Gold Nanoparticles Assembling on Smooth Silver Spheres for Surface-Enhanced Raman Spectroscopy

Weiwei Xia, Jian Sha,* Yanjun Fang, Ren Lu, Yafei Luo, and Yewu Wang*

Department of Physics and State Key Laboratory of Silicon Materials, Zhejiang University, Hangzhou 310027, People’s Republic of China

Supporting Information

ABSTRACT: A simple and cost-effective chemical method was introduced to assemble gold (Au) nanoparticles on smooth silver (Ag) spheres for realizing surface-enhanced Raman scattering (SERS) enhancement by the replacement reaction between chloroauric acid and Ag spheres. In addition, the Ag–Au core–shell spheres were fabricated when a certain amount of chloroauric acid was used in the reaction solution. We found that the Ag particles decorated with small Au nanoparticles demonstrated the strongest SERS enhancement, while Ag–Au core–shell spheres showed the weakest enhancement.

1. INTRODUCTION

Surface-enhanced Raman scattering (SERS) has been studied intensively because of its potential applications in trace detection of chemical species since its initial discovery in 1974.1 These large enhancements of the Raman signal have been demonstrated to be related to the surface roughness and the dimensions of the metallic features.2 Thus far, three common approaches have been developed to realize SERS for trace detection of molecules: reducing the gaps between adjacent metallic nanostructures to sub-10 nm because the SERS enhancement factor primarily depends upon the gap/diameter ratio (W/D),2,3 increasing the surface roughness of metallic particles,4 and approaching a metallic particle to a metallic wire or thin film.3

The most intensively investigated SERS-active metals are silver (Ag) and gold (Au).6 Currently, there has been growing interest in developing a new class of SERS-active substrates, including core–shell and alloy metallic nanostructures. Murphy et al.7 have mentioned that Ag–Au core–shell nanowires show much improvement in SERS enhancement than that of Au nanotubes or even Ag nanowires. Tsukruk et al.8 have employed a three-arm star polymer with a functional terminal as a linker to decorate the surface of Ag nanowires with gold nanoparticles, resulting in enhanced SERS ability, greatly exceeding the Raman scattering observed from isolated bare Ag nanowires, and it is also much higher than that at the gap between two neighboring Ag nanowires. Moreover, the effect significantly exceeds that reported7 for Ag–Au core–shell nanowires. However, the fabrication process is complicated, and the size and interspace of Au nanoparticles are difficult to control. Tsukruk et al.5,10 have also assembled Au nanoparticles on one-dimensional (1D) and two-dimensional (2D) Ag nanostructure surfaces as the substrates for SERS. The optimized Raman intensity is comparable to the dense array of Ag nanowires and Ag nanoparticles. Dong et al.11 have investigated the SERS activity of Ag–Au bimetallic nanostructures with hollow interiors, indicating the high enhancement SERS of the hollow nanostructures. Eychmuller et al.12 have demonstrated that the ordered macroporous bimetallic nanostructures are highly desirable for the detection of DNA bases by the SERS technique in terms of a high SERS enhancement, good stability, and reproducibility. Narayana et al.13 have synthesized Ag–Au core–shell nanoparticles with nanopores, which show much improved SERS enhancement than that of bare Ag nanoparticles. Morcillo et al.14 have investigated the SERS activity of both Au-coated Ag nanoparticles and Ag-coated Au nanoparticles, but the results show that the SERS activity of the bimetallic nanoparticles is intermediate between the activities of Ag and Au.

Herein, we introduce a simple and cost-effective chemical approach to assemble Au nanoparticles on Ag spheres by the replacement reaction between chloroauric acid and Ag spheres. The Ag–Au core–shell spheres can be fabricated when a certain amount of chloroauric acid is added in the reaction solution. The morphology evolution of the Ag–Au structures with the amount of chloroauric acid is added in the reaction solution. The morphology evolution of the Ag–Au structures is studied in detail. The Ag particles decorated by Au nanoparticles on silicon nanowires (SiNWs) are always multilayer, which offer a larger specific surface area and provide more hot spots within the laser illumination area. Moreover, the Ag–Au structures are directly assembled onto SiNWs on silicon wafer,

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which are usually very stable under ambient conditions. Therefore, the Ag–Au structures on SiNWs would be an effective substrate for SERS applications.

2. EXPERIMENTAL SECTION

SiNW arrays were prepared by the Ag-assisted chemical etching method. N-type Si (100) wafers (1 × 1 cm) with a resistivity of 0.01 Ω cm were washed with water, acetone, and water, respectively. The wafers were subsequently immersed in H₂SO₄ and H₂O₂ (4:1, v/v) solution to remove the organic contaminants. Then, the wafers were immersed in a 5% HF solution to form a H-terminated surface. Afterward, the treated wafers were immediately immersed in a solution containing HF (4.8 M) and AgNO₃ (0.02 M) to deposit Ag particles on their surface. Finally, the wafers were etched in HF (4.8 M)/H₂O₂ (0.2 M) solution for 30 min at room temperature to obtain SiNWs.

A larger quantity of Ag spheres was assembled onto the top of SiNWs via the reaction between Ag ions and Si–H bonds on the SiNW surface. After rinsing with deionized water, the SiNW arrays decorated with a large number of Si–H bonds were immersed into 5 × 10⁻³ M silver nitrate solution for 3 min. As a result, abundant and uniform Ag particles were assembled onto the top of the SiNW arrays. The sizes of Ag particles on the substrate are in the range of 200–500 nm observed using CARL ZEISS ULTRA-55 field-emission scanning electron microscopy (SEM). The morphology of Au nanoparticles on Ag microspheres is observed by transition electron microscopy (TEM, JEOL 2010).

In a typical procedure for the formation of Au nanoparticles on the smooth Ag spheres, the substrates of SiNWs were immersed into the aqueous solutions with different concentrations of HAuCl₄ for 20 min until its color became stable. The concentrations of HAuCl₄ are 0.02, 0.04, 0.07, 0.11, 0.14, and 0.17 mM. The reaction product of AgCl was removed by dissolving with a saturated solution of NaCl. The general reaction of Ag spheres and chloroauric acid can be described as follows:

\[ 3\text{Ag}(s) + \text{AuCl}_4^-(aq) \rightarrow \text{Au}(s) + 3\text{Ag}^+(aq) + 4\text{Cl}^-(aq) \]  

Xia et al. have reported that the reaction temperature plays an important role in the replacement because the solubility of AgCl and the diffusion coefficients of Ag and Au atoms were both strongly dependent upon this parameter. Therefore, the replacement reactions were performed at 60 and 90 °C to investigate the influence of the reaction temperature on the morphology evolution and SERS activities.

To evaluate the Raman-enhancing capability, the fabricated samples were submerged in the rhodamine 6G (R6G, 10⁻⁴ M) solution for 30 min and then rinsed with deionized water thoroughly. Raman measurements were performed at room temperature on a Jobin-Yvon, Labor Raman HR-800 triple Raman system with the 514.5 and 632.8 nm lines. The probed area was ~10 μm in diameter with a 50× objective lens, and the incident power was 5 mW. It should be noted that the laser power is the same for all of the Raman spectra, the integration time is 0.5 s, and the accumulation time is 5 s. The SERS spectra were collected from six different sites on each sample to clarify the reproducibility. The six different sites were randomly selected. All of the measurements were performed at room temperature.

3. RESULTS AND DISCUSSION

Figure 1 shows the SEM images of the SiNW arrays coated with Ag spheres before the replacement reaction between chloroauric acid and Ag spheres was carried out. It clearly indicates that large-quantity Ag particles are assembled onto the top of SiNW arrays. Inset a is a cross-sectional SEM image of SiNWs. Inset b reveals that the sizes of the Ag particles are in the range of 200–500 nm. Figure 2 shows the top view of the Ag spheres on the top of SiNWs before and after the replacement reactions were performed. Insets of Figure 2 are the enlarged images. Figure 2a is the SEM image of the Ag spheres before the replacement reaction occurs. The surface of Ag spheres is very smooth. At this point, the SERS signal is very weak, as shown in Figure 4a. The SEM images of Ag spheres as a function of the concentration of HAuCl₄ are shown in panels b–d of Figure 2. The representative SERS spectra as a function of the concentration of HAuCl₄ are displayed in spectra b–d of Figure 4. Tiny and sparse Au nanoparticles appear on the surfaces of Ag spheres when the concentration of HAuCl₄ in aqueous solution was 0.02 mM. The size of the Au nanoparticles is around 20 nm, as shown in Figure 2b. At this stage, the SERS signal is still weak (Figure 4b). With a further increase of the concentration of HAuCl₄ to 0.04 mM, Au nanoparticles clearly become larger and the size is about 35 nm. The TEM image is shown in the left inset of Figure 2c. The density is significantly increased (Figure 2c). The corresponding SERS signal shown in Figure 4c, in fact, shows a significant intensity increase over its initial value. The relative enhance-
ment factor (REF) between two different substrates can be calculated by applying the SERS intensity. The band having the highest relative SERS signal at around 611 cm$^{-1}$ was chosen for the estimation of the REF. The REF of the 0.04 mM sample compared to the Ag microspheres (0.00 mM HAuCl$_4$) reaches 18. The SERS spectra collected from the randomly selected six sites of the sample (Figure 2c) are shown in Figure S1 in the Supporting Information, which clearly reveal the reproducibility of the SERS measurements. Energy-dispersive X-ray spectroscopy (EDS; Figure 2f) taken from the Ag spheres decorated by Au nanoparticles in Figure 2c reveals that the resultant structures contain both Au and Ag elements. The area element scanning results of the sample shown in Figure 2c can be viewed in Figure 3. These results both confirm that the Au nanoparticles are indeed formed on the surface of Ag spheres. As the concentration of HAuCl$_4$ further increases to 0.07 mM, the size of Au nanoparticles continues to increase to $\sim 60$ nm in diameter (Figure 2d) but the SERS intensity sharply decreases (Figure 4d). Gold nanoparticles on silver microspheres become larger and then close to each other to form a gold shell, shown in Figure 2e, as the concentration of HAuCl$_4$ continues to increase (0.11 mM). At the same time, small holes form, as shown in Figure 2e (black circle). The corresponding SERS signal shown in Figure 4e almost disappears.

The hole will continue to serve as an active channel for a subsequent replacement reaction, which allows all of the species (e.g., AuCl$_4^-$, Ag$^+$, Cl$^-$, and Au) to diffuse in and out. Therefore, small gold nanoparticles can continue to deposit on the smooth surface of the gold shell when the concentration of HAuCl$_4$ was further increased. Tiny and sparse nanoparticles with an average diameter of $\sim 20$ nm appear on the surface of the Au shell when the concentration of HAuCl$_4$ was increased to 0.14 mM, resulting in a weak increase of the SERS signal (Figure 4f). The corresponding SEM image is shown in Figure 5a. As the concentration of HAuCl$_4$ was finally increased to 0.17 mM, many Au nanoparticles ($\sim 30$ nm in diameter) can be easily observed on the surface of Au shells (Figure 2e), which is similar to that in Figure 2c. The SERS signal of the structure increases obviously (Figure 4g). However, the intensity is much weaker compared to that of the sample shown in Figure 2c. Intensities of the SERS signal plotted as a function of the concentration of HAuCl$_4$ are shown in Figure 6.

The reaction temperature was also found to play an important role in the replacement reaction because the diffusion coefficients of Au and Ag atoms were both strongly dependent upon this parameter. Figure 7 shows the SEM images of the SiNW arrays coated with Ag spheres after the replacement reaction occurred with the reaction temperature of 90 °C. It clearly indicates that the morphology evolution of the samples has a similar trend compared to the results of 60 °C.

Figure 3. Area element scanning results of the Ag-capped SiNWs decorated by Au nanoparticles (the concentration of HAuCl$_4$ is 0.04 mM).

Figure 4. SERS spectra acquired from R6G adsorbed on the Ag-capped SiNW arrays (a) before and (b–g) after the replacement reaction was performed at 60 °C with different concentrations of HAuCl$_4$ aqueous solution: (b) 0.02 mM, (c) 0.04 mM, (d) 0.07 mM, (e) 0.11 mM, (f) 0.14 mM, and (g) 0.17 mM. All of the spectra are acquired at an excitation of 514.5 nm.

Figure 5. SEM images of the top view of the SiNW arrays coated with Ag spheres after the replacement reaction was performed at 60 °C with different concentration of HAuCl$_4$: (a) 0.14 mM and (b) 0.17 mM. The insets are the corresponding enlarged images.

Figure 6. Intensities of the 616, 1361, and 1694 cm$^{-1}$ bands plotted as a function of the concentration of HAuCl$_4$. The reaction temperature is 60 °C.

The reaction temperature was also found to play an important role in the replacement reaction because the diffusion coefficients of Au and Ag atoms were both strongly dependent upon this parameter. Figure 7 shows the SEM images of the SiNW arrays coated with Ag spheres after the replacement reaction occurred with the reaction temperature of 90 °C. It clearly indicates that the morphology evolution of the samples has a similar trend compared to the results of 60 °C.
However, many Au nanoparticles already appeared on the surface of Ag particles when the concentration of HAuCl₄ was only 0.02 mM. Figure 8 shows the evolution of the SERS intensity of the samples fabricated at 90 °C with the concentration of HAuCl₄. It shows a similar evolution of the SERS intensity via the concentration of HAuCl₄ compared to the results of 60 °C. However, it is worth noting that the intensity of the SERS approaches the maximum when the concentration of HAuCl₄ was only 0.02 mM (Figure 8b), which is consistent with the morphology evolution shown in Figure 7. With a further increase of the concentration of HAuCl₄, the intensity decreases (spectra c and d of Figure 8). When the concentration of HAuCl₄ was increased to 0.11 mM, the intensity is found to increase again (Figure 8e). However, the intensity is also much weaker compared to that in Figure 8b. The intensity subsequently decreases again as the concentration of HAuCl₄ increased to 0.14 and 0.17 mM, respectively (spectra f and g of Figure 8). Intensities of the SERS signal plotted as a function of the concentration of HAuCl₄ are also shown in Figure 9.

To interpret the evolution of the SERS signal, Figure 10 summarizes all morphological and structural changes involved in the replacement process between the Ag spheres and an aqueous HAuCl₄ solution that is performed at 60 °C according to the SEM investigations shown in Figures 2 and 5. Figure 10a shows the schematic illustration of the large Ag spheres with smooth surface of Ag spheres by adding different concentrations of HAuCl₄ aqueous solution: (b) 0.02 mM, (c) 0.04 mM, (d) 0.07 mM, (e) 0.11 mM, (f) 0.11 mM, and (g) 0.17 mM. All of the spectra are acquired at an excitation of 514.5 nm.

Figure 8. SERS spectra acquired from R6G adsorbed on the Ag-capped SiNW arrays (a) before and (b−g) after the replacement reaction was performed at 90 °C with different concentrations of HAuCl₄ aqueous solution: (b) 0.02 mM, (c) 0.04 mM, (d) 0.07 mM, (e) 0.11 mM, (f) 0.11 mM, and (g) 0.17 mM. All of the spectra are acquired at an excitation of 514.5 nm.

Figure 9. Intensities of the 616, 1361, and 1694 cm⁻¹ bands plotted as a function of the concentration of HAuCl₄. The reaction temperature is 90 °C.

Figure 10. Schematic illustrations of (a) original Ag spheres on the top of SiNW arrays and (b−f) gold particles assembling on the smooth surface of Ag spheres by adding different concentrations of HAuCl₄ aqueous solution: (b) 0.02 mM, (c) 0.04 mM, (d) 0.07 mM, (e) 0.11 mM, and (f) 0.14 mM.
of Ag spheres, as shown in Figure 10b. The gap between the neighboring Au nanoparticles is very large, implying that the electromagnetic gap field is still rather weak, and indeed, the SERS signal increases slightly at this stage, as shown in Figure 4b, because of the slight increase of the roughness of Ag spheres. As the concentration of HAuCl₄ was increased to 0.04 mM, many Au nanoparticles can be easily investigated on the surface of Ag spheres, as shown in Figure 10c. The gap between the neighboring Au nanoparticles decreases to about 20 nm, which is far from the sub-10 nm, indicating that the electromagnetic gap field is still rather weak. The strongest enhancements are observed when the surface Plasmon resonance wavelength is equal to \( \lambda_{SP} = (\lambda_{exc} + \lambda_{Rs})/2 \), where \( \lambda_{SP} \), \( \lambda_{exc} \), and \( \lambda_{Rs} \) are the surface Plasmon, excitation, and Raman wavelengths, respectively. Therefore, the SERS signal of Au particles caused by 632.8 nm excitation is usually more intense than that by 514.5 nm. In our study, the SERS measurements of Ag microspheres decorated by Au nanoparticles (0.04 mM HAuCl₄) were carried out upon excitation at 632.8 and 514.5 nm to study the source of the intensification of the SERS signal, and the results are presented in Figure 11. However, the SERS signal caused by 632.8 nm excitation does not show higher enhancement efficiency than that caused by 514.5 nm, suggesting that the electromagnetic coupling would be governed more by the interface of Ag microspheres and Au nanoparticles than the sparsely distributed Au nanoparticles. With a further increase of the concentration of HAuCl₄, the gap between Au particles further reduces to sub-10 nm. An intense electromagnetic field enhancement is expected. However, in fact, the SERS signal is observed to decrease abruptly. At this stage, the size of Au particles clearly becomes larger because of the Ostwald ripening and the density of particles decreases, as shown in Figures 2d and 10d. The Au particles cover most of the Ag sphere surface. The EM hot spot arising from the gap modes then becomes the main source of the SERS enhancement. The SERS signal therefore decreases sharply because of the obvious decrease of the Au particle density and the effective interfaces between Ag spheres and Au particles. Au particles connect closely and then form a smooth Au shell covering the surface of Ag spheres, as shown in Figure 10e, when the concentration of HAuCl₄ was increased to 0.11 mM. At this point, the SERS signal further decreases and is very weak, which is similar to that of smooth Ag spheres shown in Figure 4a. Small Au nanoparticles appear on the surface of the Au shell again, as shown in Figure 10e, when the concentration of HAuCl₄ was further increased. The interfaces created between a smooth surface of the Au shell and the small Au nanoparticles have been thought to be the SERS hot spots. Although the SERS signal increases, its intensity is much weaker than that of the structure shown in Figure 2c because the SERS enhancement factor for Au is much smaller than that for silver deposited on porous GaN substrates. Therefore, both the gaps between Au nanoparticles and the interface between a smooth surface of the sphere and many Au nanoparticles are thought to be the sources of the SERS enhancement.

The similar changes of the SERS signal can be observed in Figure 8, in which the reaction temperature is 90 °C. However, the intensity of the SERS signal reaches its maximum soon after the replacement reaction was performed at 60 °C with 0.04 mM HAuCl₄ aqueous solution using the 514.5 nm excitation wavelength. Therefore, the SERS enhancement factor for Au is much smaller than that for silver deposited on porous GaN substrates. Therefore, both the gaps between Au nanoparticles and the interface between a smooth surface of the sphere and many Au nanoparticles are thought to be the sources of the SERS enhancement.

ASSOCIATED CONTENT

Supporting Information
SERS spectra collected from the randomly selected six sites of the Ag-capped SiNW arrays after the replacement reaction with 0.04 mM HAuCl₄ aqueous solution (Figure S1). This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author
E-mail: phiysha@zju.edu.cn (J.S.); yewuwang@zju.edu.cn (Y.W.).

Notes
The authors declare no competing financial interest.

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