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Improve the surface-enhanced Raman scattering from rhodamine 6G adsorbed gold nanostars with vimineous branches

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ABSTRACT

The surface-enhanced Raman scattering (SERS) activity of the gold nanostars with vimineous branches has been investigated by using rhodamine 6G (R6G) as the Raman active probe. The colloidal gold nanostars have two intense localized surface plasmon resonance (LSPR) peaks in the visible and infrared ranges, respectively. Besides the visible LSPR dependent local field effect induced Raman signal enhancement, the SERS ability also greatly depends on the infrared absorption from the plasmon resonance along the aligned branches. Whether increasing the peak intensity or wavelength of the infrared absorption leads to the efficient improvement of SERS. These correlations between plasmonic absorption and SERS indicate that the lightning rod effect and creation of hot spots have been enhanced with the length and number of gold branches.

1. Introduction

Surface-enhanced Raman scattering (SERS) of molecules attached on the surface of metallic nanostructures render them appropriate candidates for applications in chemical and biological sensing. Because of the coherent oscillation of conduction band electrons, gold and silver nanoparticles exhibit a localized surface plasmon resonance (LSPR) in the visible and infrared regions. The LSPR can also generates an intense local electric field, and subsequently enhance the Raman scattering signal of nearby molecules [1,2]. Therefore, SERS becomes a useful technique in sensing and analysis, which could be used in single-molecule detection and molecular structure investigation [3]. For example, Guo et al. [4] reported an ultra-sensitive SERS-based detection for trinitrotoluene by using the gold nano-dumbbell structures. Detection of α-fetoprotein (AFP) by using SERS-based immunoassay has been studied by Wang et al. [5]. They reported a sensitive and highly specific immunoassay system by utilizing gold nanoparticles and SERS. By using their method, AFP with a very low concentration of 100 pg/mL has been detected. In the study of Seo et al. [2], SERS-based detection of cancer cells using dye molecules-embedded gold–silica core–shell nanorods has been investigated. The excellent SERS performance is enough to detect both agglomerated and single cancer cells. A Au–Si core–shell nanoparticle-based SERS biosensor for label-free glucose detection has been reported by Al-Ogaidi et al. [6]. For this gold nanostar–silica core–shell nanostructure conjugated with glucose oxidase, the SERS signal shows the response to the concentration range of glucose from 25 μM to 25 mM.

In the application of SERS-based biologic and chemical sensing, fabricating plasmonic nanostructures with hot spots is requisite. The hot spots of local electric field are resulted from the LSPR modes resonantly excited by the incident light [7]. Thus many efforts have been developed to optimize the properties of LSPR and improve the resonant SERS signal by designing and fabricating the metallic nanoparticles with different shape, structure and arrangement [3,4,8–10]. For example, the longitudinal LSPR of gold nanorods could be tuned into the infrared region by increasing the aspect ratio. By using the excellent LSPR properties of gold nanorods, the embedded methylene blue molecules present near-infrared light-induced intense SERS, which is strong enough for the single cancer cell detection [2]. Liao et al. [11] studied the LSPR and SERS biosensing of Au–Ag–Au double nanoshells. The binding of target molecule at the surface of Au–Ag–Au double nanoshells was detected based on both plasmonic absorption and SERS spectra. Besides non-aggregated SERS, aggregation of metallic nanoparticles can also provide excellent SERS. Because of the plasmon coupling between two adjacent particles, the decreasing inter-particle distance results in distinct red shift of the LSPR band

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and intense local field enhancement in the gaps between the particles [12]. Delange et al. [13] reported the plasmon focusing in short nanochains of gold nanosphere for SERS. Due to the efficient plasmonic energy trapping and focusing, stronger field enhancement could be created in the short chains of gold nanospheres, which provides the need of SERS. Recently, Pilo-Pais et al. [7] used DNA origami to organize the gold nanoparticles and form the tetramers structure. The resulting assemblies exhibit hot spots of enhanced local field in the gaps between the particles. And a significant SERS signal from the molecules attached to the assemblies has been observed.

In recent years, star-shaped gold nanoparticles are particularly interesting because their tunable plasmonic properties result from tip effect, large aspect ratio of the branches, and plasmon hybridization between core and the tips [14–17]. The using of gold nanostars for SERS has also been studied [18]. In the report of Fales et al. [19], gold nanostars have been demonstrated as one of the best nanostructures for producing SERS in a non-aggregated state. Raman scattering from individual gold nanostars had been observed by Hrelescu et al. [20]. The SERS signal could be detected without the aggregations of nanoparticles. By using the finite-difference time-domain simulation, great local field enhancement and excellent SERS response of the four-pointed gold nanostar array have been demonstrated [21]. By using the seed-mediated growth method, gold nanostars were prepared in aqueous solutions [22]. It has been found that the SERS activity of the star-shaped gold nanoparticles was much stronger than that of the spherical gold nanoparticles with similar size. In the report of Su et al. [16], the SERS efficiency as a function of morphology of gold nanostar has been studied. They found that the gold nanostars with longest branches could generate the best SERS efficiency.

However, in these previous reports, the branches or tips of the nanostars are relative short, and the corresponding LSPRs are shorter than 900 nm. Recently, by using Triton X-100 in the seed-growth synthesis, five-branched gold nanostars were prepared, and the corresponding LSPR could be tuned into the wavelength ranges of 1100–1600 nm [17]. How about the SERS ability of the gold nanostars with vimineous branches? In this letter, the SERS activity of the gold nanostars has been evaluated by using rhodamine 6G (R6G) as the Raman active probe. It has been found that the SERS activity of gold nanostars greatly depends on the infrared absorption induced from the LSPR of aligned branches.

2. Experimental

2.1. Synthesis of gold nanostars

The colloidal gold nanostars in this study were synthesized according to the Triton X-100 participant seed-growth method developed by Pallavicini et al. [17] with slight modification. Initially, the Au seed solution was prepared by mixing the aqueous $HAuCl_4$ (5×10^{-4} M, 5 mL) with Triton X-100 (0.2 M, 5 mL) solution in a test tube of 15 mL. After gentle hand-shaking, a pale yellow colour of the solution is obtained. Secondly, the previously prepared ice-cold aqueous solution of $NaBH_4$ (0.01 M, 0.6 mL) was added. After gentle hand-shaking, a reddish-brown colour appeared. Then the seed solution was kept in ice for next use. The growth solution was prepared in a 10 mL test tube. Aqueous $AgNO_3$ (0.004 M, 125 μL), $HAuCl_4$ (0.001 M, 2.2 mL) are added in this order to aqueous Triton X-100 (0.2 M, 2.5 mL) solution. In order to obtain gold nanostars with different branch lengths, the $HAuCl_4$ amount in the growth solution has been increased to 2.3 mL, 2.4 mL, 2.5 mL and 2.6 mL in our experiment. Then, an aqueous solution of ascorbic acid (0.0788 M, 85 μL) was added. After gentle hand-shaking, the mixture was gradually changed from yellow to colourless transparent liquid. At last, the seed solution (5 μL) were added, and the mixture gradually changed from colourless to pink and then quickly became a turquoise liquid, finally appeared as dark green solution. The samples are allowed to equilibrate at 27 °C for 1 h.

2.2. Preparation of SERS samples

2.2.1. The surfactant replacement

In order to increase the particle concentration of gold nanostars, the surfactant replacement is processed at first. Aqueous CTAB (0.1 M, 1 mL) solution was mixed with gold nanostar colloid (4 mL). After intense hand-shaking for 1 min, keep the samples equilibrate at room temperature and the surfactant replacement will finish in 2 h. Then, the centrifugation (12,000 rpm, 15 min) was carried out and removed the supernate, finally the samples were resuspended into ultra-pure water (4.5 mL), respectively.

2.2.2. R6G-adsorbed gold nanostars with different $HAuCl_4$ volumes in the growth solution

Gold nanostar colloid (2 mL) with different branch lengths (the $HAuCl_4$ amounts in the growth solution for each sample were 2.2 mL, 2.3 mL, 2.4 mL, 2.5 mL, 2.6 mL, respectively) were taken for centrifugal (12,000 rpm, 25 °C, 15 min) firstly. Then, remove the supernatant carefully, and the remaining is 0.45 mL. Secondly, aqueous R6G solutions (1×10^{-6} M, 50 μL) were added in the remaining, so the final concentration of R6G is 1×10^{-7} M. At last, the samples were sonicated for 10 min (45 kHz, 25 °C) prior to the measurements.

2.2.3. R6G-adsorbed gold nanostars with different particle concentrations

Took five centrifuge tubes (10 mL) and then added 5.5 mL gold nanostar colloid (the $HAuCl_4$ amounts in the growth solution was 2.2 mL), respectively. Then, the centrifugation (12,000 rpm, 25 °C, 15 min) was carried out for two times. After getting rid of the supernate, the samples were resuspended into 0.8 mL, 1.0 mL, 1.2 mL, 1.4 mL and 1.6 mL ultra-pure water, respectively. Thus the gold nanostar colloids with different particle concentrations have been obtained. At last, different amount of aqueous R6G was added into each samples, and then the volume of each sample finally reached 1.0 mL, 1.25 mL, 1.5 mL, 1.75 mL and 2.0 mL, respectively. So that the R6G in each sample finally reached the same concentration of 2×10^{-7} M. The specific content has been reported in Table 1.

2.2.4. R6G-adsorbed gold nanostars with different plasmonic resonance wavelengths

Gold nanostar colloid (2 mL) with different branch lengths (the $HAuCl_4$ amounts in the growth solution for each sample were 2.2 mL, 2.3 mL, 2.4 mL, 2.5 mL, 2.6 mL, respectively) were injected into five test tubes, and then different amounts of ultra-pure water were added in each tube to make the third absorption peak reached the same intensity. After centrifugation (12,000 rpm, 25 °C, 15 min), the supernatants of each sample were removed, and the volume of the remaining is 0.27 mL. At last, aqueous R6G (1×10^{-6} M, 30 μL) were added into the remaining, so the final concentration of R6G in each sample is 1×10^{-7} M. In these samples, the R6G-adsorbed gold nanostars with 2.2 mL $HAuCl_4$ in the growth solution was also used in the experiment of comparison between gold nanostars and gold nanorods.

2.2.5. Equipment

The Raman spectra were collected in a back scattering geometry through a 50× (NA = 0.75) objective HORIBA JOBIN YVON Raman spectrometer (HORIBA, France). The wavelength of laser excitation was 785 nm, the integration time was 30 s, and the radius of the laser spot was 1.28 μm. The laser power focused on samples was