# Influence of local environment on the intensity of the localized surface plasmon polariton of Ag nanoparticles*

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A combined Ag nanoparticle with an insulating or conductive layer structure has been designed for molecular detection using surface enhanced Raman scattering microscopy. Optical absorption studies revealed localized surface plasmon resonance, which shows regular red shift with increasing environmental dielectric constant. With the combined structure of surface enhanced Raman scattering substrates and rhodamine 6G as a test molecule, the results in this paper show that the absorption has a linear relationship with the local electromagnetic field for insulating substrates, and the electrical property of the substrate has a non-negligible effect on the intensity of the local electromagnetic field and hence the Raman enhancement.

**Keywords:** silver nanoparticles, resonance absorption, surface enhanced Raman scattering, local environment

**PACC:** 7320M, 3220F, 3320K

Noble metal nanoparticles (NPs) embedded in dielectric substance exhibit extraordinary optical resonances in the visible region.[1−3] In the case of small particles with a diameter comparable to the mean free path of the electrons, they can be excited by an electromagnetic radiation, and exhibit localized surface plasmon resonance (LSPR) due to the collective oscillations of their conduction electrons, leading to selective photon absorption and enhancement of the local electromagnetic (EM) field near the surface of NPs.[3,4] The optical and electromagnetic characteristics enable the noble metal NPs to be promising for a wide range of application in chemical[5] and biological sensors,[6] optical filters,[7] optical tweezers[8], ultrafast optical switching,[9] and surface enhanced Raman spectroscopy (SERS).[6,10,11] SERS has recently evolved into an important laser spectroscopic characterization technique applied to biomedically significant molecules to investigate their structural functional properties.[11,12] The SERS effect is remarkable; however, the detailed mechanisms for the sensitivity enhancement are complex.[13] So far the theoretical and experimental investigations clearly demonstrate that the strong EM field enhancement induced by LSPR, which leads to so-called 'hot-spots', makes a major contribution to the Raman enhancement.[14,15] Over the past few years, various experimental studies have been carried out to manifest the SERS effect, including changing the NPs' size, shape, interparticle separation, alignment and the shape/dielectric constant of the substrate, etc.[15−18] But the influence of the electrical property of the substrate has not been investigated yet. In this paper, we demonstrate that the electrical property has a non-negligible effect on the EM field intensity and hence on the SERS effect.

The sensitive SERS material used in this work is Ag NPs, produced by thermal evaporation. The thermal evaporation technique has been proved to be a simple and reproducible method for fabrication of Ag NPs with high SERS enhancement factor.[19] With this method, control of particle morphology and optical property is relatively easy.[20] To obtain different electric conductive substrate, we deposited the electrically insulating $Al_2O_3$ layer and the trans-

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parent conductive oxide ITO layer by reactive thermal evaporation with different $O_2$ flux on borosilicate glass substrates. Compositional analysis of $Al_2O_3$ and ITO thin films was performed by means of XPS (not shown in this paper). The amount of Ag, $Al_2O_3$ and ITO evaporating on the glass was recorded with a quartz crystal oscillator, and converted to equivalent mass thickness ($d_m$) for ideal continuous film with bulk density. In order to reduce the fluorescence and photoreactivity,[10,21] we choose NIR–FT Raman, which uses a 1064-nm excitation wavelength (Nd:YAG laser) with an output power of 200 mW. FT-Raman spectroscopy has an experimental limitation that the excitation laser is limited to 1064 nm, and the Raman scattering intensity is much smaller than the confocal Raman which uses 325, 488, 514 and 633 nm excitation wavelengths, etc. So the SERS is more important to the NIR–FT Raman and it has the advantage that the laser light does not raise the sample temperature to a great extent, which is suitable for analysis of biological samples. The SERS performances are investigated using a rhodamine 6G (R6G) molecule ($10^{-3}$ M solution), since R6G is extensively studied and well characterized by SERS.[15,22]

Scanning electron microscopic (SEM) images were collected at an acceleration voltage of 15 kV in vacuum ($\sim 10^{-6}$ Pa) using a JEOL Rigaku 6700F. Figure 1 shows the images of Ag, $Al_2O_3$, ITO thin films deposited on glass and Ag NPs deposited on $Al_2O_3$ and ITO films. The borosilicate glass substrates were boiled in cleaning agent and ultrasonically cleaned in ethanol subsequently for 15 min, respectively, and then dried with pure nitrogen flow. To obtain insulating substrate with different dielectric constant from glass, a 3-nm $Al_2O_3$ layer (equivalent mass thickness $d_m$ recorded by quartz crystal oscillator) was deposited on the glass before the Ag NPs. Correspondingly, a 80-nm ITO layer was deposited to make the substrate conductive (the sheet resistance is 56 Ohm/sq). Figures 1(b) and 1(c) show that the $Al_2O_3$ and ITO are so flat that we could see no morphology at a magnification factor of $1\times10^5$. Theoretical and experimental results clearly show that the so-called 'hot-spots', induced by LSPR coupling between the NPs, make a major contribution to the Raman enhancement.[14,15] The Ag NPs deposited on $Al_2O_3$ and ITO thin films exhibit the same morphology to those deposited on glass, having a random configuration which provides numerous contacts and thus achieving a sufficient hot-spot effect.[13] So the Ag NPs we obtained may be capable of obtaining a high enhancement factor.

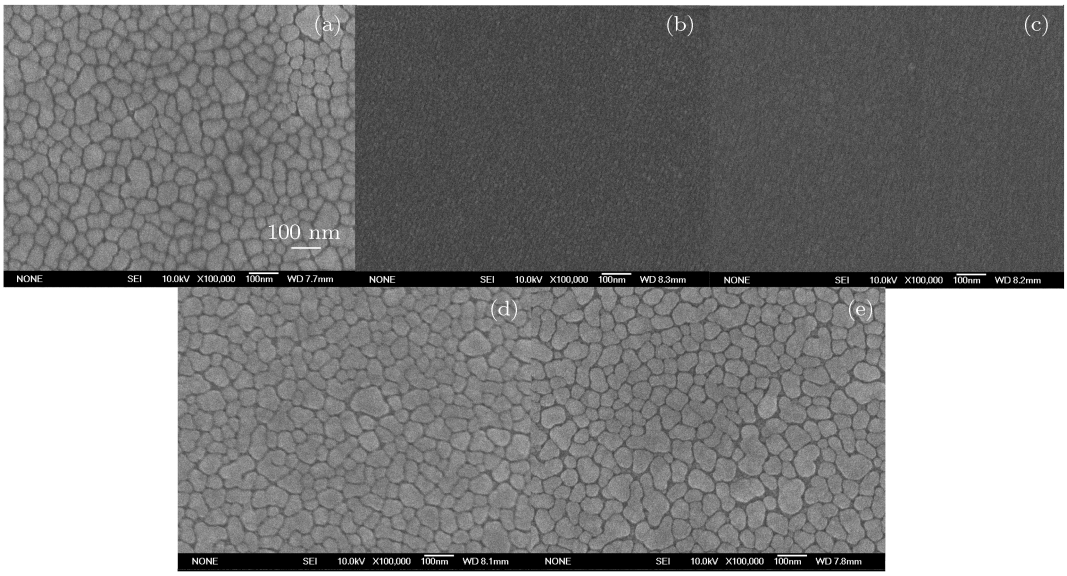



**Fig. 1.** The SEM images of (a) Ag NPs deposited on glass, (b) $Al_2O_3$ deposited on glass, (c) ITO deposited on glass, (d) Ag NPs deposited on $Al_2O_3$ film, (e) Ag NPs deposited on ITO film. The deposition conditions of Ag NPs in figures (a), (d) and (e) were the same: $d_m = 17$ nm (equivalent mass thickness), $r_d = 0.1$ nm/s (deposition rate), $T_s = 160$ °C (substrate temperature), in a vacuum of $10^{-5}$ Torr (1 Torr=133 Pa).

Calculations and observations indicate that the extinction cross-section is dominated by the scattering corss-section for surface plasmon resonance.[1] Therefore we could extract the resonant wavelength from the optical spectra conveniently.[2] Ultraviolet–visible–near infrared (UV–VIS–NIR) absorption spectra of Ag NPs on different substrates were recorded using a UV-3600 spectrophotometer (Shimadzu Corporation, Japan) fitted with an integrating sphere. The absorption of $Al_2O_3$ and ITO films indicates that the two kinds of transparent film have neglectable absorption in the visible and infrared regions. So the salient features in the absorption spectra are mainly related to the LSPR property of Ag nanoparticles. The resulting spectra for 14-nm Ag NPs deposited onto different substrates, referenced to a certain measurement area, are displayed in Fig. 2(a). These spectra show a broad band of LSPR absorption. With background materials of different dielectric constants, the interaction between the photons and the electrons will change. In fact, the substrate induces degenerate dipolar plasmon mode splitting by the inhomogenous electromagnetic field and hence changes the resonant wavelength.[23] In the case of these evaporating samples, the surrounding material consists of the substrate and air, and the plasmon resonance peak shifts due to the dielectric constant changes in the adjacent medium of Ag NPs.[23] As the mass thickness of the $Al_2O_3$ layer increases, the resonant wavelength of LSPR shows a regular red shift from 466 nm to 495, 500 and 507 nm respectively, and the attached figure in Fig. 2(a) shows the increasing absorbance at near-infrared regions. In Fig. 2(b) the spectra exhibit a stronger absorption and the resonance wavelength for Ag NPs on glass redshifts from 466 nm to 482 nm with the equivalent mass thickness of Ag layer increasing to 17 nm. The resonant wavelength also shows regular redshift (482 nm, 512 nm and 625 nm) with the increase in dielectric constant[1,23] ($n_{\rm glass} \approx 1.5$, $n_{\rm Al_2O_3} \approx 1.76$ and $n_{\rm ITO} \approx 2$ in the visible and near infrared regions). Moreover, the absorption of Ag NPs deposited on ITO is significantly larger in the infrared region and the absorption peak at 300 nm which arises from the free carrier in ITO. When adding a thin layer of $Al_2O_3$ to the ITO substrate, the absorption peak blueshifts. Since the peak exhibits significant sensitivity to the local dielectric constant,[1,23] it shows that the $Al_2O_3$ layer has successfully covered the ITO substrate.

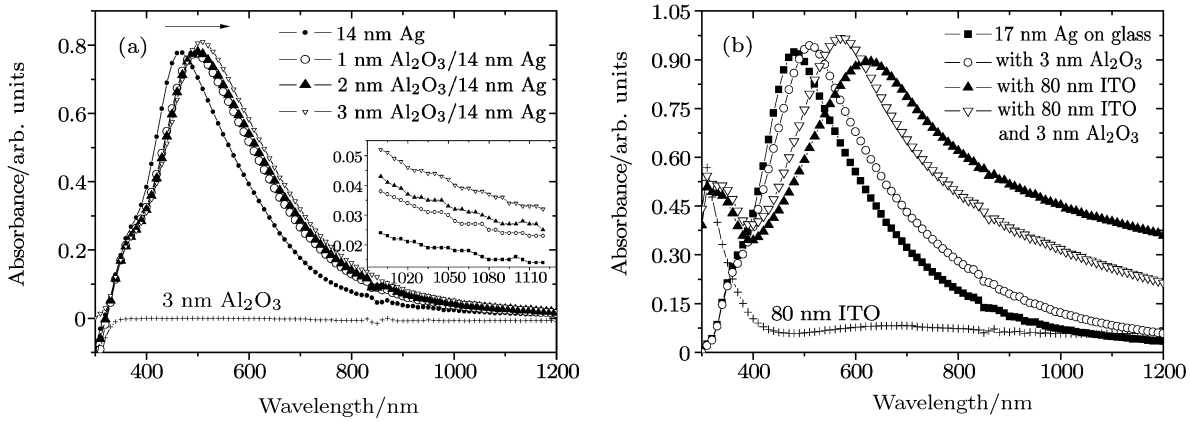



**Fig. 2.** Optical extinction spectra for Ag NPs deposited on substrates with different mass thicknesses and dielectric constants. (a) The mass thickness of the electrically insulating $Al_2O_3$ layer is 0, 1, 2 and 3 nm respectively, the thickness of the Ag layer is 14 nm. (b) 17-nm Ag NPs deposited on glass, $Al_2O_3$ and ITO thin films respectively.

R6G dissolved in ultrapure water (filtered by a Milli-Q reagent water system at a resistivity of $> 18$ MΩ·cm) was used as the SERS active molecule, which was deposited on the surface of the substrate using a micropipette resulting in a 4-$\mu$l drop. The water was allowed to evaporate, creating a 0.3-cm$^2$ drop area. As a reference, the Raman spectra from the $10^{-3}$-M and $10^{-2}$-M R6G solution deposited on glass substrate were also recorded in Fig. 3. A comparison of the spectra reveals a significant enhancement of the Raman scattering intensity caused by different combined SERS substrate layers. Numerous peaks are distinctly observed in the spectra. The most pronounced ones are 1306, 1360, and 1507 cm$^{-1}$, which can be assigned to be aromatic stretching vibrations, whereas the peak at 606 cm$^{-1}$ is due to the in-plane deformation vibration of the ring.[24] The Raman signals

have subtracted the background signal and the SERS enhancement factor ($EF$) is shown in Table 1, which was obtained by the method described in Ref. [25] as

$$EF = \left|\frac{I_{\rm SERS}}{I_{\rm Raman}}\right| \times \left|\frac{N_{\rm Raman}}{N_{\rm SERS}}\right|, \tag{1}$$

where $I_{\rm SERS}$ is the intensity of a vibrational mode in the surface-enhanced spectrum, and $I_{\rm Raman}$ is the intensity of the same mode in a normal Raman spectrum, $N_{\rm Raman}$ is the number of molecules adsorbed and sampled on glass, and $N_{\rm SERS}$ is the number of molecules on the SERS-active substrate. As a certain measurement area is used on different substrates, the sampled molecules ratio $N_{\rm Raman}/N_{\rm SERS}$ is equivalent to the sampled concentration ratio 10 as $10^{-3}$ M on SERS-active substrate and $10^{-2}$ M on glass.

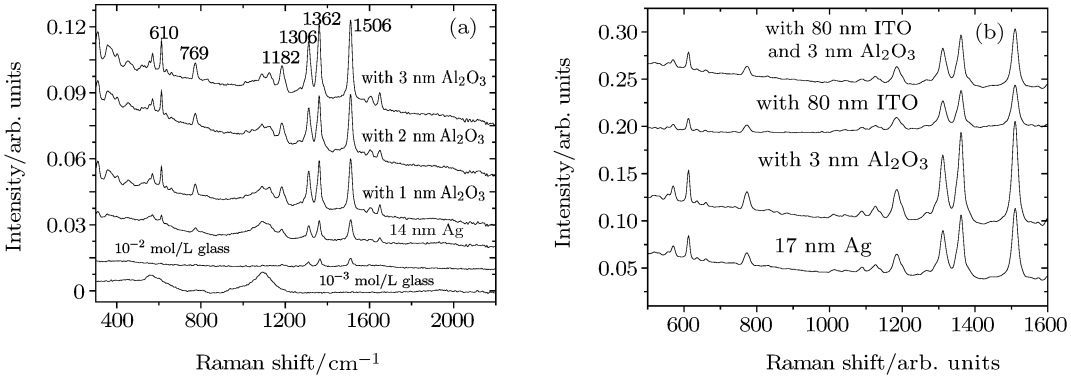



**Fig. 3.** FT-Raman spectral comparison of Ag NPs on different substrates. (a) 14-nm Ag NPs on 1, 2 and 3-nm $Al_2O_3$ layers compared only on glass, in order to compare the Raman intensity at different variation frequencies, $10^{-3}$-M and $10^{-2}$-M R6G directly dipped on glass are shown as references. (b) 17 nm Ag NPs on insulating and conductive substrate, $Al_2O_3$ as an insulating layer and ITO as a conductive layer, furthermore deposited $Al_2O_3$ on ITO to decrease the conductivity of the substrate.

As the SERS enhancement is mainly related to the large EM field intensity which leads to sufficient 'hot-spots' caused by the surface plasmon polariton and near-field coupling mode,[14,15] the significant Raman scattering enhancement we obtained in Fig. 3 shows that even the near-infrared region (1064 nm) could lead to the localized surface plasmon polariton on the Ag NPs' surface with different surroundings. Raman scattering is caused by nuclear motion induced by the distortion (polarization) of the electron cloud around the nucleus. The Raman intensity is related to:

$$I_j \sim I_0 \left(\nu_0 - \nu_j\right)^4 \left(\frac{\partial \alpha}{\partial Q_j}\right)^2 \langle \phi_f \left| Q_j \right| \phi_i \rangle^2 , \tag{2}$$

where $I_j$ is the Raman intensity of vibration frequency $\nu_j$, $I_0$ is the intensity of incident light, $\nu_0$ and $\nu_j$ are the Rayleigh frequency and Raman frequency respectively, $Q_j$ is the nuclear coordinate in a crystal lattice, $\phi_f$ and $\phi_i$ are the density of states function for the end-state $f$ and start-state $i$ respectively. The most important of all, $\partial\alpha/\partial Q_j$, which is usually described as polarization, is related to vibration of the electron cloud and dominated by the electrostatic force and van der Waals attraction which enable the conjugation of molecules. The factors would not change but the polarization would when the local EM field is enhanced by LSPR. Since the intensity of vibration will not the same at different frequencies, the polarization and FT-SERS enhancement will not be the same as that induced by the same local EM field intensity. According to Ref. [26], the SERS enhancement factor is simplified as the fourth power of the local electric field enhancement, so we define the local electric field enhancement as having a direct ratio of the quarter power of the SERS enhancement factor:

$$I_j \sim \left|\frac{E_{\rm loc}}{E_0}\right|^4 , \tag{3}$$

$$E_{\rm loc} \sim |EF|^{1/4} . \tag{4}$$

The enhancement factor for the different SERS substrates listed in Table 1 shows that absorption has some relation to the enhancement. Though the enhancement factors are different at each Raman shift

for one sample because the polarization has different relationships with the local EM field, the factors for one sample at different Raman shifts have uniform trends. In other words, the one quarter power of enhancement factors could characterize the local EM field intensity by different Raman enhancement as shown in Fig. 4, which contains the first six samples in Table 1 for insulating substrates. Figure 4 shows that for insulating substrates the enhancement factors have a linear relationship with the absorption. So the absorption can be attributed to the fact that the photons interact with the conduction electrons on the surface of Ag NPs and excite the localized surface plasmon polariton which leads to sufficient 'hot spots' on the surface and enhances the Raman scattering intensity. With the coherence of the absorption with EM field enhancement for insulating substrates, we clearly see that the Ag NPs deposited on conductive substrates have larger absorption but smaller Raman enhancement. In other words, the extinction of photons on conductive substrates was not all used to excite the 'hot spots'. When decreasing the conductivity of the substrate by depositing a thin layer of insulating $Al_2O_3$, the enhancement becomes bigger as shown in Table 1. We conclude that when Ag NPs are deposited on a conductive substrate, the excited surface plasmon may transmit along the conductive layer, the localization and coupling between surface plasmons may be weakened, and hence the intensity and number of the 'hot spots' will be smaller. In the case of an insulating substrate, the localization and coupling will be well satisfied, and then lead to a very sensitive SERS substrate.

**Table 1.** Enhancement factor for different samples.

| sample | absorbance at 1064 $cm^{-1}$ | $EF$ at 1507 $cm^{-1}$ | $EF$ at 1360 $cm^{-1}$ | $EF$ at 1306 $cm^{-1}$ | $EF$ at 606 $cm^{-1}$ | $\|EF_{ave}\|^{1/4}$ |
|---|---|---|---|---|---|---|
| 14-nm Ag on glass | 0.018 | 28.48 | 27.57 | 32.87 | 28.08 | 2.46 |
| 14-nm Ag with 1-nm $Al_2O_3$ | 0.027 | 69.09 | 65.89 | 80.28 | 99.87 | 3.04 |
| 14-nm Ag with 2-nm $Al_2O_3$ | 0.031 | 83.62 | 78.82 | 90.5 | 119.49 | 3.17 |
| 14-nm Ag with 3-nm $Al_2O_3$ | 0.039 | 113.28 | 104.33 | 127.35 | 168.08 | 3.42 |
| 17-nm Ag on glass | 0.056 | 225.62 | 209.38 | 260.33 | 285 | 4.01 |
| 17-nm Ag with 3-nm $Al_2O_3$ | 0.095 | 329.64 | 301.56 | 378.4 | 416.92 | 4.39 |
| 17-nm Ag with 80-nm ITO | 0.418 | 135.68 | 121.78 | 165.03 | 153.85 | 3.49 |
| 17-nm Ag with 80-nm ITO and 3-nm $Al_2O_3$ | 0.28 | 187.54 | 172.37 | 210.11 | 210 | 3.77 |

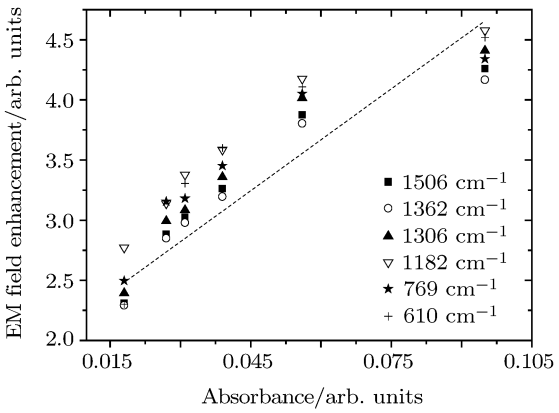



**Fig. 4.** The EM field enhancement at different absorption points for insulating substrates. The enhancement at each Raman shift maintains a good linear relationship with the absorption of the substrate. The average enhancement gives an overall impression.

In conclusion, a sensitive FT–SERS substrate has been obtained by a simple and reproducible evaporation method. Changing the permittivity of the substrate by depositing a thin-layer $Al_2O_3$ film on glass with different thicknesses shows that the absorption at 1064 nm, the excitation wavelength of the NIR–FT Raman spectroscopy we used, has a linear relationship with the local EM intensity caused by LSPR. Furthermore, this method also offers an easy way to obtain enormous enhancement factors by enhancing the absorption of Ag NPs deposited on the dielectric substrates at the excitation wavelength. In comparison with the SERS sensitivity of Ag NPs on substrates with different electrical properties, it shows that the

conductive substrate may lead to the surface plasmons transmitting along the substrate layer, then reducing the localization and coupling of the enhanced local EM field, and hence weakening the enhancement of Raman intensity. To sum up, we point out that the permittivity and electrical property of SERS substrate has a non-negligible effect on the EM field intensity, and this may lead us to obtain further enhancement of Raman scattering intensity for detection of trace quantities of analytes.

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