Facile Fabrication and Raman Scattering Enhancement Properties of Mixed Gold and Silver Nanoparticle Layers

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I have fabricated gold and silver nanoparticle layers on amino-terminated glass substrates by immersion processes from aqueous colloidal solutions of gold and silver nanoparticles. The composition ratio of nanoparticles on the modified substrates was varied by the mixing ratio of corresponding colloidal solutions of nanoparticles. Raman signals of rhodamine 6G were observed on the nanoparticle-modified substrates. In the case of the mixed gold and silver nanoparticle-modified substrates, the intensities of the Raman signals were larger than the intensities expected from a simple proportional sum of the Raman signals obtained using a gold nanoparticle layer or a silver nanoparticle layer. The nonlinear enhancement properties of the Raman signal intensities may be attributable to unique localized surface plasmon resonance between the gold and silver nanoparticles.

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Keywords: Surface-enhanced Raman scattering; Gold nanoparticle; Silver nanoparticle; Localized surface plasmon resonance

I. INTRODUCTION

Gold and silver nanoparticles have received considerable attention as next-generation optical materials. These nanoparticles, with diameters ranging from several nanometers to sub-micrometers, can interact with ultraviolet-visible-near infrared (UV-vis-NIR) light because they exhibit appreciable surface plasmon bands in this wavelength region. Localized surface plasmon resonance (LSPR) is observed on the surface of gold and silver nanoparticles, and it produces a highly localized electromagnetic field under illumination. LSPR has made it possible to greatly enhance the sensitivity of Raman scattering; the enhanced scattering is known as surface-enhanced Raman scattering (SERS) [1–6]. LSPR can also excite surface-adsorbed materials as light, which is essential for enhancing the efficiencies of fluorescence emission of organic and inorganic fluorescent materials [7–12], photovoltaic conversion of photovoltaic devices [13–21], and so on.

Controlling the near-surface electromagnetic field is an important factor for the application of plasmonic nanoparticles. For example, the enhancement factor of SERS is largely dependent on the size and shape of the nanoparticles. It is well known that strong Raman signals are observed at junctions of two adjacent particles, at protrusions of particles, and so on [1, 22–24]. At such a local nanospace, extremely strong LSPR is generated, which can also be estimated theoretically.

Combinations of different metal (ex. gold and silver) nanoparticles and core-shell architecture nanoparticles are quite interesting for developing plasmonic materials. Indeed, several groups reported that the considerably larger SERS was observed using bimetal plasmonic materials than that using corresponding monometal plasmonic material [25–27].

In this research, we have prepared mixed gold and silver nanoparticle layers on amino-terminated glass substrates by an immersion process, in which the mixing ratio of gold and silver nanoparticles was varied systematically. Raman scattering spectra of rhodamine 6G on the nanoparticle-modified substrates were measured and compared with each other.

II. EXPERIMENTAL

All chemicals were used as received. Water was used following distillation. Aqueous colloidal solutions of gold and silver nanoparticles (AuNPs and AgNPs) were prepared by the reduction of HAuCl₄ and AgNO₃ with trisodium citrate salt, which were based on the previous report [28]. Briefly, 190 mL of aqueous HAuCl₄ solution (2.5 × 10⁻⁴ M) was refluxed. Next, 1.4 mL of aqueous trisodium citrate solution (1 wt%) was added to the refluxing solution, which was then refluxed for 1 h to obtain a colloidal AuNP solution. For the preparation of AgNPs,

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36 mg of AgNO₃ was dissolved in water (200 mL). After refluxing the solution, 4.0 mL of aqueous trisodium citrate solution (1 wt%) was added, and refluxing continued for 1 h.

Hydrophilic amino-terminated glass slides (MAS⃝coated) were obtained from Matsunami Glass Co. and used as received. Mixed solutions (20 mL) of AuNPs colloidal solution and AgNPs colloidal solution (100:0, 25:75, 50:50, 75:25, and 0:100, v/v) were prepared. MAS⃝coated glass slides were dipped in the mixed colloidal solution of AuNPs and AgNPs and left overnight [12]. The glass slides were then washed well with distilled water and dried with a stream of N₂ gas. The obtained nanoparticle-modified glass slides were denoted as AuNPs(n):AgNPs(m)/MAS (n:m = 100:0, 25:75, 50:50, 75:25, and 0:100).

R6G solution was dropped on the AuNPs:AgNPs/MAS substrates such that the solution spread uniformly, and then, the substrates were spin-coated (500 rpm for 5 s, then 2000 rpm for 60 s), followed by drying in air to obtain R6G/AuNPs(n):AgNPs(m)/MAS (n:m = 100:0, 25:75, 50:50, 75:25, and 0:100) (Fig. 1). R6G-modified MAS⃝coated glass (R6G/MAS) was also fabricated by spin-coating as a corresponding reference.

Extinction spectra of the aqueous colloidal solutions and nanoparticle-modified glass slides were measured by a UV-vis-NIR spectrophotometer (V-670, JASCO). Raman scattering spectra of R6G-nanoparticle-modified substrates and the corresponding reference were obtained by a micro-Raman spectrometer (NRS-5100, JASCO). The excitation source was a 532 nm CW laser with a power of approximately 30 mW. The laser was focused onto the sample by using an objective lens (×100). To reduce the degradation of the samples, the excitation laser was passed through a neutral density filter (OD = 3). Raman signals were averaged from 10 independent measurements, which were obtained by one-shot measurements with 1 s of sampling time on each measurement point.

Extinction spectra of aqueous colloidal solutions of (a) gold nanoparticle and (b) silver nanoparticle.

III. RESULTS AND DISCUSSIONS

Extinction spectra of aqueous colloidal solutions of AuNPs and AgNPs are showed in Fig. 2. A characteristic plasmon absorption band attributable to gold nanoparticles was observed around 530 nm in the solution of AuNPs. An obvious absorption peak around 410 nm attributable to a plasmon band of silver nanoparticles was also observed in the solution of AgNPs.

The extinction spectra of nanoparticle-modified substrates AuNPs(n):AgNPs(m)/MAS (n:m = 100:0, 25:75, 50:50, 75:25, and 0:100) are shown in Fig. 3. AuNPs(100):AgNPs(0)/MAS had absorption peaks around 520 and 750 nm; the former was mainly attributable to the plasmon band of isolated AuNPs, whereas the latter was attributable to interparticle plasmon coupling of aggregated AuNPs. In AuNPs(0):AgNPs(100)/MAS, a similar pattern of absorption peaks was observed, with absorption bands around 400 and 670 nm. The former was attributable to isolated AgNPs, and the latter was attributable to interparticle plasmon coupling of aggregated AgNPs. For the mixed nanoparticle-modified substrates, the absorption profiles can nearly be interpreted as a mixture of AuNPs and AgNPs.

The extinction intensity at 532 nm for all nanoparticle-modified substrates is plotted in Fig. 4. The extinction intensity increased linearly with increasing ratio of AgNPs solution in the mixed AuNP:AgNP nanoparticle solution for preparation of nanoparticle modified substrates. Therefore, no obvious interaction between AuNPs and AgNPs was observed from the viewpoint of light absorption at 532 nm on the nanoparticle-modified substrate. On the other hand, the extinction intensity of R6G on AuNPs(n):AgNPs(m)/MAS at 532 nm was negligibly smaller than that of AuNPs(n):AgNPs(m)/MAS itself. Because, obvious extinction peak due to R6G was not observed in R6G/AuNPs(n):AgNPs(m)/MAS.
FIG. 4: Extinction intensity of nanoparticles modified glass substrates at 532 nm.

FIG. 5: Raman scattering spectra of R6G on nanoparticles modified glass substrates and amino-terminated glass without nanoparticles. (a) R6G/AuNPs(0) : AgNPs(100)/MAS, (b) R6G/AuNPs(25) : AgNPs(75)/MAS, (c) R6G/AuNPs(50) : AgNPs(50)/MAS, (d) R6G/AuNPs(75) : AgNPs(25)/MAS, and (e) R6G/AuNPs(100) : AgNPs(0)/MAS, (f) R6G/MAS

As obtained Raman scattering spectra of R6G adsorbed onto AuNPs(n):AgNPs(m)/MAS (n:m = 100:0, 25:75, 50:50, 75:25, and 0:100) without any spectral correction are shown in Fig. 5. Clear Raman scattering peaks at 1128, 1184, 1310, 1361, 1509, 1573, and 1648 cm\(^{-1}\) from R6G were observed on the nanoparticle-modified substrates. In contrast, in the case of R6G spin-coated MAS glass slides (R6G/MAS), no obvious peak of Raman scattering from R6G was observed under same measurement condition. As described before, the extinction intensity of R6G on nanoparticle-modified substrates was almost negligible comparing with that of AuNPs and AgNPs. Therefore, AuNPs and AgNPs deposited on MAS-coated glass enhanced Raman scattering from R6G; qualitatively, AgNPs are more effective for enhancing Raman scattering than AuNPs.

Figure 6 shows the relative Raman scattering spectra of samples after these spectral correction: 1) linear baseline suppression, 2) normalization for the extinction intensity at 532 nm. Interestingly, R6G/AuNPs(50):AgNPs(50)/MAS and R6G/AuNPs(25):AgNPs(75)/MAS showed higher intensity of Raman scattering than R6G/AuNPs(0):AgNPs(100)/MAS. The intensities of the characteristic Raman scattering peaks of R6G at 1361 and 1648 cm\(^{-1}\) in Fig. 6, which are assignable to aromatic stretching vibrations of R6G. Relative intensities of Raman signals at 1361 and 1648 cm\(^{-1}\) are plotted for all R6G/AuNPs(n):AgNPs(m)/MAS, in Fig. 7. At both wavenumbers, the intensities of Raman signals in the mixed AuNPs and AgNPs layers, R6G/AuNPs(n):AgNPs(m)/MAS (n:m = 25:75, 50:50, and 75:25), were higher than the intensity of Raman signals from AuNPs or AgNPs alone.
signals expected from the proportional addition of R6G/AuNP(m)/AgNP(n)/MAS (n/m = 100:0 and 0:100).

These nonlinear enhancement properties of Raman scattering are quite interesting from a viewpoint of similarity with the enhancement of Raman scattering using combinations of gold and silver nanoparticles, core-shell nanoparticles and nano-sized hetero dimer [25–27].

In this research, detailed mechanism of the nonlinear enhancement of Raman scattering is not clear at stage. However, at least, the mixed layer of AuNPs and AgNPs may cause larger LSPR field between nanoparticles than that of monometal nanoparticle (AuNPs or AgNPs) layer. As a result, a nonlinear enhancement profile of Raman signals of R6G was seemingly obtained, which was depended on the mixing ratio of AuNPs and AgNPs solutions. After considering the effect of nanoparticle sizes and AuNPs-AgNPs ratio on glass substrates, a more detailed mechanism of enhanced Raman signals will be discussed. In addition, fluorescence emission enhancement of photoexcited dye molecules (e.g., porphyrins) using AuNP-AgNP-modified substrates will also provide valuable information about strong electric fields around nanoparticles or charge transfer between gold and silver nanoparticles. My current work focuses on this objective.

IV. CONCLUSION

I have succeeded in the fabrication of mixed gold and silver nanoparticles layers on amino-terminated glass substrates using immersion processes. Gold and silver nanoparticle layers with several mixing ratios of gold and silver nanoparticles were obtained from the mixed colloidal solutions of gold and silver nanoparticles. Raman signals from rhodamine 6G were strongly enhanced by the nanoparticle layers. The intensities of Raman signals of rhodamine 6G on mixed gold and silver nanoparticle layers were larger than that expected when gold or silver nanoparticle layers were used individually.

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