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

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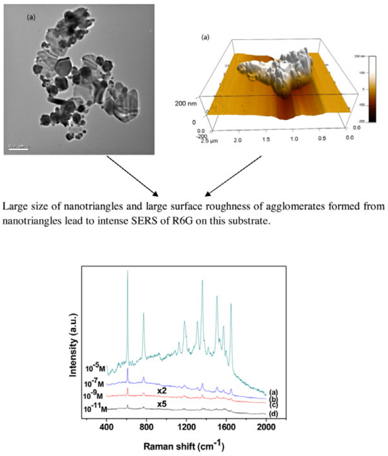
HIGHLIGHTS

- An efficient SERS-active agglomerates prepared by mixture of Ag truncated nanotriangls and quasi-spherical nanoparticles.
- The large size of nanotriangles benefit to enhance SERS efficiency.
- The detection limit for R6G by this easy-obtained SERS-active agglomerates can be 1×10^{-11} M.

GRAPHICAL ABSTRACT



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

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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.

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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 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 with 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 sliver 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.

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

	0.01 mL	0.1 mL	1 mL
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

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 an 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)–(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 1 mL 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.

The UV–vis-NIR spectra of the three samples are shown in Fig. 3. The absorption spectra are the intergrated features of the nanosphere and nanotriangle. Generally the spherical silver nanoparticles exhibited only one dipole plasmon resonance at about 400–440 nm depending on their size [19,20]. But when the content of nanopsphere was small, it may have been that their resonance occurred as a little shoulder peak at 413 nm as shown in Fig. 3.