

Fabricating Au–Ag core-shell composite films for surface-enhanced Raman scattering

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Abstract Surface-enhanced Raman scattering (SERS) integrates high levels of sensitivity with spectroscopic precision, and thus, has tremendous potential for chemical and biomolecular sensing. The key to the wider application of Raman spectroscopy using roughened metallic surfaces is the development of highly enhancing substrates for analytical purposes, i.e., for better detection sensitivity of trace contaminants and pollutants. Here, we have prepared Au, Ag, AuAg multilayer, and Au@Ag films on glass substrates for SERS-active substrates. The Au@Ag film shows a much stronger SERS signal for *trans*-bis(4-pyridyl)ethylene (BPE) molecules than those from pure Au, Ag, and AuAg films, indicating the Au@Ag film is more powerful than pure Au, Ag, and AuAg film as SERS active substrates. The enhanced surface Raman scattering signals were attributed to the local field enhancement in the core-shell structure.

Introduction

Surface-enhanced Raman scattering (SERS) integrates high levels of sensitivity with spectroscopic precision and thus has tremendous potential for chemical and biomolecular sensing [1, 2]. The key to the wider application of Raman spectroscopy using roughened metallic surfaces is the development of highly enhancing substrates for analytical purposes, i.e., for better detection sensitivity of trace contaminants and pollutants [3]. Controlled methods for preparing nano-structured metal substrates might provide more useful correlations between surface structure and signal enhancement. Recently the fabrication of nano-structures or nanoparticles has increased interest throughout the fields of pure and applied science and technology due to their unique physical, optical, and chemical properties [4]. Some new methods of generating macroscopic metal surfaces, based on self-assembly of nanometer-scale colloidal gold, and silver particles from solution onto various solid substrates have been reported by many research groups in the past several years [5, 6]. It has been found that a well-defined and uniform nanometer-scale architecture of silver or gold colloid, can be generated and many possible applications, including SERS substrates, have been demonstrated [2, 7]. Especially, the AuAg composite nanoparticles often exhibit improved physical and chemical properties over single component counterparts, making them attractive from both scientific and technological viewpoints [8–10]. We have reported the SERS properties of gold-coated silver and silver-coated gold composite nanoparticles by measuring the Raman spectra of Rhodamine 6G on these composite nanoparticles at 532 nm [9]. However, the SERS properties of silver-coated gold nanoparticles and AuAg multilayer adsorbed with different molecules at different excited laser

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wavelength is also interesting. Here, we prepared Au, Ag, and silver-coated gold composite nanoparticles and self-assembled on glass substrates as sensitive SERS substrates. Their SERS properties were studied by using trans-1,2-bis(4-pyridyl)ethylene molecules at 488 nm. The strongest SERS signals were observed in silver-coated gold nanoparticle film and attributed to the electronic ligand effect and localized electric field enhancement in core-shell nanoparticles under laser excitation.

Experimental details

Briefly, gold and silver colloids were prepared by the method of Na(cit)₃ thermal reduction [10]. In the process of thermal reduction, a gold sol was prepared by adding 1 mL of 1 wt% HAuCl₄ aqueous solution and 2 mL of 38.8 mM sodium citrate aqueous solution into 90 mL boiling water. The citrate ion acted as both a reductant and a stabilizer. After the solution had turned purple red within 30 s, it was cooled quickly in the ice bath in order to prevent the further growth of gold nanoparticles. This resulted in a stable dispersion of gold particles with an average diameter of around 15 nm. The silver colloid was prepared by thermal reduction of 10 mM AgNO₃ aqueous solution in the presence of 20 mM trisodium citrate at 70 °C [11]. After the solution had turned green around 10 min, it was quickly cooled in the ice bath. This resulted in a stable dispersion of silver nanoparticles with an average diameter of around 30 nm.

Au-core/Ag-shell nanoparticles (Au@Ag) were prepared by using a seed colloid technique as follows [12]. As prepared Au colloids and 1 mL of 38.8 mM Na(cit)₃ solution were added into 30 mL H₂O. Later, 1.2 mL of 10 mM AgNO₃ aqueous solution was added, and then 0.4 mL of 100 mM ascorbic acid aqueous solution was added to the above solution drop-by-drop, while stirring for 1 h at room temperature. The monolayer Au, Ag, and Au@Ag films were self-assembled on 3-aminopropyltrimethoxysilane (APTMS)-modified (4 g APTMS in 36 g methanol) glass slides by immersing the slides for 12 h in the solution, as reported previously [10], and the AuAg multilayer was prepared by immersing the Au monolayer in the APTMS/methanol solution and Ag solution for 12 h, respectively. Finally, these films were heat-treated at 300 °C for 10 min in H₂/N₂ atmosphere in order to remove some organic agents.

The surface morphology of these films were examined with dynamic force mode (DFM) using an atomic force microscope (Seiko II, SPA-300HV). UV–Vis spectra of these films were measured with a Jasco Ubest 570 UV–Vis–NIR spectrophotometer. SERS measurements were performed by a Jasco NRS-2000 model microscopy Raman

spectrometer with a LN₂-cooled charge-coupled-device (CCD) detector and a holographic notch filter. The molecule probe used in this study was trans-1,2-bis(4-pyridyl)ethylene (BPE), which exhibited high Raman scattering cross section [13, 14]. All samples for SERS measurement were prepared by dropping 30 μL of 1 mM BPE in methanol onto the Au, Ag, AuAg, and Au@Ag films and allowing the solvent evaporate. The Raman spectral of 100 mM BPE in methanol was also measured. The SERS excitation wavelength was provided by the 488.0 nm line of a NEC Ion laser. The laser power density at the sample position was about 12 W/cm² for BPE on the SERS substrates. All the spectra reported here were the results of a single 10-s accumulation at room temperature.

Results and discussion

Structural analysis

The packing structures and topographies of Au, Ag, AuAg multilayer, and Au@Ag films were investigated by AFM. These particles are spherical and have good uniformity, as shown in Fig. 1. The average diameters of pure Au and Ag nanoparticles are 15 and 30 nm, respectively, as shown in Fig. 1a and b. While the Ag nanoparticles in AuAg multilayer (Fig. 1c) shows the same diameter as that in Ag NP film. The average diameter of Au@Ag composite nanoparticles (Fig. 1d) is 50 nm and larger than those diameters of pure Au and Ag nanoparticles, which indicates that gold nanoparticles are coated by silver nanoparticles.

Optical and SERS properties

The UV–Vis–NIR absorption spectra of the Au, Ag, AuAg and Au@Ag films are shown in Fig. 2. The Au and Ag monolayer shows the absorption bands at 520 and 415 nm, which are attributed to the surface plasmon resonance (SPR) of Au and Ag nanoparticles, respectively [9]. In addition, the weak absorption band around 620 nm (Au) and 700 nm (Ag) can be attributed to the SPR coupling band of aggregated Au and Ag nanoparticles, respectively. The AuAg monolayer shows two distinctive absorption bands at 515 and 370 nm due to the SPR of Au and Ag nanoparticles, respectively. While the Au@Ag monolayer show only one absorption band at 460 nm, which indicates that the gold nanoparticles are capped by silver shell [15, 16] in the Au@Ag monolayer.

One of the major goals of the present study is to prepare SERS active substrates that can be useful for investigating the molecules adsorbed on them. Figure 3 shows the surface-enhanced Raman spectra of trans-1,2-bis(4-pyridyl)ethylene (BPE) adsorbed on these nanoparticles at

Fig. 1 AFM images of (a) pure-Au, (b) Ag [reproduced from ref. [9] with permission] and (c) AuAg multilayer and (d) Au@Ag films

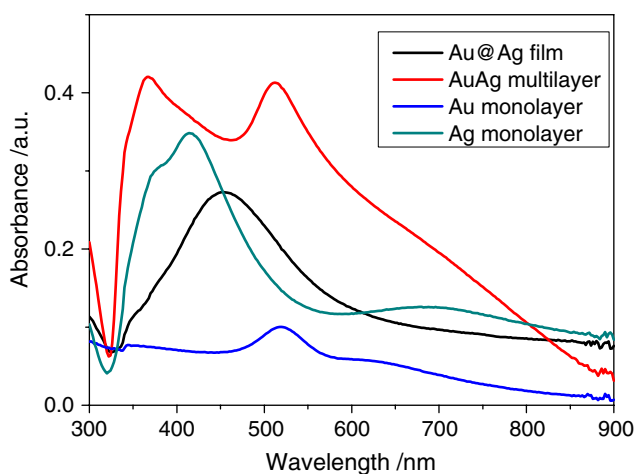
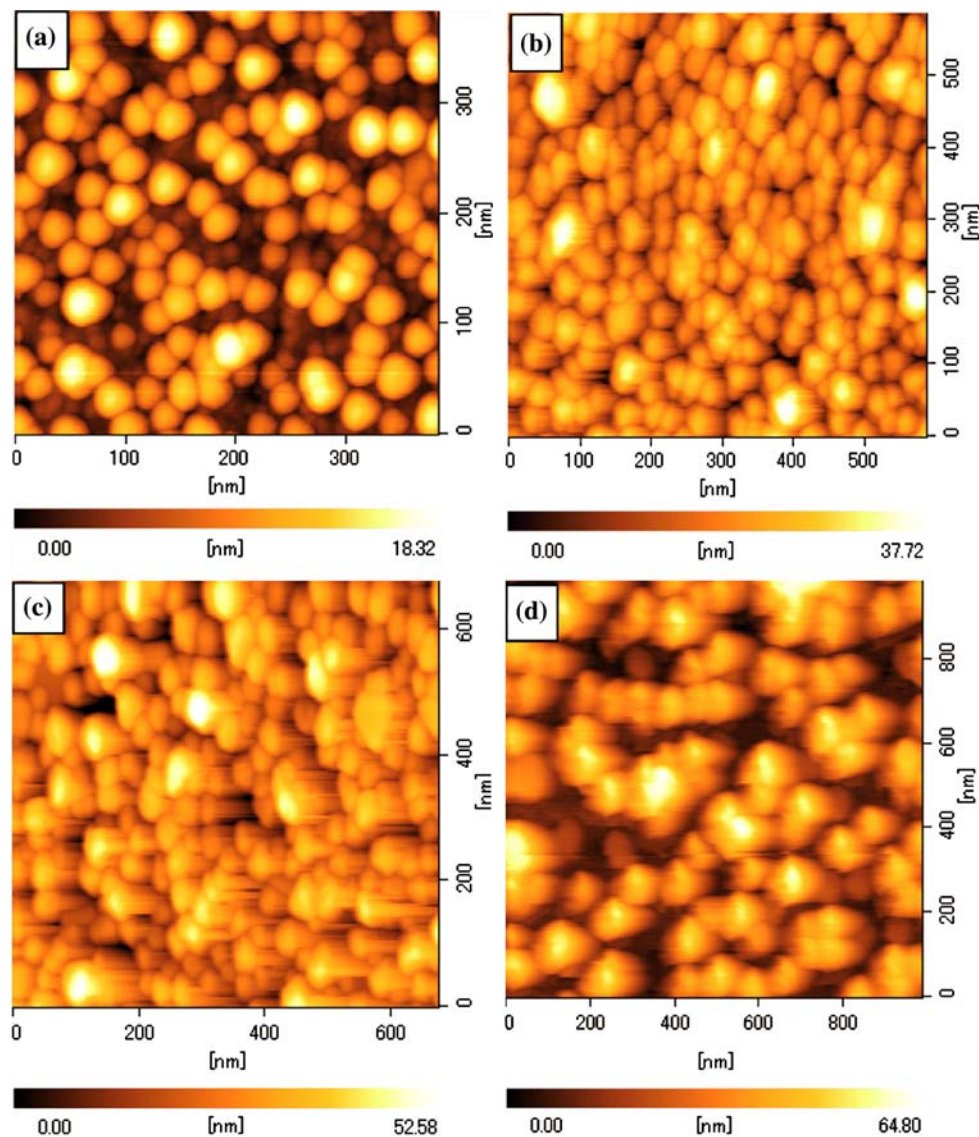


Fig. 2 The UV-Vis-NIR absorbance spectra of self-assembled Au, Ag, AuAg multilayer and Au@Ag films

an excitation wavelength of 488.0 nm for Au, Ag, AuAg, and Au@Ag films. These peaks around 1,200, 1,600 cm^{-1} are attributed to BPE signals [13]. The Au nanoparticle monolayer deposited on glass shows a very weak Raman spectrum, which indicates that gold is SERS-inactive at the excitation wavelength 488.0 nm [2, 14]. The Ag nanoparticle monolayer shows a strong Raman signal, indicating Ag nanoparticles are SERS-active substrates. The AuAg multilayer exhibits stronger Raman signal than pure Ag monolayer, which can be attributed to the coupling of dipole plasmon between Au and Ag nanoparticles [17]. What is more, the Au@Ag film shows a much stronger SERS signal from BPE than those from pure Au, Ag, and AuAg films, indicating the Au@Ag film is more powerful than Ag, Au, and AuAg film as SERS active substrates.

The surface enhancement factor (SEF) was calculated for BPE on our samples according to the equation [13], as follows:

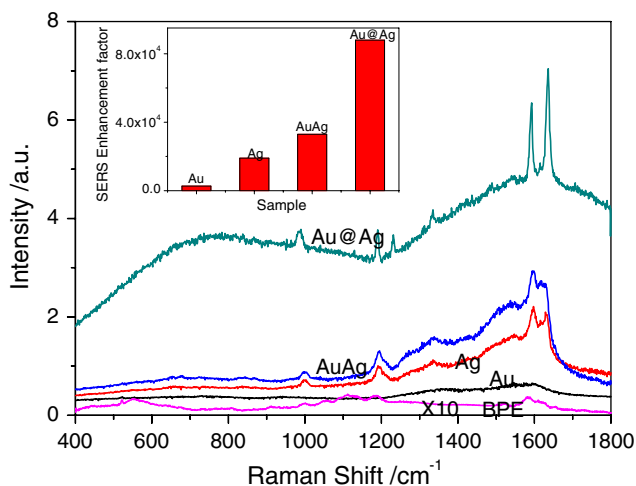


Fig. 3 SERS spectra of BPE solution and BPE adsorbed on Au, Ag, AuAg and Au@Ag films

$$\text{SEF} = \frac{I_{\text{surf}}/N_{\text{surf}}}{I_{\text{bulk}}/N_{\text{bulk}}} \quad (1)$$

where I_{surf} and I_{bulk} denote the integrated intensities for the $1,600 \text{ cm}^{-1}$ band of the BPE adsorbed on the sample surface and BPE in solution, respectively, whereas N_{surf} and N_{bulk} represent the corresponding number of BPE molecules excited by the laser beam. The calculated SERS SEF for our samples is shown in the inset of Fig. 3. The SEF of Ag nanospheres is evaluated to be 1.9×10^4 , the same order of magnitude with the reported Ag nanoparticles with the diameter of 60 nm excited at 497 nm [14] and higher by one order of magnitude than that of gold nanoparticles monolayer. Furthermore, the SERS enhancement factor observed on Au@Ag films is ~ 5 times higher than that of the Ag monolayer. The larger SERS enhancement for Ag-capped Au monolayer is due mainly to electronic ligand effect and localized electric field enhancement in core-shell nanoparticles under laser excitation [18]. Recently theoretical studies on core-shell structures suggest that the local field effects can be enhanced several orders of magnitude and are responsible for the enhanced SERS signals [19].

Conclusions

In summary, we have prepared Au, Ag, AuAg multilayer, and Au@Ag nanoparticles and self-assembled on glass substrates by layer-by-layer technique for SERS-active substrates. The Au@Ag film shows a much stronger SERS

signal than those from pure Au, Ag, and AuAg multilayer films, indicating the Au@Ag film is more powerful than pure Au, Ag, and AuAg multilayer as SERS active substrates. The larger SERS enhancement for Ag-capped Au monolayer is due mainly to electronic ligand effect and localized electric field enhancement in core-shell nanoparticles under laser excitation.

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