

Homogeneous surface-enhanced Raman scattering observed from self-assembled gold nanoparticle films deposited from the liquid–liquid interface

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Abstract

The self-assembled gold nanoparticle film deposited from the liquid–liquid interface has been fabricated, and homogeneous surface-enhanced Raman scattering (SERS) of R6G molecules on the film has been observed. The SERS enhancement factor of the film is estimated to be in the range 10^8 – 10^{10} . Occasionally, there are some sudden jumps in the Raman signal, where the signal is increased a few times. Such jumps are probably caused by single-molecule SERS in some extremely “hot” sites.

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1. Introduction

Surface-enhanced Raman scattering (SERS) [1] discovered nearly three decades ago, has recently gained more focuses since it was demonstrated to be possible even for single-molecule detection [2–4]. Further research attracted on increasing interest, not only in the fundamentals of physics and chemistry, but also in the large potentials of various applications in ultra-sensing technologies [5]. High SERS enhancement, however, also means an ultra-spatial inhomogeneity, since enormous SERS effects usually only happen in so-called “hot sites”, e.g., the very small volumes in the cavities between metallic nanoparticles [6–8]. The common problems of instability and irreproducibility of SERS are most likely caused by such inhomogeneity, where other causes could be chemical reasons and molecule hopping. The theoretical studies show that the local electromagnetic field near metallic nanoparticles is strongly confined to the “hot sites” by the surface plasmon

resonance, resulting in an inhomogeneous electromagnetic energy distribution [7]. This is the principal obstacle if one wants to get both a spatial SERS homogeneity and a high sensitivity.

However, such inhomogeneity cannot be exactly distinguished by an ordinary optical microscopy, since its scale is far below the diffraction limit of light. By increasing the density of “hot sites”, homogeneities in the scale of the diffraction limit of light can be achieved, when ordinary optical microscopes are used to collect the Raman signals. Since metallic nanoparticle arrays can supply a high density of nanocavities between neighboring nanoparticles, i.e. SERS “hot sites”, they should be the ideal substrates for the aim of both SERS homogeneity and high sensitivity. Recently, a theoretical investigation based on the RLC circuit analogy shows that the averaged SERS enhancement factor can reach to the order of 10^{11} , which is comparable even to the enhancement factor obtained in discrete nanoparticle systems [9]. If this enhancement factor is not overestimated, metallic nanoparticle arrays will be good substrates for SERS sensors.

Usually, there are two kinds of methods to make metallic nanoparticles arrays. One is to use lithographic (top-down)

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approaches [10–13], typically electron beam lithography, to design and grow nanoparticle patterns. The other is to use chemical (bottom-up) approaches to form self-assembling nanoparticle arrays, by controlling the attraction and repulsion potentials between nanoparticles [14,15]. The lithographic method seems more controllable, but due to the resolution of the electron beam, it is difficult to make the separation between nanoparticles less than 10 nm with current techniques. As is known, smaller separations between nanoparticles are crucial for large SERS enhancement [7,11,16]. This method, at least presently, drastically limits high SERS sensitivities. Although the chemical method is usually less controllable, the separation between nanoparticles can reach the sub-nanometer scale, thus high SERS sensitivities can be obtained. Recently, Wei et al. have successfully made SERS-active resorcinarene-encapsulated gold nanoparticle arrays at the air–water interface [14]. The enhancement factors ranged between 10^4 and 10^7 . SERS-active Langmuir–Blodgett films of Ag nanoparticles and Ag nanowires were reported as well [17,18].

In this study, we report on an SERS study of gold nanoparticle films, formed at the liquid–liquid interface. The investigation will be focused on both the high SERS enhancement and the spatial SERS homogeneity.

2. Experiment

Gold particles were synthesized according to Ref. [19]. This synthesis gave mono- and polycrystalline spherical particles with a rather narrow size distribution (16 ± 2 nm). Two milliliters of this solution was mixed with 2 ml of toluene containing 15 mg of mercapto undecanol. Upon agitation, the water phase turns colorless, while the interface turns violet/blue with a metallic gold shine. The film was deposited on a microscopy glass slide (Menzel-Gläser, artikel nr 011101), which had been made hydrophilic by chemical etching in a 3.75 M NaOH solution. The glass slide was thoroughly rinsed with distilled water before use. The film was deposited using a modified beaker with a hole in the bottom. A piece of parafilm was used to seal the hole. The beaker was filled with water, and the glass microscopy slide was placed on a support so that it lay with a slight angle below the water surface. The gold film, in the water/toluene solution, was poured on the water surface and allowed to spread at the interface. A small hole was made in the parafilm, allowing the water to drain slowly. As the water level lowered, the gold film reached the glass slide and deposited onto it (see Fig. 1). The glass slide was allowed to dry in air. The film obtained is resistant to washing by water and toluene. Chemicals were obtained from commercial sources (ABCR, Aldrich) and used without further purification.

Five microliters of 10^{-6} M rhodamine-6G (R6G) was taken by a pipette and put on the gold nanoparticle film, then dried with a weak nitrogen gas flow. A ~ 50 mm² slightly

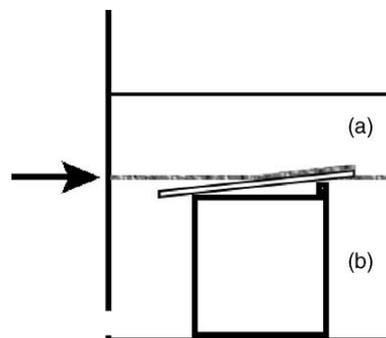


Fig. 1. A scheme of the deposition process (not to scale). A beaker with a hole in the bottom is used. The hole is sealed with parafilm. A microscopy glass slide is put on a support, tilted at a shallow angle. During deposition, the water phase (b) drips slowly through a pinhole made in the parafilm. The gold nanoparticle film (arrow) is located at the water(b)/toluene(a) interface. As the water level is lowered, the nanoparticle film is deposited onto the glass slide.

reddish R6G mark was left on the gold nanoparticle film after drying. The R6G marked region was then investigated by a fiber coupled confocal micro-Raman-setup, consisting of an Olympus BX41 microscope equipped with an XY scanning stage (minimum scanning step 100 nm) and Z motorization (1 μ m/step), and a fiber coupled rack mounted spectrometer (InduRAM) equipped with a TE air cooled 1024×256 CCD detector. Raman spectra were excited by a He–Ne laser at the wavelength of 632.8 nm. The incident intensity is about 5 μ W on the sample. The Raman mapping was obtained by scanning the R6G marked region, where with each scanning point consisted of one spectrum. With a $100\times$ objective (Nikon, N.A. 0.95) and the confocal arrangement, each investigated point has an area of ~ 1 μ m². The extinction spectrum of the gold nanoparticle film is recorded by a fiber-optic spectrometer (Avantes, 2048 pixel CCD detector) with a tungsten–halogen light source. For the R6G sample, 10^{-4} M (14.4 mg R6G (Sigma) dissolved in 300 ml (MilliQ) water) was first prepared in a plastic bottle, and then 10 μ l of this solution was diluted in 1 ml water in a plastic cuvette to obtain a concentration of 10^{-6} M. Total number of rhodamine-6G molecules (5 μ l of 10^{-6} M) put on the gold nanoparticle film is about $(5 \times 10^{-6}) \times (1 \times 10^{-6}) \times (6 \times 10^{23}) = 3 \times 10^{12}$. These molecules were spread on the area with 50×10^6 μ m². Each spot with 1 μ m² has about $(3 \times 10^{12}) / (50 \times 10^6) = 60,000$ R6G molecules.

3. Results and discussions

Fig. 2a shows a typical TEM image of the gold nanoparticle film formed at the liquid–liquid interface. The film is mainly composed of single monolayer of gold nanoparticles. In the islands of dense nanoparticles, slight overlaps of nanoparticles are observed. Fig. 2b shows the extinction spectrum of the gold nanoparticles film and the

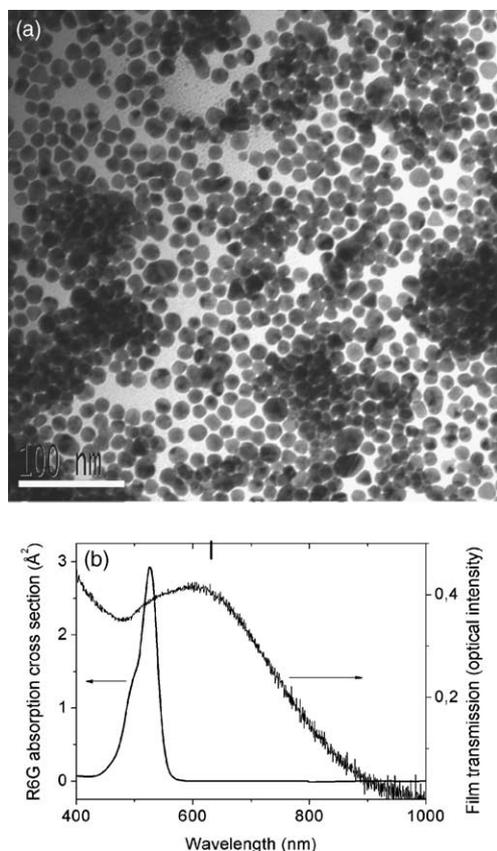


Fig. 2. (a) TEM image of a gold nanoparticle film, formed at the liquid–liquid interface; (b) the transmission spectrum of the film (to the right) and the absorption cross-section of the R6G molecule (to the left). The scale bar in (a) is 100 nm, and the laser wavelength in (b) is indicated by a short black line.

absorption cross-section of the R6G molecule. From the extinction spectrum, the excitation wavelength used here is well matched to the surface plasmon resonance peak of the film. Obviously, it is far away from the molecular resonance of R6G. Hence, the SERS enhancement is caused by the film, no resonant Raman effects.

Fig. 3a shows a typical Raman map of a R6G/film with a size of $20\ \mu\text{m} \times 20\ \mu\text{m}$. The scanning step is $1\ \mu\text{m}$. Each scanning point contains one Raman spectrum (see, e.g. Fig. 3c). The corresponding data for each point in Fig. 3a is obtained by averaging the Raman intensity in the window of $1100\text{--}1690\ \text{cm}^{-1}$, which includes rich Raman information of the R6G molecule. From the histogram in Fig. 3b, the Raman map of Fig. 3a has a very narrow intensity distribution, centered at the value of 65 counts. The minimum value of about 50 counts is very close to the center value. The majority of the values lie between 50 and 80 counts. The small spatial variation of SERS could be caused by the spatial inhomogeneity of the gold nanoparticle film in the scale of about 100 nm, although the inhomogeneity may have been drastically averaged out under a larger scale of the diffraction limit of the light.

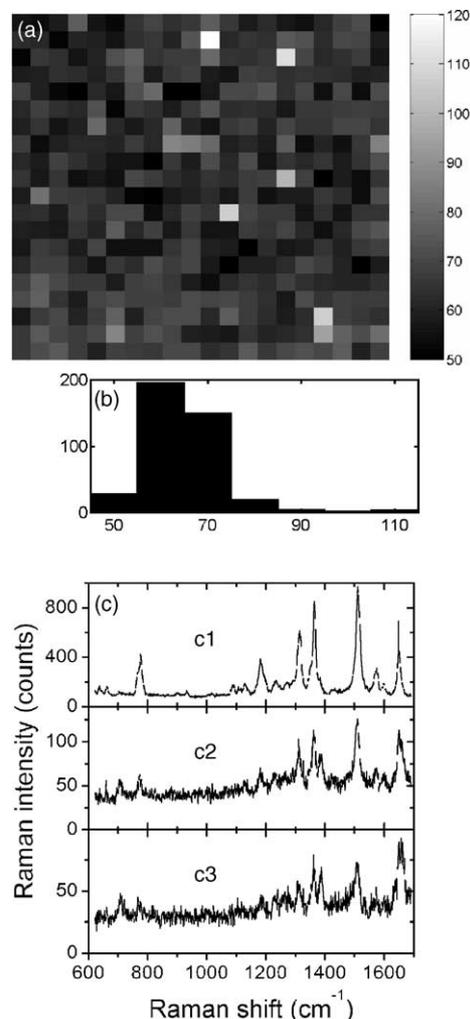


Fig. 3. (a) Raman map of R6G molecules on a gold nanoparticle film ($20\ \mu\text{m} \times 20\ \mu\text{m}$, $1\ \mu\text{m}$ per scanning step) with the average intensities integrated from 1100 to $1690\ \text{cm}^{-1}$ and the integration time 30 s; (b) the histogram of all intensities in (a); (c) Raman spectra of (c1) the brightest point in the second row of (a), (c2) the typical mean-value point and (c3) the darkest point. The incident wavelength was $632.8\ \text{nm}$ with the intensity about $5\ \mu\text{W}$.

Occasionally, the huge enhancement was observed, as for the brightest point with a value of 220 counts in the second row of Fig. 3a. The ratio between the maximum and the minimum is a little bit more than three times. The reason for this huge enhancement is probably from an extremely “hot” site, which could be caused by both multipole couplings of neighboring particles and in-phase dipole couplings from other array particles far away. The dipole couplings are analog to those in the fractal structures of nanoparticle aggregates, as predicted by the theory [20]. In the corresponding Raman spectrum in Fig. 3c1, the largest peak intensity, at $1509\ \text{cm}^{-1}$, is over ~ 8 times above the background, while only ~ 3 times in the typical Raman spectrum (with an averaged Raman intensity at ~ 65 counts as in Fig. 3b) shown in Fig. 3c2. This evidence may indicate some huge single-molecule SERS contribution(s) stemmed

from the extremely “hot” site(s). Except those extremely “hot” sites, the gold nanoparticle film is in general homogeneous for SERS. It is pertinent to compare the homogeneity with discrete nanoparticle systems, where the SERS signals can vary a few orders of magnitude, depending on the configurations and incident polarizations [21–23].

The SERS sensitivity of the nanoparticle gold film is also quite high. With our experimental conditions, about 60,000 R6G molecules contribute to each Raman spectrum. The Raman intensity in a typical Raman spectrum, e.g. in Fig. 3c2, is comparable to those in the single-molecule SERS studies, with a proper normalization of the incident intensity [3,8,24]. It should be noted that our experiment is non-resonant for R6G, while other single R6G molecule SERS studies were for the resonant case. The resonant Raman scattering may contribute more than 1000 times to the enhancement factor. Hence, the enhancement factor of the gold nanoparticle film is about two orders smaller than other single-molecule SERS studies. The claim of 10^{14} – 10^{15} times enhancement for single-molecule SERS [2,3] by comparing the Raman cross-section of a dye molecule to a different small colorless molecule, e.g. a methanol molecule is overestimated, since the factors of the resonance and the larger Raman cross-section of a dye molecule, as compared to a small molecule are ignored. The absolute surface enhancement required for single-molecule SERS in a resonant case should be much smaller, probably in the range 10^{10} – 10^{12} . Hence, the SERS enhancement factor of the nanoparticle film in the excitation wavelength used here may be estimated to be in the range 10^8 – 10^{10} , although the exact value could not be obtained here. This estimation roughly agrees with the recent theoretical prediction [9].

Recently, Wei et al. [14] have reported an SERS enhancement ranging from 10^4 to 10^7 on the planar gold nanoparticle arrays, which are a few orders smaller than our result here. Due to the different procedures to make the film, the exact comparison may be difficult. But, there are two notable reasons which may cause this big difference. The first reason is the different roughness of the films. In our film, there are dense secondary nanostructures (gold nanoparticle islands), while not the case for Wei et al.’s film. These secondary nanostructures can function as a dense large gold particle layer which will give additional surface plasmon resonances to favorite the SERS enhancement. Recent experiment shows the large gold particle layer can give 10–20 times extra SERS enhancement factor [25]. The second reason is the different experimental conditions. Wei et al. used the objectives with N.A. ≤ 0.75 , while we used the objective with N.A. = 0.95. According to the Wei et al.’s study, the increase N.A. from 0.4 to 0.75 can increase the SERS enhancement factor about one order more due to the angle-dependent SERS enhancement on rough metal surfaces with a maximum between 55° and 60° relative to the surface normal [26]. This maximum can be collected by an objective with N.A. = 0.95 (72°), while not with N.A. ≤ 0.75 ($\leq 49^\circ$). Hence, more SERS enhancement

can be expected with the increase of the N.A. from 0.75 to 0.95.

4. Summary

As a summary, we made self-assembled gold nanoparticle films deposited from the liquid–liquid interface, and the homogeneous SERS effect has been observed from the film with R6G molecules. The SERS enhancement factor of the film is estimated to be in the range 10^8 – 10^{10} . The easy fabrication, high SERS homogeneity and the huge SERS enhancement factor means that the gold nanoparticle film introduced in this study has a large potential for SERS sensors.

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