

Surface-enhanced Raman Scattering Effect of Ordered Gold Nanoparticle Array for Rhodamine B with Different Morphologies^{*}

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Abstract In this study, well-ordered gold nanoparticle array on silicon substrate was adopted as an active surface-enhanced Raman scattering substrate for detecting rhodamine B (RB), and the influence of RB morphologies on surface-enhanced Raman scattering (SERS) properties was discussed. The Au nanoparticle array was prepared by using patterned P4VP nanodomains of poly(styrene-*b*-4-vinylpyridine) (PS-*b*-P4VP) diblock copolymer thin films as nanoreactors which is a simple and economical approach. The results show that Raman spectra of RB on the Au nanoparticle array have much stronger intensity than those on the bare silicon substrate by detecting same RB solution. It indicates that the prepared Au nanoparticle array on silicon substrate has a significant Raman enhancement for RB. Interestingly, the Raman intensity of RB from its ethanol solution is much stronger than that from its aqueous solution due to the special morphologies of RB formed in their ethanol solutions. This work provides an effective approach to prepare highly sensitive and stable surface-enhanced Raman scattering substrate.

Keywords: Nanoparticle array; Rhodamine B; Raman spectroscopy; Nanowire; Nanograin.

INTRODUCTION

Surface-enhanced Raman scattering (SERS) has received increasing attention in recent years as a powerful and extremely sensitive analytical technique with applications in biochemistry^[1, 2], chemical production^[3] and environmental monitoring^[4]. Typically, SERS is a Raman spectroscopic technique aimed at enhancing Raman signals due to the interaction between molecules and metal surfaces or nanoparticles. Thus, it is affected by the interparticle gap, the size and shape of nanoparticles, and the excitation frequency^[5, 6]. Chen *et al.*^[7] reported Au@Ag core-shell nanoparticle dimers and trimers, and measured the ensemble-averaged SERS enhancement factors at hotspots of the isolated colloidal nanoclusters. They found that the ensemble-averaged enhancement factors at the hotspots of the dimers and trimers were about 100 times higher than the monomers. Yin *et al.*^[8] fabricated the SERS dye encoded gold nanoparticles *via* ligand exchange and surface-initiated atom transfer radical polymerization, and they could sensitively and selectively detect cadmium ion (Cd²⁺) by taking advantage of the interparticle plasmonic coupling generated in the process of Cd²⁺-selective nanoparticle self-aggregation.

Benefiting from the advance in nanofabrication techniques, many new kinds of substrates have been reported for SERS, such as nanowire arrays^[9], nanowire/nanoparticle composite arrays^[10, 11], nanodimple array^[12], Si/Au nanopillar arrays^[13] and particle-in-bowl arrays^[14]. Many exploited SERS substrates are the noble

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metal nanoparticles and their assemblies prepared from the wet chemical methods. Unfortunately, they have a poor detection reproducibility caused by the stochastic aggregation of nanoparticles^[15, 16]. More recently, template-assisted methods, such as electron-beam lithography^[17], nanosphere lithography^[18, 19] and porous anodic aluminum oxide (AAO) template^[20, 21], have been utilized in fabricating uniform periodic arrays of metallic nanostructures for sensitive SERS detection. However, simple, large-area and economical fabrication of sensitive and stable SERS substrate continues to be a major challenge. Furthermore, the relationship between the morphologies of detective molecules and SERS properties has not been reported.

In this paper, we report a simple and economical approach for fabricating large-area and well-ordered Au nanoparticle arrays on silicon substrates for detecting rhodamine B (RB) by SERS. The well-ordered Au nanoparticle array was prepared by using PS-*b*-P4VP film with patterned nanodomains as a template. The SERS properties and morphology of RB adsorbed on Au nanoparticle array with solutions of different concentrations and solvents were systematically investigated.

EXPERIMENTAL

Materials

PS-*b*-P4VP diblock copolymer (M_n : 300 kg/mol for PS and 175 kg/mol for P4VP, $M_w/M_n = 1.10$) was purchased from Polymer Source Inc. Hydrogen tetrachloroaurate(III) trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, > 99.9%) was purchased from Alfa Aesar. Rhodamine B (analytical grade) was purchased from Aladdin. Chloroform was purchased from Guangzhou Chemical Reagent Factory. Methanol (analytical grade) was purchased from Tianjin Baishi Chemical Reagent Co. Ltd. Toluene (> 99.9%), tetrahydrofuran (analytical grade), *N,N*-dimethylformamide (DMF, analytical grade) and trisodium citrate dehydrate ($\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$, > 99.9%) were purchased from Tianjin Damao Chemical Reagent Factory.

Synthesis of Ordered Au Nanoparticle Array

PS-*b*-P4VP thin film was fabricated with 0.2 wt% PS-*b*-P4VP chloroform solution by a spin-coating and solvent annealing method. Then, the PS-*b*-P4VP film was immersed in 0.05 mol/L HAuCl_4 solution with methanol as solvent for 30 min to fully load HAuCl_4 solution in the P4VP nanodomains. Then the sample was rinsed with de-ionized water. After that, Au nanoparticle array on silicon substrate was obtained by treating Au-loaded film with air plasma (Schwarze) for 20 min and calcining at 600 °C for 10 h.

Detection of RB Solution with Different Solvents

The Au nanoparticle array on silicon substrate was immersed in 10^{-4} mol/L RB aqueous and ethanol solutions, respectively. The samples were kept for 6 h to realize molecule adsorption and then taken out to dry in room temperature. For comparing, RB on bare silicon substrates was also prepared with 10^{-4} mol/L RB solution by the same method. Besides, the Au nanoparticle arrays on silicon substrates were also immersed in 10^{-6} mol/L and 10^{-8} mol/L RB aqueous and ethanol solutions for 6 h, respectively.

Characterization

The atomic force microscopy (AFM) images were obtained using a Bruker MultiMode 8 AFM. The morphologies of the samples were analyzed by scanning electron microscopy (SEM) images using a Hitachi S4800 SEM. Raman measurements were performed on a HORIBA Jobin Yvon Raman system (LabRAM Aramis) with 633 nm HeNe laser (the maximum power of 10 mW) as excitation source, and the diameter of the laser spot is about 1.03 μm . The integration time was 15 s.

RESULTS AND DISCUSSION

PS-*b*-P4VP diblock copolymer was dissolved in chloroform which is a good solvent for both PS and P4VP blocks. When the 0.2 wt% PS-*b*-P4VP chloroform solution was spin-coated on silicon substrate at 3000 r/min and solvent-annealed at 30 °C under mixed vapors of toluene and THF (20:80, *V/V*) for 24 h, the polymer molecules self-assembled into ordered P4VP nanodomains surrounded by a PS matrix^[22, 23]. Figures 1(a) and

1(b) show the AFM images of PS-*b*-P4VP film with well-ordered cylindrical P4VP nanodomains and PS matrix. The average center-to-center distance of the P4VP nanodomains was (90 ± 3) nm with an average diameter of (45 ± 2) nm. When the thin film was immersed in HAuCl_4 -methanol solution, the P4VP nanodomains were swollen but not the PS matrix because methanol was a good solvent for P4VP blocks but non-solvent for PS blocks. As a result, HAuCl_4 was only absorbed into P4VP nanodomains, and selectively coordinated to the pyridine units of the P4VP nanodomains. Then well-ordered Au nanoparticle array was obtained on silicon substrate by combining air plasma and calcination methods. The resultant morphologies of the Au-loaded film and Au nanoparticle array are shown in Figs. 1(c) and 1(d), respectively. Clearly, Au nanoparticles were formed in the P4VP nanodomains (Fig. 1c), and well-ordered Au nanoparticle array with the average center-to-center distance (91 ± 3) nm and particle size (30 ± 2) nm was obtained (Fig. 1d). The pattern of the Au nanoparticles is essentially identical to the template.

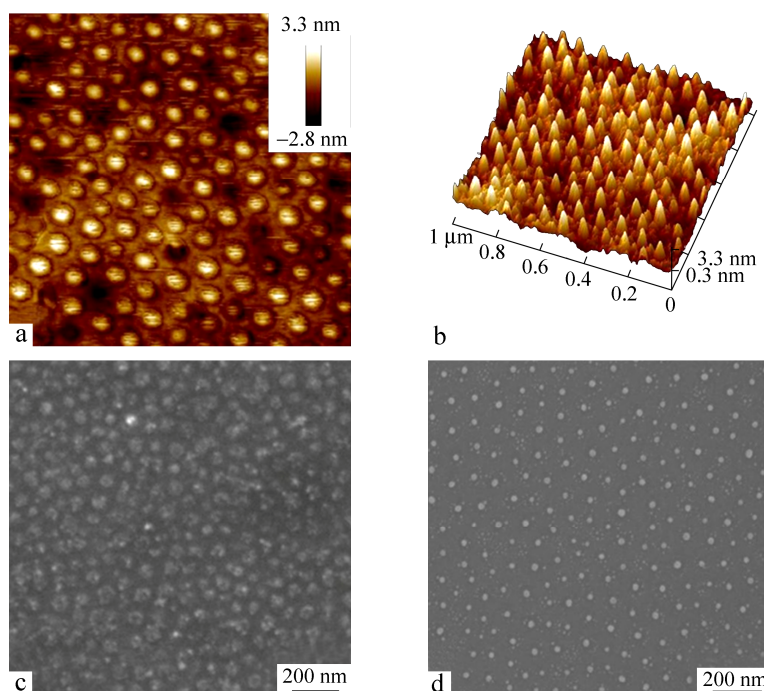


Fig. 1 AFM (a) height and (b) 3D images of the PS-*b*-P4VP film on silicon substrate (image size: $1 \mu\text{m} \times 1 \mu\text{m}$); SEM images of (c) Au-loaded PS-*b*-P4VP film and (d) Au nanoparticle array prepared by using patterned P4VP nanodomains as nanoreactors

In order to demonstrate the SERS performance of the well-ordered Au nanoparticle array on silicon substrate, RB was used as the target molecule. RB solutions with water and ethanol as solvents were both discussed systematically. Figure 2 shows the SEM images of RB on Au nanoparticle array with different concentrations and solvents. It showed that there was no special morphology for RB from its aqueous solution as shown in Figs. 2(a), 2(c) and 2(e). Interestingly, when the active substrate was immersed in 10^{-4} mol/L RB ethanol solution for 6 h, RB nanowires generated with the average diameter ~ 100 nm and length $\sim 3 \mu\text{m}$ as shown in Fig. 2(b). When it was used to detect 10^{-6} mol/L RB ethanol solution, RB nanograsses with the average width ~ 600 nm and length $\sim 7 \mu\text{m}$ were observed as shown in Fig. 2(d). Furthermore, when the active substrate was used to detect 10^{-8} mol/L RB ethanol solution, a wrinkle RB film was formed on Au nanoparticle array as shown in Fig. 2(f). It is speculated that the RB molecules in ethanol solution are easier to be adsorbed on the Au nanoparticle array on silicon substrate than those in aqueous solution, and they are easier self-assemble to form special morphologies during the immersing and drying processes when ethanol solutions are used.

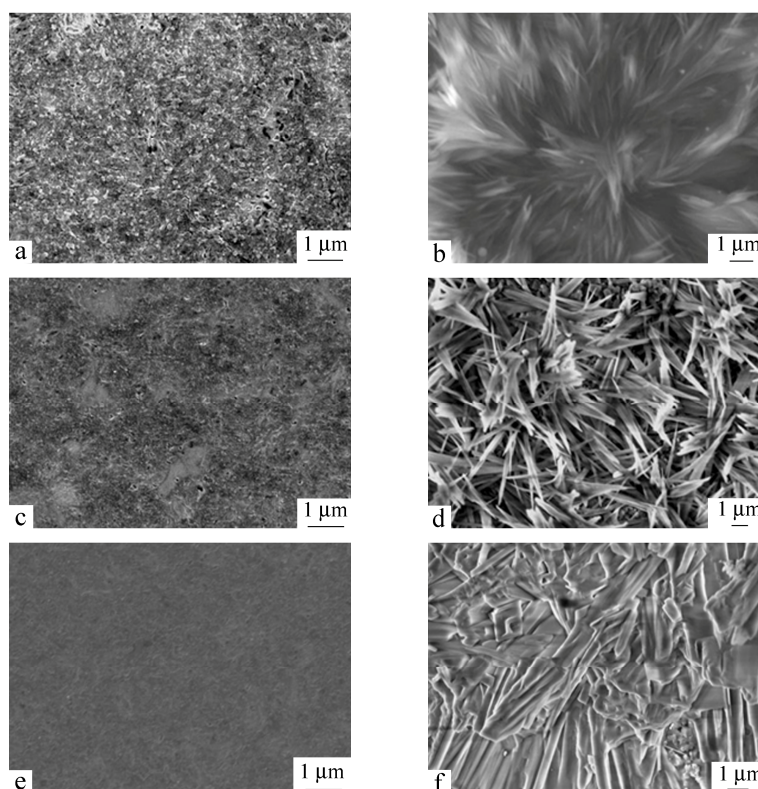


Fig. 2 SEM images of RB on Au nanoparticle array with different concentrations and solvents: (a) 10^{-4} mol/L, water, (b) 10^{-4} mol/L, ethanol, (c) 10^{-6} mol/L, water, (d) 10^{-6} mol/L, ethanol, (e) 10^{-8} mol/L, water and (f) 10^{-8} mol/L, ethanol

Figure 3 shows the Raman spectra of RB on bare silicon substrate and Au nanoparticle array prepared by immersing in 10^{-4} mol/L aqueous and ethanol solutions, respectively. The peak signals from RB on bare silicon substrate with 10^{-4} mol/L aqueous and ethanol solution were both very weak, and some main peaks of RB were not observed. Compared to the bare silicon substrate, the SERS spectra of RB on Au nanoparticle array were improved greatly. When the Au nanoparticle array was used to detect 10^{-4} mol/L RB aqueous solution, it was observed clearly that all of RB peaks appeared, and the intensity of main peaks at 620, 1198, 1277, 1356, 1505 and 1646 cm^{-1} were all enhanced obviously. It indicates that the Au nanoparticle array on silicon substrate has a significant Raman enhancement for RB. Interestingly, the Raman peaks of RB on Au nanoparticle array from its 10^{-4} mol/L ethanol solution were all further enhanced greatly, especially at 620, 1505 and 1646 cm^{-1} . The enhancement factor is about 10^3 based on the reported calculation method^[24]. It indicates that the SERS properties are also influenced by the morphologies of RB adsorbed on Au nanoparticle array formed in different solutions significantly.

In order to further demonstrate the influence of solvents and sensitivity of the well-ordered gold nanoparticle arrays as SERS substrates, low concentrations of RB in water and ethanol were both detected as shown in Fig. 4. When the gold nanoparticle array on silicon substrate was used to detect 10^{-6} mol/L RB aqueous solution, the Raman peaks of RB were still detected. But the intensity of RB Raman peaks decreased obviously. During detecting 10^{-8} mol/L RB aqueous solution, it was difficult to observe Raman peaks of RB. Interestingly, when the gold nanoparticle array on silicon substrate was used to detect 10^{-6} mol/L RB ethanol solution, the Raman peaks of RB were still strong, even much stronger than those for 10^{-4} mol/L RB aqueous solution. When detecting 10^{-8} mol/L RB ethanol solution, the SERS enhancement was still observed clearly. It is speculated that the reason for higher sensitivity by using ethanol as solvent is due to the special morphologies of RB on Au nanoparticle array formed in their ethanol solutions^[25].

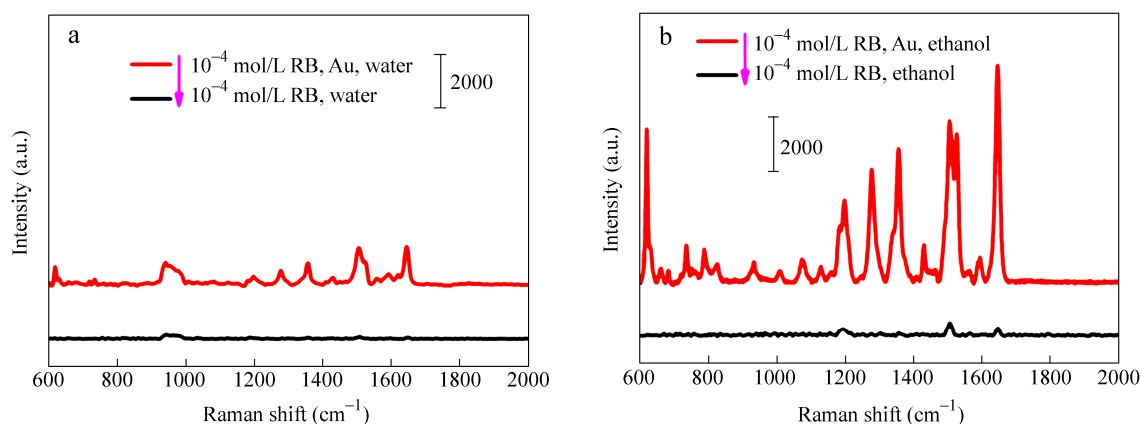


Fig. 3 Raman spectra of RB on bare silicon substrate and Au nanoparticle array with 10^{-4} mol/L concentration and different solvents: (a) water, (b) ethanol

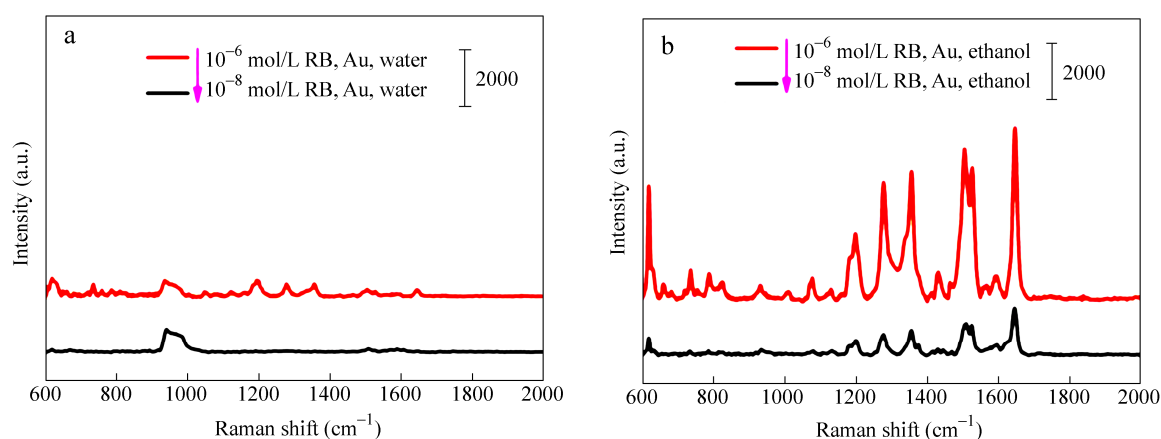


Fig. 4 SERS spectra of RB on Au nanoparticle arrays with different concentrations and solvents: (a) water and (b) ethanol

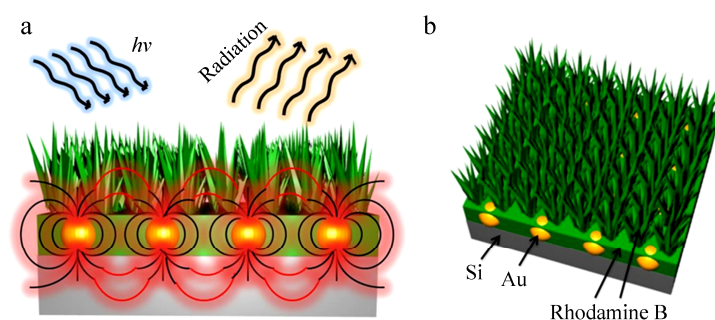


Fig. 5 Illustration of (a) the SERS mechanism and (b) the structure of RB on Au nanoparticle array with ethanol as solvent

Figure 5 shows the SERS mechanism and the structure of RB on Au nanoparticle array formed in its ethanol solution. When the Au nanoparticle array with RB was irradiated by 633 nm laser, the local electromagnetic field of each gold nanoparticle was enhanced based on the localized surface plasmon resonances. Because the Au nanoparticles were well-ordered and close, the induced electromagnetic fields of single nanoparticles coupled with each other and gave rise to the total field, resulting in great Raman enhancement. Furthermore, the well-ordered array as a role of a light-guide antenna can guide the radiation

direction in the reemission process of SERS, and the directional radiation in far field further enhance the SERS signal based on propagating surface plasmons^[26, 27]. Besides, the higher Raman enhancement from ethanol was due to the strong interactions between RB with special morphologies and surface plasmons^[28].

CONCLUSIONS

In summary, we developed a simple and economical technique to fabricate large-area Au nanoparticle array to detect minute amounts of RB, and found the great influence of detective molecules morphologies on surface-enhanced Raman scattering properties. Well-ordered Au nanoparticle array was fabricated with the average center-to-center distance (91 ± 3) nm and particle size (30 ± 2) nm by using patterned P4VP nanodomains of PS-*b*-P4VP film as nanoreactors. The Raman intensity of RB on Au nanoparticle array was much stronger than those on the bare silicon substrate due to electromagnetic enhancement based on the localized surface plasmon resonances and propagating surface plasmons. More importantly, the Raman enhancement was higher enough from ethanol than from water due to the special morphologies of RB formed in different ethanol solutions. This technique has great potential applications in the detection and sensing of biomolecules and chemical materials.

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