonance, most researcher have concluded that the highest SERS intensity should be obtained only when the excitation laser wavelength overlaps the wavelength of the localized surface plasmon resonance (LSPR) [10-13]. But the results of Kleinaman et al. [14] and Samal et al. [15] have indicated that in a hot-spot dominated SERS system, such as aggregated nanoparticles-formed substrates, the enhanced SERS properties showed little correlation to the spectral properties of the corresponding nanoparticle's LSPR. This then raises the question of what factors influence the SERS intensity of aggregated nanoparticles. As is well known, the formation of hot-spots relies on the shape and size of the nanoparticles and the distance between two adjacent nanoparticles. Some efforts [15-17] refer the dependency of SERS properties on the shape and size of nanoparticles. For example, Samal et al. [15] mentioned that the SERS efficiency increased with Au@Ag nanoparticles size regardless of the selected laser line. A strategy was introduced to prepare SERS-active Ag nanoparticles on a roughened Au substrate in the report by Ou et al. [16]. With an increase in the deposition time, the size of the dendritic Ag nanoparticles will increase along with an increase in SERS intensity using Rhodamine 6G (R6G) as probe molecule. Gao et al. [6] fabricated a silver nanosheet-assembled film as SERS substrate and found that with an increase in the concentration of the reactant, the length of the sheet increased and SERS intensity increased as well. Jana et al. [17] reported that for the spherical Au/Ag nanoparticles, the optimum size range for a good Raman spectra signal was 20-70 nm. Their results didn't comply with the previously mentioned rule; that the larger

the nanoparticles, the higher the intensity of the SERS signal. Also the SERS sensitivity produced from anisotropic nanoparticles is higher than that obtained from isotropic nanoparticles when the morphology is platelet or rod or a special morphology that contained many tips [12]. The triangular shape as an anisotropic morphology, with the virtues of a tunable LSPR position by size and three tips on each nanoparticles, the relationship between the size of these nanotriangles and the corresponding SERS signal of the agglomerates comprised of nanotriangles has not been reported. In this report, three different-sized Ag nanotriangles formed agglomerates were prepared on a glass slide and their SERS behavior with R6G was studied. The relationship between the sizes of the nanotriangles and the SERS intensity was discussed from the view of the hot spots generated in the agglomerates and the surface roughness of the agglomerates.

2. Experimental section

The preparation of Ag nanotriangles was conducted according to the procedure of Wu et al. [18] in which a seed-mediated growth method was used. The different sizes of Ag nanotriangles were prepared by a two step process. This preparation procedure consisted of the chemical reduction of Ag nanoparticle seeds using sodium borohydride, followed by seed growth of the Ag nanoparticles by the reduction of AgNO_3 in the presence of poly(vinylpyrrolidone) (PVP). The size of Ag nanotriangles was tuned by varying the amount of seed concentration, while maintaining the concentration of the other reagents constant. Finally, the resulting Ag nanotriangle solution was purified by centrifuging for three times and then redispersed in alcohol as a thirty-fold concentration over that of the original reactant solution.

A Perkin Elmer Lambda 950 UV/VIS/NIR spectrophotometer was used to measure the absorbance of Ag nanoparticles solution. In parallel analyses, the three different-sized nanotriangles were characterized by transmission electron microscope (TEM, FEI Tecnai F30). The surface morphology and roughness of the Ag agglomerates on the glass slide were obtained using an atomic force microscopy (AFM, Asylum Research MFP-3D) experiments. The root mean surface roughness (RMS) was automatically calculated using the program

attached to the instrument. Raman spectroscopy was performed with a HORIBA Jobin Yvon HR800 spectrometer with a 532 nm diode laser as excitation source. Spectral data were collected over the range 400-2000 cm^{-1} with a 0.1 s acquisition time. All spectra were calibrated with respect to silicon wafer at 520 cm^{-1} .

SERS substrates were prepared by dropping 10 μL of the concentrated Ag nanotriangles suspension with the Ag mass concentration of 5.4 mg/mL onto the glass slide and allowing it dry in air. During the process of solvent evaporation, the aggregation state was achieved via random deposition of the Ag nanotriangles on the surface of the glass slide. Then, 10 μL of the probe molecule-R6G solutions with concentrations in the ranges 10^{-5} - 10^{-11} M were redropped onto the prepared SERS substrate for SERS investigations.

3. Results and Discussion

Fig. 1 (a), (b) and (c) show the TEM images obtained for the Ag nanoparticles that were synthesized with the addition of three different volume seed (0.01, 0.1 and 1 mL) solutions while keeping the other conditions constant. As shown, each contains both quasi-spherical nanoparticles and the truncated triangular platelet (or quasi-disc). The evolutionary process from triangle to truncated triangle and disc is shown in Fig. 1(d). The more the seeds added, the more ratio of nanotriangles were truncated and they are almost composed of nanodiscs for the product synthesized under 1ml seeds. The average sizes of the nanoparticles and nanotriangles for each samples is listed in Table 1 based on a statistical analysis employing Nano Measurer 1.2 software and the TEM images. The corresponding size distribution histograms were shown in Fig. 2.

Fig. 1. TEM images of Ag nanoparticles with three different sizes prepared with (a) 0.01 mL, (b) 0.1 mL and (c) 1 mL of seed solution and (d) the schematic diagram of the morphology when the triangular particles were truncated

Fig.2 Diameter distributions histogram for nanoparticles with seeds volume as (a) 0.01 ml, (c) 0.1 ml and (e) 1 ml; edge length or diameter distribution histogram for truncated nanotriangles and nanodiscs with seeds volume as (b) 0.01 ml, (d) 0.1 ml and (f) 1 ml.

Table 1 Average size of the samples prepared using various seed volumes and the resulting roughness of the corresponding agglomerates

	0.01ml	0.1ml	1ml
Diameter of nanoparticles (nm)	73	45	27
Edge length of triangles (nm)	259	112	
Diameter of nanodiscs (nm)			41
Root mean surface roughness	68	58	40

The UV-VIS-NIR spectra of the three samples are shown in Fig. 3. The absorption spectra are the integrated features of the nanosphere and nanotriangle. Generally the spherical silver nanoparticles exhibited only one dipole plasmon resonance at about 400-440nm depending on their size [19, 20]. But when the content of nanosphere was small, it may have been that their resonance occurred as a little shoulder peak at 413 nm as shown in Fig. 3. For nanotriangles there were three dominant peaks corresponding to different modes of plasmon excitation. From the long to short wavelength, the three SPR peaks can be attributed to the in-plane dipole, the quadrupole plasmon resonance and the out-of-plane quadrupole resonance modes. The in-plane dipole and in-plane quadrupole plasmon resonances were red-shifted when the edge length of the nanotriangles increased from 41 nm to 259 nm. This red-shift was attributed to the increased charge separation during the plasmon oscillation as enabled by the increase in size. The band at 339 nm (or 340 nm) refers to the bluest resonance, namely the out-of-plane quadrupole resonance, which was nearly unaltered despite the variation of the edge length of the triangles. The in-plane dipole resonance position of the nanotriangle often shows some dependence on its edge length as has been reported in some theoretical calculation [21]. According to the results in Fig. 1 reported by Hermoso [21] for silver nanotriangle, a linear formula can be obtained between the in-plane dipole position and its edge length in the format, $y=460.1+3.745x$ (y denoted the in-plane resonance position, x denoted the edge length of the triangle, the units for x and y are nm). Thus, three edge length values of 164.4, 85.3 and 23.0nm were obtained for the three different size of samples. The

calculated values were somewhat different from the results obtained from the TEM images listed in Table 1, because in Fig. 1, it is can be seen that other than the nanospheres, the products were truncated triangles. However, the LSPR character of truncated nanotriangles or nanodiscs were similar to the prefect nanotriangles, but LSPR position was little slightly blue shifted compared to the perfect nanotriangles.

Fig. 3. UV-VIS-NIR absorption spectra of different sized Ag nanotriangles solution; (a),(b) and (c) for the seed dosage of 0.01, 0.1 and 1ml.

The normal Raman scattering of the pure R6G was not observable when the concentration of R6G was 10^{-5} M. But in the presence of Ag nanotriangles formed agglomerates no matter the size of the nanotriangles, the Raman scattering of R6G can be observed distinctly as shown in Fig. 4. It is characteristic of Raman spectra of R6G [22, 23] and the assignment for several peaks are listed in Table 2.

Table 2 Assignment for Raman Spectra of R6G molecule

Wave number (cm ⁻¹)	610	770	1125, 1180	1310, 1575	1360, 1510, 1650
Vibration mode	C-C-C	C-H	C-H	N-H	C-C

ring	out-of-plane	in-plane	in-plane	stretching
in-plane	bend	bend	bend	
vibration				

Through comparing the SERS signals with the morphologies of the three agglomerates formed from different-sized Ag nanotriangles, it was found that the agglomerate with the largest edge length (259 nm) in the nanotriangles exhibited the highest SERS intensity. In fact, the SPR 548 nm of the Ag nanodiscs with average diameter of 41 nm was closest to the excitation laser wavelength (532 nm). The enhancement was apparently independent of the SPR spectral position, but was related to the size of nanotriangles. Fig. 4 is a plot of the

Fig. 4. SERS spectra of R6G adsorbed on Ag agglomerates formed by nanotriangles synthesized with seeds volume of 0.01 mL (a), 0.1 mL (b) and 1 mL (c) at $1 \times 10^{-5} \text{M}$

SERS intensity coming from different substrates prepared by three batches as-prepared products which contained different-sized Ag nanotriangles and, the reasons for different SERS intensity should be considered in terms of the hot-spots. Hot spots are defined as a junction or close interaction of two or more plasmonic objects. Agglomerates necessarily contain hot spots, but the characteristics of hot spots relied on the shape and the size of the built unit-nanoparticles. In this reported work, three SERS-active substrates consisted of agglomerates that were obtained using three different-sized Ag nanotriangles. The hotspots can be built by several nanospheres, several nanotriangles or mixed of them. The quantity of built nanoparticles can be two or more, so the possible quantity of the hot spots can be large.

But from the view of type of the unit-component which is the nanosphere and nanotriangle, we just define three forms of geometric hotspots. The first form is the gap or junction between the adjacent Ag quasi-spherical nanoparticles. The second form is the corner sites of a quasi-spherical nanoparticle in proximity to the surface of a nanotriangle. The third form is the zone between two parallel Ag nanotriangles. Two nanotriangles perpendicular to each other was seldom observed, so this condition was not considered to produce hot spots. The three kinds of hot spots can coexist in the three agglomerates formed from three different-sized Ag nanotriangles. Since the second hot spots are located outside the junction between the quasi-spherical nanoparticles and the flat surface of the nanotriangles, it processes the virtue of high accessibility for detection as discussed in the literature [10]. The second and third hot spot as efficient hot spots will become more abundant when the size of the nanotriangle increased, which ultimately led to the enhanced SERS intensity. In particular, the third form of hot spots in agglomerate will provide more hot spot area and volume for target molecules to absorb. So the SERS intensity of such a substrate increased with the increased size of nanotriangle. As reported in the literature [24,25], the nanoscale surface roughness of the SERS-active substrate has a strong effect on the SERS signals for R6G or methylene blue (MB) probe molecules. A surface microstructure with higher roughness will provide more chance for probe molecules to adsorb on the SERS-active substrate. The morphology of the surface of three agglomerates was examined by AFM and shown in Fig. 5. The surface roughness increased with the average size of the nanotriangles and the root mean surface roughness was 40, 58 and 68nm for the three substrates formed by 41 nm, 112 nm and 259 nm nanotriangles.

Fig. 5. AFM images of Ag agglomerates formed by (a) 259 nm, (b) 112 nm and (c) 41 nm nanotriangles

The SERS spectra of R6G at different concentrations were measured using the substrate formed by 259 nm nanotriangles. As shown in Fig. 6, the spectral intensities decreased as the concentration of the R6G decreased. The typical bands of R6G molecule were clearly observed even when the R6G concentration was reduced to $1 \times 10^{-11} \text{ M}$, demonstrating the high sensitivity of this substrate. These results confirmed that the Ag nanotriangles agglomerates could be used to achieve detection of trace quantities of R6G molecules.

Fig. 6. SERS spectra of R6G adsorbed on Ag agglomerates formed by 200 nm nanotriangles with different concentration: (a) $1 \times 10^{-5} \text{ M}$, (b) $1 \times 10^{-7} \text{ M}$, (c) $1 \times 10^{-9} \text{ M}$, (d) $1 \times 10^{-11} \text{ M}$

To quantify the SERS enhancement using this substrate, the peak at 610 cm^{-1} was used to calculate the SERS EFs (enhancement factors) using the following equation:

$$EF = (I_{SERS} / I_{bulk}) \times (N_{bulk} / N_{SERS})$$

Where I_{bulk} and I_{SERS} are the intensities of the same peak for the Raman spectra of bulk and SERS; N_{bulk} and N_{SERS} are the numbers of solid R6G molecules and R6G molecules on the agglomerate formed from Ag nanotriangles within the laser spot. For determination of N_{bulk} and N_{SERS} , 10 μL of R6G solution (10^{-3}M) was spread onto a glass slide with the diameter of 1 cm and the R6G solution ($1 \times 10^{-11}\text{M}$, 10 μL) was dropped onto the most efficient substrate with the same area. The ratio of N_{bulk}/N_{SERS} was calculated to be 10^8 under the same area of laser spot. The two samples were measured by Raman spectroscopy using same conditions, and the ratio of I_{SERS}/I_{bulk} was calculated to be 0.68 from the intensity of peak at 610 cm^{-1} . The EF value was founded to be 6.8×10^7 . These results indicated that the 259nm Ag nanotriangles aggregates could be employed as an efficient SERS substrate for trace detection.

4. Conclusions

In summary, SERS-active substrates were prepared by deposition of three different-sized Ag nanotriangle solutions onto a glass slide. The SPR of Ag nanotriangles solutions was tuned by varying the edge length of the nanotriangles. Although the SPR of Ag nanotriangles with the smallest edge length was very close to the source laser wavelength, the SERS efficiency of the substrate formed from them is lowest. The results indicated that the SERS intensity increased with the size of Ag nanotriangles, which can be ascribed to the type of hot spot generated. When the size of the nanotriangles increased, the quantity of the produced hot spots between two parallel triangular nanoplates increased, which provided more space for adsorption of the target molecule resulting in an enhanced Raman spectral intensity. The reported results showed that the probe molecule R6G can be detected in a concentration range from 10^{-5} - 10^{-11}M . A SERS enhancement factor up to 6.8×10^7 was obtained by the substrate formed by the largest size of Ag nanotriangles.

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Large size of nanotriangles and large surface roughness of agglomerates formed from nanotriangles lead to intense SERS of R6G on this substrate.