

Effect of Au nanorod assemblies on surface-enhanced Raman spectroscopy



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ABSTRACT

Monolayer and multilayer arrangements (consisting of disorder, parallel alignment and perpendicular superlattice) of hydrophobic gold nanorods have been prepared on silicon substrates via the evaporation-based self-assembly and the heat treatment methods, and the substrates were provided for the surface-enhanced Raman spectroscopic (SERS) examination. The perpendicular superlattice assembly of gold nanorods maximally enhanced intensities of Raman bands in comparison with parallel and disorder assemblies. Moreover, multilayer films of gold nanorods were more effective on SERS than monolayer films. The motive force of the Raman enhancement should be the adequate resonance coupling of localized surface plasmon waves at the reasonable density of spaces between neighboring rods. Moreover, the adsorption ability of analytes on the hydrophobic peripheral octadecyltrimethoxysilane groups will also improve the detection limit and develop the detection scope from aqueous to organic solutions.

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1. Introduction

Nanosized noble metal particles have attracted significant attention, because they exhibit remarkable optical nonlinearity and surface-enhanced spectroscopic effect due to the local field enhancement near the surface plasmon wave. Gold nanoparticles particularly provide a prospective type of surface-enhanced spectroscopic substrates [1]. Since gold nanoparticles are chemically stable and easily modified their surfaces with compounds as represented by thiols, they possess potential applications to the detection of chemicals [2]. Moreover, theoretical calculations have indicated that gold nanorods (NRs) are expected to be more greatly surface-enhancement-active than spherical gold nanoparticles because of a strong longitudinal plasmon band at near-infrared wavelength [3–5]. More importantly, because the Plasmon electric fields are large on assembled or aggregated particles, the extremely large surface-enhancement can occur on these architectures [4,6,7].

Various efforts have been made to design suitable techniques for fabricating arranged NR films such as adsorption [8], electronic deposition [9], and layer-by-layer assembly approach via electrostatic interaction [10] as well as adsorption methods at an air/liquid or liquid/liquid interface for disordered multilayer gold NR films [11,12]. However, the aggregated NR films mentioned above were mainly prepared from hydrophilic NRs, and few simple methods have been reported so far for preparing horizontally well-ordered gold NR films as surface-enhanced substrates [12], but there was no report for perpendicular arrangement by such NRs. Alternatively, hydrophobic NRs, which were prepared by surface-modification with hydrophobic thiols, have produced the perpendicularly arranged film and the ordered superlattice structure [13–15], although nobody has studied the corresponding surface-enhanced spectroscopic effect of NR superlattices so far, as our knowledge.

In this work, various films with different arrangements of hydrophobic gold NRs including perpendicular superlattices on silicon substrates are simply prepared, based on the evaporation-induced self-assembling [15], and then the surface-enhanced Raman scattering phenomenon of dye molecule, rhodamine 6G (R6G), on perpendicular superlattices is studied in comparison with architectures of disorder and parallel arrangements. The most effective architecture of gold NPs for surface-enhanced

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Raman spectroscopy (SERS) is revealed and the principle is discussed.

2. Experimental

Hydrophobic gold NRs with an aspect ratio of *ca.* 3.5 were prepared by treating with mercaptopropyltrimethoxysilane (MTS) and subsequently octadecyltrimethoxysilane (ODS), according to the previously reported methods [13–15]. A longitudinal plasmon resonance band of these NRs were around 800 nm. The gold NR films on silicon substrates were prepared via the evaporation-induced self-assembling method [15]. Through controlling of NR concentration, the suprastructures of the gold NR films with disorder, parallel or perpendicular orientation were fabricated. All films of gold NRs were annealed at 150 °C for 30 min, that is, at the condition that the suprastructures of NRs were stable. Moreover, the transmission electron microscopic (TEM, Philips, TECNAI SPIRIT) images as well as X-ray diffraction results (the corresponding data are not shown here) elucidated no structural changes even after annealing at *ca.* 170 °C.

The surface morphology of the films and the ordering of NRs were examined by high-resolution scanning electron microscope (SEM) (Hitachi, S-5000) and TEM (Philips, TECNAI F20) prior to the SERS measurements. R6G (Wako Co. Ltd., Tokyo) was used without further purification. An ethanol solution of R6G (5 mm³, *ca.* 1 nmol/cm³) was dropped on the gold NR films and allowed to spread uniformly (the diameter is approximately 5 mm), followed by drying in air. The quantity of R6G molecules in the observed area could be supposedly the order of 0.1 pmol, assuming that the area of the laser spot on the specimen is *ca.* 3 mm². The measurements of the Raman spectra were carried out by a Raman microspectrophotometry at 532.3 nm and 634.8 nm excitation wavelengths, which equipped with a liquid nitrogen-cooled CCD camera and an Olympus BH-2 microscope in the back scattering geometry using a 50× microscope objective to focus the laser beam on the specimen. The spectral resolution of the whole system was 8 cm⁻¹. The observed Raman spectra were averaged repetitious measurements over large (mm size) areas except in a comparison at different laser excitation wavelengths where spectra were measured *in situ* at the same position on the same film.

3. Results and discussion

The evaporation-induced self-assembling technique was adopted for the preparation of gold NR films [15]: along with the evaporation of solvent, the combination of top-down surface patterning and bottom-up material assembling induced the deposition of gold NRs on silicon substrate. Via this procedure, the self-assembled films of NRs can be enlarged up to several square millimeters, which is very important as a preparation of prospective SERS substrates.

The surface morphology of the films was confirmed by SEM measurements, as shown in photographs (A–E) in Fig. 1, where A and C were taken on monolayer and B, D, and E were on multilayer. SEMs of A and B displayed the disorder texture, textures of C and D were the parallel alignment, and a photograph of E revealed the perpendicular arrangement of close-packed NRs.

TEM observation was carried out to elucidate the “hot site” feature of the perpendicular two-dimensional (2D) nanostructure. A spacing (*ca.* 3 or 4 nm) between two adjacent NRs (shown in Fig. 1F) was supposed to be the “hot site” [16]. Theoretically, the size of “hot site” affects the intensity of SERS bands. The well-ordered and close-packed 2D nanostructure may give us the regular and uniform distribution of the “hot site” [17]. In this work, the horizontally and vertically aligned gold NR films were annealed

at 150 °C for 30 min. This treatment will allow the rearrangement between adjacent gold NRs as well as between NRs and silicon substrate [18].

The SERS spectra were measured on the parallel multilayer film with different laser excitation wavelengths of 532.3 nm and 634.8 nm, and the results are plotted in Fig. 2. Raman bands of R6G could be observed correspondingly at the same Raman shifts in both spectra: Intensities of main six bands at 1520–750 cm⁻¹, which are intrinsic for R6G and assigned CC stretching, CC stretching + CN stretching, and in-plane and out-plane CH bending vibration modes [19], were scarcely dependent on excitation wavelength. However, intensities of CC stretching vibration bands at 1652 and 1572 cm⁻¹ were stronger at 532.3 nm excitation than at 634.8 nm excitation. The reason is that the 532.3 nm excitation wavelength is close to the absorption band of R6G (at 524 nm) and thus induces the Raman resonance effect on an electronic transition mode (with a direction of the long molecular axis) of R6G excited at 524 nm [13]. In addition, due to the same resonance phenomenon, Raman bands as indicated by arrows in Fig. 2 were also intensified more at 532.3 nm excitation wavelength. Bands were at 1605 and 1543 cm⁻¹ (CC stretching vibration mode) and at 1289 cm⁻¹ (C–O–C stretching vibration mode). These results are consistent with the previous report [19].

SERS spectra at 532.3 nm excitation were compared among three multilayer structures in Fig. 3. For disorderly, horizontally and vertically arranged multilayers, band profiles both in Raman shift and relative intensity do not change but absolute intensities of all Raman bands varied. The band intensities were strongest on the perpendicularly aggregated NR film, stronger on the parallel NR film and weak on the disorder NR film. The intensity ratio was roughly 4:2.5:1. Moreover, the resonance bands at 1652, 1605, 1572, 1543 and 1289 cm⁻¹ were also intensified along with surface-enhanced bands for three NR films, indicating the similar orientation of adsorbed R6G molecules on the films.

The intensity difference between NR arrangements was apparent even on monolayer NR films. On Raman spectra of monolayers in Fig. 4, although band profiles were again similar to each other, almost of Raman bands for the parallel arrangement were stronger than those for the disorder firm with an intensity ratio of 4:1. In addition, it can be noticed by comparison of Fig. 4 with Fig. 3 that the surface-enhancement effect of multilayer films was superior to that of monolayers: the effect on the former was 2.5 times for parallel alignment and 4 times for disorder arrangement as large as on the latter.

It should be noted that a Raman band at 530 cm⁻¹ was observed on monolayer films. It, especially on the disorder film, was evidently strong as against other bands. Since no obvious corresponding Raman band was clearly distinguished from Figs. 2 and 3, this band can be attributed to a Raman band of single crystal silicon in substrate but not of R6G. For these assembly architectures, a Raman band of silicon was enhanced due to the lower surface coverage by NRs in monolayer alignment, as apparent from Fig. 1 (compare A and B or C and D).

From the above estimation of Raman enhancement factor, the reasonable ordering was perpendicular multilayer > parallel multilayer > disorder multilayer = parallel monolayer > disorder monolayer with a scale of 16 > 10 > 4 = 4 > 1. This tendency is in agreement with a previous qualitative report, where gold NRs with perpendicular arrangement are indicated more powerful as SERS active substrates [4].

It is a general knowledge that the enhancement factor of SERS depends on the condition of metal surface (metal element, shape, domain size, roughness and so on). These factors are strongly related to the existence of “hot spots” having intense electromagnetic fields, from which highly efficient Raman scattering can be obtained. Moreover, in SERS enhancement, the electromagnetic

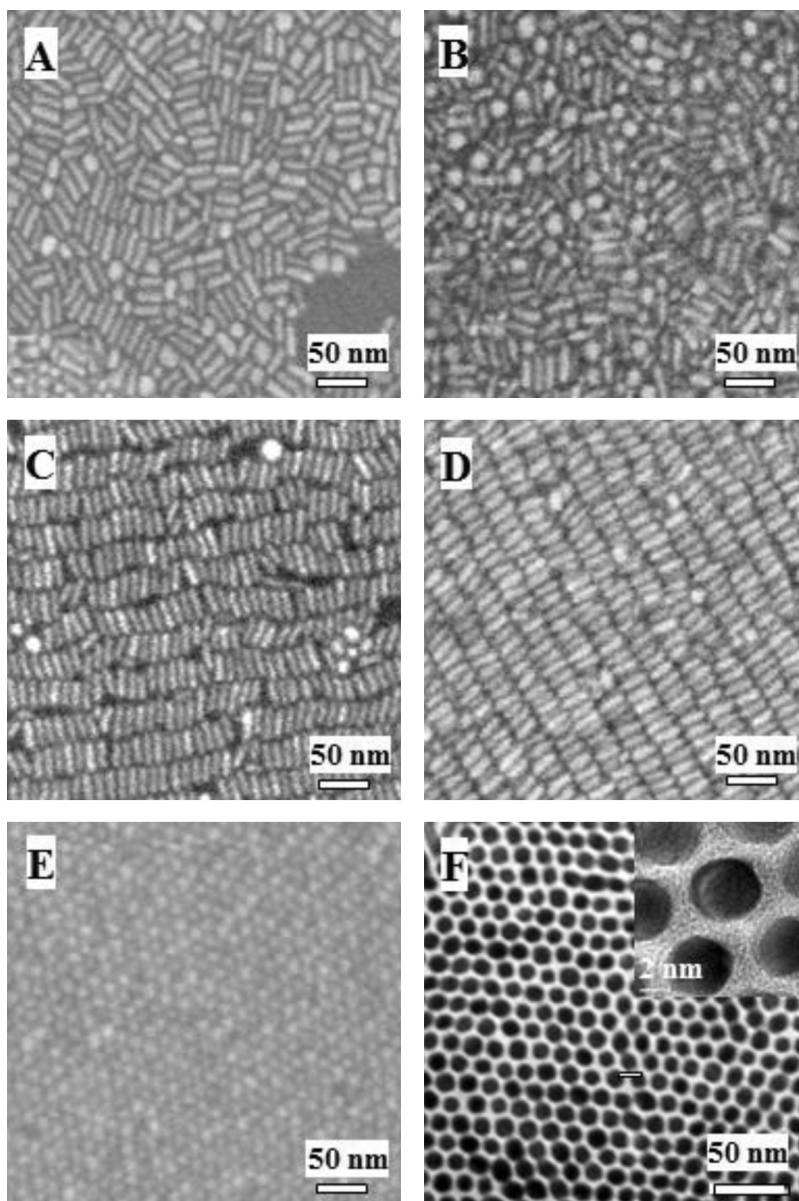


Fig. 1. (A)–(E) SEM images of gold NRs in different arrangements. (A) disorder monolayer; (B) disorder multilayer; (C) parallel monolayer; (D) parallel multilayer; (E) perpendicular multilayer. (F) TEM images of gold NRs in perpendicular multilayer. The insert is a high-resolution image.

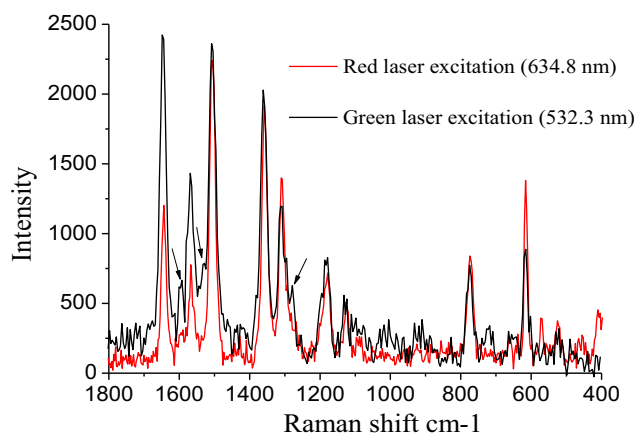


Fig. 2. SERS spectra of R6G adsorbed on parallel multilayer of gold NRs. Laser excitation wavelength was at 532.3 nm (black) and 634.8 nm (red). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

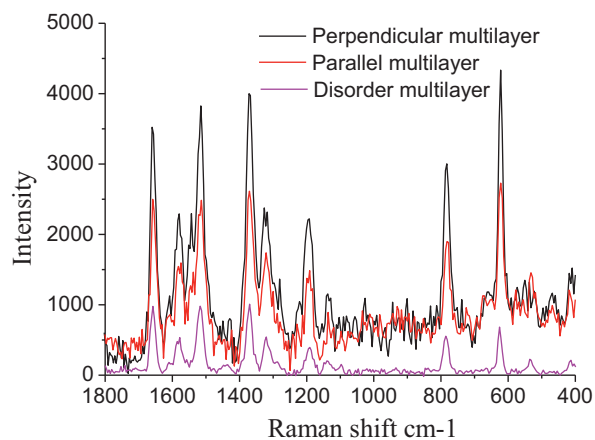


Fig. 3. SERS spectra of R6G adsorbed on disorder, parallel and perpendicular multilayers of gold NRs. Laser excitation wavelength was at 532.3 nm.

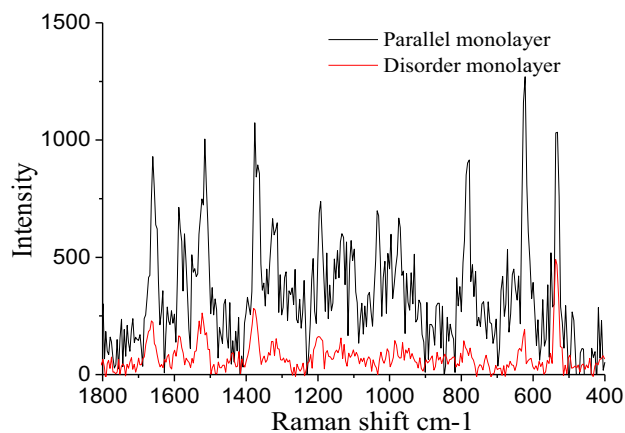


Fig. 4. SERS spectra of R6G adsorbed on disorder and parallel and monolayers of gold NRs. Laser excitation wavelength was at 532.3 nm.

contribution is always dominant over the chemical contribution (due to the molecule) [16].

Based on the results described above, the possible reasons for strongest Raman enhancement from the perpendicular multilayer assembly can be discussed as below. First, the vertical arrangement of gold NRs in a well-ordered suprastructure would potentially allow each rod in each 2D layer array to be involved individually at the integration at <5 nm separation. More efficient separation is achievable at the close-packed NR/NR interface rather than at the NR/NR interface in random or horizontal NR assembly [20]. With the adequate density of spaces between neighboring rods in the close-packing structure, where hot spots or enhancement sites may reside, the enhancement factor can be even enlarged. Then, the resonance coupling of localized surface plasmon waves occurs in the close-packed arrangement of the NR arrays and leads to the further enhanced electric field contributing to the SERS enhancement.

As seen in Fig. 1, since parallel assemblies are 2D layers consisting of horizontally arranged NRs, domains with highly close-packed structure like perpendicular assembly are not promised and then the resonance coupling of localized surface plasmon waves should be weaker. The disorder assemblies take less ordering and, therefore, exert the less enhancement effect. Moreover, NR packing of both disorder and parallel monolayers is inferior to the corresponding multilayers. Then the ordering of Raman enhancement factor determined in the present work (see above description) is reasonable.

The NR density in the aggregates greatly relates to the suprastructure of NR assemblies. The density should increase in the order of disorder assembly $<$ parallel assembly $<$ perpendicular assembly and be higher in multilayer than in monolayer, as estimated from TEM images in Fig. 1. As R6G molecules adsorb on the surface of NRs, the density, namely the total surface area, of NRs in the aggregates directly relates to the density (amount) of adsorbed R6G in the target area of Raman measurement and to the Raman intensity in consequence. Therefore, the ordering of Raman enhancement factor observed in the present work can be interpreted even from side view of the density of NRs in the films.

In addition, it has been also experimentally proved that the enhancement on a surface-enhanced resonance Raman spectroscopy from a silver NR depends on both the directions of laser polarization and particle orientation, and it is largest when the direction of the laser polarization coincides with the long axis of the NR [21]. Therefore, the utilization of the polarized laser will also be a significant vehicle to enhance the Raman spectra.

Furthermore, the advantage of the present substrates is that the affinity of analyte compounds to the ODS-modified SERS-active surface can be driven by the hydrophobic interaction, since the surface of NRs is coated by hydrophobic alkylchains [13,22]. Thus the present SERS-active system can be used in both aqueous and non-aqueous media. However, for the SERS study, the only expectation is the discriminative detection in Raman bands of the analytes as they adsorb, and therefore the appearance of only Raman bands attributable to analytes is desirable. In fact, any unexpected Raman bands were not monitored, at least on NR multilayer films, even as the coexistence of protectants, MTS and ODS, on NRs.

4. Conclusions

As SERS-active systems, self-assembled aggregates of gold NRs have been prepared on silicon substrates via evaporation-based self-assembling deposition of NRs, and the stable structure of the systems was obtained through the successive heat-treatment procedure. It was rather easy to prepare stable and ordered multilayer films, consisting of hydrophobic gold NRs, especially films with perpendicular arrangement.

These NR assemblies displayed a potential as highly sensitive substrates for SERS-based investigations. The Raman enhancement effect had greatly relations with the suprastructure of assemblies, and the SERS bands increased, being dependent on the packed extent of NR arrangement at the order of disorder monolayer $<$ disorder multilayer = parallel monolayer $<$ parallel multilayer $<$ perpendicular multilayer. The motive force of the Raman enhancement can be assumed from the suprastructure prepared. That is, the well-ordered, especially close-packed, arrangement of NRs is preferable because of the adequate resonance coupling of localized surface plasmon waves due to the reasonable density of spaces between neighboring rods.

In addition, ODS molecules chemically bound on gold nanorods via a functional siloxane group can serve the dual purpose of particle stabilization and surface modification. Most importantly, by promoting the adsorption of guest molecules (analytes) from solutions (e.g. heterocyclic compounds in wastewater) through the hydrophobic interaction with peripheral ODS groups, the ODS shell surrounding NRs will improve the detection limit and develop the detection scope from organic solutions to aqueous solutions.

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