

SERS activity of Au nanoparticle films

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The core-shell gold nanoparticle film is fabricated by using nanolithography and self-assembly monolayer technology. The film exhibits unique optical properties and has strong surface enhanced Raman scattering (SERS) activity. The relationship between nanostructure and surface electrical field is studied by employing pyridine as the SERS probe. It is found that particle size and inter-particle space are important factors. The enhancement ratio is measured to be more than 10^4 .

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Noble metal nanoparticles (MNPs) exhibit strong absorption in the ultraviolet (UV) to visible band because of the resonant collective conduction oscillation known as localized surface plasmon resonance (LSPR)^[1–3]. The resonance wavelength depends on the MNP size, shape, and inter-particle space. The extinction peak of the LSPR wavelength is very sensitive to the surrounding environmental dielectric constant change, which makes the LSPR much more attractive in bio-sensing applications. Currently, man-made noble metal nano and sub-wavelength structures, by virtue of their unique optical and electronic properties, are the hot topic in nanophotonics and biotechnology. The underlying mechanism of how the structure contributes to the LSPR is a key factor for the improvements in nanostructure design and detection sensitivity. Surface enhanced Raman scattering (SERS), as a sensitive surface analysis tool, has been applied widely in biotechnology, electrochemistry, and photonics^[4–9]. SERS was first observed in 1970s. When molecules was deposited on a rough noble metal electrode, greatly enhanced Raman scattering was obtained. The further detailed experimental and theoretical work proved that this great enhancement was not simply caused by the increase of the surface area due to the roughness. The localized electromagnetic phenomenon associated with the roughness of such noble metal surfaces was one of the dominant factors attributing to the enhancement. Noble MNPs and some man-made nano and sub-wavelength structures were proved to have SERS activity. The enhancement was caused by the LSPR of the structure. In this letter, we report the fabrication of a core-shell gold nanoparticle film. The surface field enhancement associated with the structure is studied by SERS.

A core-shell gold nanoparticle film was fabricated based on nanolithography technique. In brief, the process can be described as follows. The template of polystyrene nanospheres was made by chemical self-assembly technology^[10,11]. Then a golden layer with specific thickness was deposited onto the template by thermal evaporation coating. The core-shell gold nanoparticle film which consisted of polystyrene core and gold shell was thus obtained.

The SERS experiment was carried out on an RM1000 Renishaw system, equipped with a $50\times$ Leica Microscope with ultra-long working distance. A He-Ne laser with the excitation wavelength at 632.8 nm was used.

$5\text{-}\mu\text{L}$ pyridine solutions at the concentrations of 1 mol/L and 1 mmol/L were prepared. The core-shell gold films with the polystyrene sphere sizes of 50, 100, 200, and 350 nm were fabricated by the method described above. Planar gold surface with the thickness of 50 nm was also prepared by thermal evaporation deposition for comparison.

Figure 1(a) shows the scanning electron microscopy (SEM) image of the gold nanoparticle film. The template composed of polystyrene showed a sub-monolayer dense assembly. Figure 1(b) shows the optical density (OD) spectrum of the gold film of the template in Fig. 1(a). The OD spectrum had an extinction peak around 565 nm. This extinction peak was template dependent. Several other templates with the polystyrene sphere sizes of 50, 200, and 300 nm were also made. These films exhibited different colors as brown, green, and pink, respectively, due to their different extinction peaks in the OD spectra. Also several templates composed of multi-layer

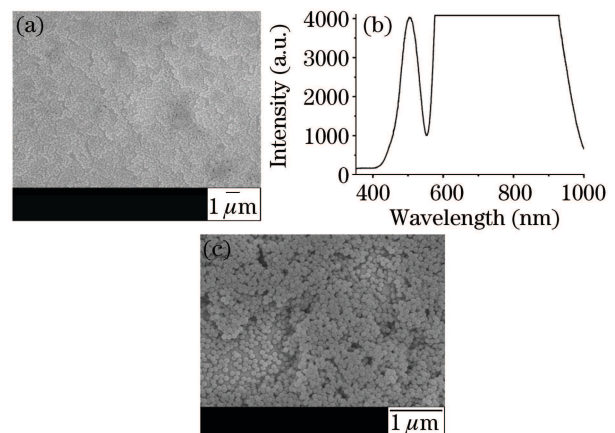


Fig. 1. Structure and OD spectrum of the core-shell gold nanoparticle film. (a) SEM image of sub-monolayer structure of the template; (b) OD spectrum of the gold film with the particle size of 100 nm; (c) SEM image of multi-layer deposition of particles around the border of the template.

assemblies of polystyrenes were fabricated. Several colors showed up on the different parts of the same film due to the unhomogeneous distribution of the particles. The film exhibited blue around the border where multi-layers were dominant. The color changed into violet in the center of the sample. The SEM image in Fig. 1(c) was taken around the border, showing the assembly of multi-layers of polystyrenes.

The extinction peak in the gold nanoparticle film was caused by the LSPR effect. It resulted from the enhancement of the electromagnetic field around the nanoparticles. According to Raether^[12], when the particle size $a \ll \lambda$ in which λ is the incident wavelength, the outside electric field of the particle was described as

$$E(a) = 2 \frac{\varepsilon_1 - 1}{\varepsilon_1 + 2} E_0 + E_0 = \frac{3\varepsilon_1}{\varepsilon_1 + 2} E_0, \quad (1)$$

where ε_1 is the dielectric constant of the metal, E_0 is the incident electric field. When the real part of ε_1 is equal to -2 , the surface electric field enhancement factor could be

$$T_{el} = \left| \frac{E(a)}{E_0} \right|^2 = \left| \frac{3\varepsilon_1'}{\varepsilon_1'} \right|^2. \quad (2)$$

Equation (2) shows that the enhancement results from the surface electric field associated with the particle structure. Thus the enhancement provides us a way to further study how the structure contributes to the surface electric field that is also associated with LSPR.

5 μ L of 1-mol/L pyridine solution was dropped onto the planar gold surface. The typical vibration mode of

pyridine was measured, as shown in Fig. 2(b). There are two typical peaks at 1002 and 1034 cm^{-1} . A 1000-fold dilution of the pyridine solution was then dropped onto the planar gold surface, and no peak was observed, as shown in Fig. 2(a). This 1-mmol/L pyridine solution was then dropped onto the gold nanoparticle film. As expected, the enhanced signal was measured. In the result measured from the 100-nm polystyrene gold nanoparticle film (Fig. 2(b)), three peaks are seen clearly. Compared with the pyridine peaks on the planar gold surface in Fig. 2(b), the signal enhancement was more than 10^4 . The first peak was split into two, and the second peak had a red shift. The mechanism of SERS was well recognized from electromagnetic enhancement associated with LSPR and chemical enhancement. Based on the mechanism, the localized surface plasmon properties depending on the nanostructure of the template were exhibited by SERS.

Comparing the results in Fig. 2(b), it is obvious that the particle size has a great influence on the enhancement. Sizes of 50 and 100 nm are much better than 200 and 350 nm. It is clearly shown that the size of 50 nm has the best enhancement.

In conclusion, the surface electric field enhancements by nano and sub-wavelength structures were studied by SERS. The nanoparticle size of the template plays a dominant function of enhancement, as expressed in Eq. (2). This theory is mainly based on the single-particle model. However, for man-made films, due to the fact that particles are close to each other, the particle interaction would be another factor to be studied in our future work.

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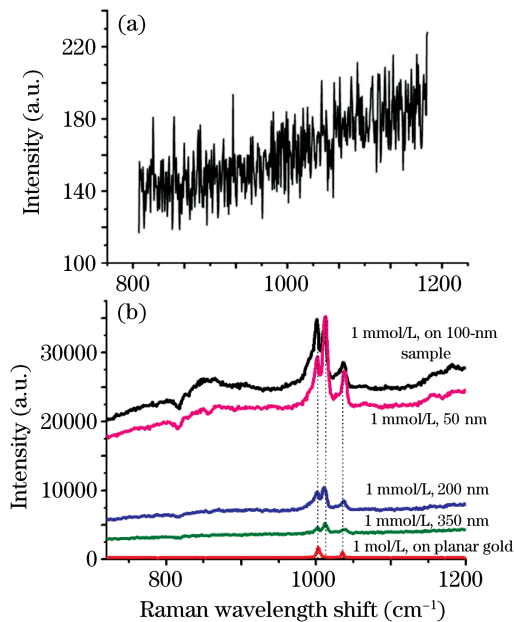


Fig. 2. SERS activity of gold nanoparticle films. (a) No signal was detected for the diluted pyridine solution (1 mmol/L) on planar gold surface; (b) SERS of 1-mmol/L pyridine on gold nanoparticle films with the particle sizes of 50, 100, 200, and 350 nm, compared with 1-mol/L pyridine on planar gold surface.