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Nanogaps in 2D Ag-nanocap arrays for surfaceenhanced Raman scattering

Yongjun Zhang,^{a,b} Wenting Gao,^{a,b} Shuo Yang,^c Shanshan Liu,^{a,b} Xiaoyu Zhao,^{a,b} Ming Gao,^{a,b,c} Yaxin Wang^{a,b}* and Jinghai Yang^{a,b,c}

The surface-enhanced Raman scattering substrate of Ag–Ag nanocap arrays are prepared by depositing Ag film onto twodimensional (2D) polystyrene colloidal nanosphere templates. When the original colloidal arrays are used as the substrate for Ag deposition, surface-enhanced Raman scattering (SERS) enhancements show the strong size-dependence behaviours. When O₂-plasma etched 2D polystyrene templates are used as the substrate for Ag deposition to form nanogaps, the gap sizes between adjacent Ag nanocaps from 5 to 20 nm generate even greater SERS enhancements. When SiO₂ coverage is deposited to isolate the Ag nanocaps from the neighbours, the SERS signals are enhanced more. The significant SERS effects are due to the coupling between Ag nanocaps controlled by the distance, which enhances the local electric-field intensity. Copyright © 2013 John Wiley & Sons, Ltd.

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Keywords: surface-enhanced Raman scattering spectroscopy; nanogap; Ag nanocap; local surface plasmon resonance; 2D PS arrays

Introduction

Surface-enhanced Raman scattering (SERS) is of nondestructive and ultrasensitive characteristics with enhancement factor up to 10¹², which makes SERS a powerful spectroscopic technique with the resolution down to the single molecule.^[1,2] The solution-phase Au and Ag colloidal nanoparticles are the most widely studied SERS platforms, and the ultrahigh Raman enhancement factors could be obtained in areas of 'hot spots' from the dispersed nanoscale systems.^[3-7] The subwavelength SERS 'hotspots' can be created by illuminating metallic nanoparticles,^[8–11] gaps,^[12–15] or sharp tips^[16-18], and the dramatically enhanced Raman signals are produced from the adsorbates. The enhanced electric field around the noble metal nanostructure, which is known as electromagnetic (EM) enhancement, is regarded as the dominant driving force for the tremendous enhancement.^[19] Local surface plasmons (LSPs) can substantially enhance the local EM field as a result of the collective motion of the conduction electrons, while the evanescent nature of the LSPs permits their energy to be localized to subwavelength dimensions.^[20,21]

The unique size-dependent properties of nanometer-scale particles and templated surfaces have received great attentions in a variety of fields, for instance, medicine and microelectronics.^[22-24] Assembled nanostructures have been testified lately to possess strong surface plasmon coupling, which creates amplified EM fields at the nanogaps with perfect SERS signals.^[25,26] A few promising approaches are used to fabricate nanogap structures, for example, electron-beam lithography,^[27] electromigration,^[28] nanosphere lithography,^[29–35] and electro-chemical metal growth.^[36]

In this communication, we report a SERS substrate which consists of Ag–Ag nanocap arrays by Ag deposition on the ordered PS colloid sphere array. Ag nanocap arrays show good surface uniformity over large areas. Size-dependence SERS enhancement is observed when different size PS beads are chosen for Ag deposition. The distances between two Ag nanocaps are controlled to optimize the coupling between Ag nanocaps. It indicates that the gap size adjacent Ag nanocaps regions separated by air ranges from 5 to 20 nm generate greater SERS enhancements.

Experiment

Two-dimensional (2D) arrays of polystyrene colloids were prepared by self-assembly technique on the Si wafer. Suspension of monodispersed PS microsphere (10 wt. %) was purchased from the Duke scientific corporation and used as received. The etching process was performed in a plasma cleaner (Model 1020, E.A. FischioneInstruments Inc.), and the working gas was a mixture of 80% O and 20% Ar.

The Ag film deposition was carried out in magnetron sputtering system by dc sputtering Ag target. The base pressure was 2.0×10^4 Pa and the argon pressure was 0.6 Pa during film deposition. The deposition rate was estimated as 0.0589 nms⁻¹ under the reaction pressure 0.6 Pa.

The 1 mM 4-mecaptopyridine (4-MPy) aqueous solution was used to evaluate the substrate Raman-enhancing capability, and 4-MPy (96%) was obtained from Aldrich. The sample was immersed in a 1 mM 4-MPy aqueous solution for 3h. Raman

- * Correspondence to: Yaxin Wang, Institute of Condensed State Physics, Key Laboratory of Functional Materials Physics and Chemistry, Jilin Normal University, Ministry of Education, Siping 136000, PR China. E-mail: wangyaxin1010@126.com
- a Institute of Condensed State Physics, Jilin Normal University, Siping136000, PR China
- b Key Laboratory of Functional Materials Physics and Chemistry, Jilin Normal University, Ministry of Education, Siping136000, PR China
- c Key Laboratory of Excited State Physics, Changchun Institute of Optics Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun130033, PR China

spectra were measured using Renishaw inVia Raman system under a 514.5 nm (or 2.41 eV) Ar⁺ ion laser (20 mW) excitation. The Raman emissions, dispersed in a 0.5 m single monochromator equipped with a grating of 1800 grooves cm⁻¹, were detected with CCD. A 50 × 0.50 NA Leica object focused the excitation beam onto the samples with a spot size of ca 1 µm. The signal acquisition time was 10 s in a 180° backscattering geometry. According to manufacturer specifications, the solid angle of collection, Ω , was 0.37 steradians.

Results and discussion

Figure 1a shows 2D PS templates obtained by self-assembly technique on Si wafer and the nanospheres sizes are 100 nm, 200 nm, 500 nm, and 700 nm, respectively. The continuous ordered areas are over 1 cm² in size. The uniform reflected color of film indicates that the PS monolayer is distributed on silicon wafer homogenously from point to point. Figure 1b is the SEM image of PS colloid spheres with diameter 200 nm. The 2D PS template shows the perfect hexagonal arrangements, and the PS beads show the spherical shape and the homogeneous size.

When silver films are deposited onto 2D PS template, Ag nanocaps are forming on PS top. The nanocap thickness decreases gradually from the top to the brim, which is confirmed SEM image in Fig. 2a after Ag nanocap array is transferred to another substrate and the PS nanospheres are etched away. Figure 2b shows the 4-MPy Raman spectrum obtained on the Ag nanocap arrays when 30 nm silver film is sputtered. No Raman peaks are observed from 4-MPy for the flat Ag film on silicon wafer. For the Ag nanocap on PS bead, 4-MPy Raman peaks become obvious and the spectra show twelve dominant peaks at 711, 780, 1010, 1039, 1069, 1101, 1218, 1276, 1470, 1497, 1604, and 1615 cm⁻¹. The peak at 1604 cm⁻¹, the aromatic C–C stretching vibrational mode, is used to study the evolution of the peak intensity for different Ag nanocap substrates quantitatively. When 100 nm PS is chosen for the colloidal template, the 4-MPy Raman peak shows the largest increase for the Ag nanocap substrate. Several authors have shown the maximum SERS signals when the size of the surface roughness ranges from 80 to 100 nm, consistent with our results.^[37,38] Figure 2c shows Raman spectrum of 4-MPy obtained on Ag nanocap array for 100 nm polystyrene colloids and Ag film is 5, 10, 20, 30, and 40 nm in thickness. The intensity of the Raman signal reaches a maximum when the silver film is 30 nm. With the increase of the film thickness, Raman signal is gradually weakened. When the thickness of the metal film is too thin, it cannot provide a full EM field and the random dipole–dipole interactions between Ag shells lead to the broad optical extinction peaks.^[39] When the thickness of the metal film is close to the bead size, the top of the nanosphere is covered completely. The surface morphology is similar to the flat film, and no SERS signals are observed.

When 2D Ag nanocap array on 700 nm PS is used for SERS substrate, the signals are small from 4-MPy in spite of the obvious SERS effects. To improve the signals, nanogaps are created between the Ag nanocaps by silver film deposition onto the etched 2D PS arrays. Figure 3a shows SEM image of the 30 nm Ag nanocaps on the original template of 700 nm PS colloids without gaps, which shows no obvious differences from the PS template. Figure 3b shows the final nanogap sizes ranges from 5 nm to 20 nm, when the etching time is 60 s. Figure 3c shows that the nearly 150 nm nanogap sizes are obtained when the oxygen plasma etching is applied for 150 s. Figure 3d shows the SERS spectra of 1 mM 4-MPy adsorbed on the Aq-nanocap substrates with varied O₂-plasma etching times. As expected, when the etching time is 60 s, the Raman peak shows the significant increase. The SERS signals are enhanced nearly 100 times compared to the SERS signals from the original 700 nm PS array for the aromatic C–C stretching mode. When O₂-plasma etching time increases over 80 s, for example, to 150 s, the gap sizes are around 100 nm and the Raman peak almost disappears. These results indicate that the SERS performance can be essentially improved by optimizing the plasmon coupling between the neighbour nanospheres if O2-plasma etching time is varied. SERS intensity is directly related to the intensity of the localized EM fields that are enhanced by the LSPs between neighbour nanounits. To realize efficient coupling of the localized surface plasmons, the gaps between the adjacent nanosphere are optimized via control of the O2-plasma etching times. The large EM fields have been taken advantage by a few promising approaches for generating even greater SERS enhancements, which can be generated between adjacent metal regions separated by a dielectric gap (typically air) of 5–20 nm.^[40]Resonant light absorption by void plasmons is accompanied by high local-field enhancement to trigger the SERS effects.^[41] Since the absorption and local-field properties of these types of nanogap structures can be effectively tailored by varying the diameter of the gap, the amplification factors can be actively tuned and optimized by plasma etching and film deposition for our research.

Figure 4 shows SERS spectra of 1 mM 4-MPy on Ag-nanocap substrates and the Ag nanocaps are prepared on 100 nm



Figure 1. (a) PS templates scale up to continuous areas cm² in size. (b) SEM image shows the colloid sphere array 200 nm.



Figure 2. (a) SEM images acquired from the silver nanocap arrays. (b) Raman spectra of 1 mM 4-MPy molecules adsorbed on 30 nm silver film. (c) Raman spectrum of 1 mM 4-MPy obtained on 100 nm PS bead arrays with Ag thickness of 5, 10, 20, 30, and 40 nm.



Figure 3. SEM of the nanogaps array with the 30 nm Ag film, and the anisotropic oxygen plasma time is (a) 0 s (b) 60 s (c) 150 s. (d) The SERS spectra of 1 mM 4-MPy adsorbed on the Ag-nanocap substrates at varied O_2 -plasma etched times.

nanospheres after O_2 -plasma etching for different times. The inset shows the corresponding SEM for the nanogaps substrate with 30 nm Ag film. When the etching time is 80 s and more, PS arrays are etched up and the substrate is close to the flat Ag film, so that there are almost no Raman signals. When the etching time is 40 s, the gap sizes between adjacent Ag nanocaps are

from 5 to 20 nm. SERS intensity from nanogap is about twice that from Ag nanocap array on the original PS template, which can be attributed to a strong coupling between the Ag nanocaps because silver nanocaps allow direct coupling between the electric field arising from the incoming radiation and resonant electron plasmon oscillations. This observation suggests the





Figure 4. Comparison of the measured SERS spectra of 1 mM 4-MPy of different etching time nanogap arrays: 80 s, 40 s, 0 s (The silver film thickness is 30 nm. PS nanosphere size is 100 nm). The inset shows the corresponding SEM of nanogap arrays with 30 nm Ag film.

mutual coupling of EM fields between adjacent Ag nanocaps. It has been reported that the SERS signal decreases with increasing distance between the Raman label and the metal surface, which is modeled by the EM field enhancement theory.^[42,43] A continuous nanometric gap is created along the perimeter of the patterned metal areas, providing a wide variety of design freedom for making SERS substrates and plasmonic devices such as waveguides and resonators.^[44]

In order to examine the stronger plasmonic coupling from the edge of two Ag nanocap, 500 nm PS array is chosen as the substrate after etched for 60 s. $SiO_2/Ag/SiO_2$ nanocaps are prepared by sputtering the Ag and SiO_2 targets. Figure 5a schematically illustrates a cross-section image of the $SiO_2/Ag/$ SiO₂ nanocap-SERS substrate, which indicates that the insulator SiO₂ puts Ag isolated, favorable for perfect SERS signals. Thirty nanometer SiO₂ shields top part of Ag nanocap from SERS effects and only the Ag film near the nanocap brim works if coupling happens. The inset is the SEM of the SiO₂/Ag/SiO₂ nanostructures deposited on 500 nm PS spheres after 60 s etching. Figure 5b shows the strong SERS spectra of 1 mM 4-Mpy on Ag (30 nm) nanocap, $SiO_2/Ag/SiO_2$ (30 nm/30 nm/30 nm) nanocap, $SiO_2/Ag/SiO_2/Ag/$ SiO₂ (30 nm/50 nm/30 nm) nanocap, and SiO2/Ag/SiO2 (30 nm/ 70 nm/30 nm) nanocap, and 1 mM R6G on an ordinary Si substrate coated with Ag as a reference. Compared to the Ag nanocap array (Ag 30 nm), the SERS intensity is enhanced nearly four times after SiO₂ coverage. As the Ag thickness increases, the SERS signal becomes gradually stronger. The biggest enhancement is obtained on SiO2/Ag/SiO2 (30 nm/70 nm/30 nm) nanocap, which is enhanced ten times compared to the 30 nm Ag nanocap array. The probing molecules cannot penetrate into the solid dielectric material; therefore, collective charge oscillations only occur at nanogap. When the Ag deposition time increases, the thickness of the edge of Ag increases, resulting in the reduced gap sizes between the edges of Ag nanocaps. When the gap size decreases, the coupled plasmon resonance shifts to red and the enhanced EM field increases at the junction of the particles.^[45] This confirms that the nanogap between the two nanocaps contributes to enhanced Raman signal. The Raman signal on the SiO₂/Ag/SiO₂ nanocap substrate is much stronger than the Raman signal on the Ag nanocap substrate, because the SiO₂ put each pair of Ag nanocaps isolated so that strong coupling between LSPs can be achieved to substantially enhance the near electric-field intensity.^[46] The SiO₂/Ag/SiO₂ nanocap substrate is similar to the structure of the dimers, producing intense EM fields in the interstices of a reasonably simple structure because the dipole coupling is enhanced.^[47] SiO₂ layer is very thin near the nanocap edges, which is another important factor contributing to SERS enhancement. The ultrathin SiO₂ layer is essential to extend the strong EM field from the metal to the probed surface.[48,49]

In order to compare the SERS effect on nanogap arrays, we calculate the enhancement factor $\text{EF} = (I_{\text{SERS}}*N_{\text{vol}})/(I_{\text{RS}}*N_{\text{surf}})$, where I_{SERS} and I_{RS} are the intensities of the band 1604 cm⁻¹ from the SERS substrates and reference solution, respectively. $N_{\text{Vol}} = c_{\text{RS}}V$ is the average number of molecules in the scattering volume (V) for the Raman (non-SERS) measurement and N_{Surf} is the average number of adsorbed molecules in the scattering volume for the SERS experiments. It is assumed that 4-MPy forms a homogeneous monolayer on the substrate after absorption, and the surface area occupied by a single 4-Mpy adsorbed molecules on the silver substrate value is estimated to be 0.30 nm^{2} .^[50] The spot of laser is a circle with a diameter of 1 μ m. N_{Surf} can be calculated to be 2.6×10^6 . For the optical configuration and microscope employed, the effective focused depth is 1 μ m. The molar concentration of the 4-Mpy analyte



Figure 5. (a) Schematic illustration (not to scale) of the cross section of the SiO2/Ag/SiO2 nanostructures on the Si substrate. The inset is the SEM of the SiO2/Ag/SiO2 nanogap arrays. (b) SERS spectra of 1 mM 4-MPy of SERS spectra of SiO2/Ag/SiO2(30 nm/30 nm/30 nm) on Si wafer, Ag(30 nm) nanocap-SERS, SiO2/Ag/SiO2(30 nm/30 nm) nanocap-SERS, SiO2/Ag/SiO2(30 nm/30 nm) nanocap-SERS, SiO2/Ag/SiO2(30 nm/30 nm) nanocap-SERS.

on the reference region is 1 mM. $N_{Vol} = c_{RS}V$ is about 4.7× 10⁷. I_{SERS}/I_{RS} is 22 for SiO₂/Ag/SiO₂ nanogap substrate and 11 for Ag nanogap substrate. So the EF is calculated to be 1.1× 10⁵ for SiO₂/Ag/SiO₂ nanocap substrate and 0.5× 10⁴ for Ag nanocap substrate, respectively. The substrates show good repeatability of the fabrication and the reproducibility of the SERS spectra (see Figs. S1 and S2 in Supporting Information).

Conclusions

In summary, we report the fabrication of nondestructive and large-area metal nanosphere arrays with fine surface uniformity and a tunable adjacent gap by Ag deposition onto 2D polysty-rene colloid sphere template. Strong size dependence of SERS enhancement is demonstrated when Ag nanocap substrates are etched to form nanogap by O₂-plasma. The gaps with size from 5 nm to 20 nm give significant SERS enhancements. Stronger plasmonic coupling from the edge of two Ag nanocap arrays is well demonstrated by SiO₂/Ag/SiO₂ nanocap substrate when the insulator SiO₂ puts Ag isolated.

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Supporting information

Supporting information may be found in the online version of this article.

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