Surface-enhanced raman scattering from a layer of gold nanoparticles

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Abstract. We studied to prepare substrates for Surface-Enhance Raman Scattering (SERS). Gold nanoparticles were produced by laser ablation of gold plate in ethanol. The average size of gold nanoparticles is 13nm. The gold nanoparticle colloid was allowed to dry on a silicon wafer to prepare SERS substrate. Using the gold nanoparticle substrates we could obtain SERS spectrum of Rhodamine 6G molecules adsorbed on gold nanoparticles. The Raman signal was enhanced strongly by our SERS substrate. This result demonstrates that the metal nanoparticles synthesized by laser ablation in clean liquid can be used to prepare SERS substrate for molecular detection in our laboratory.
Key words: Surface plasmon, Plasmon resonance, laser ablation, Raman Scattering

1. Introduction

The Surface-Enhanced Raman Scattering (SERS) technique is widely used as a high sensitive analytical tool for molecular detection and characterization of a wide range of adsorbate molecules down to the single molecule detection limit [1].

Estimated enhancement factors for the Raman signals in SERS started from modest factors of 10^3 to 10^5 in the initial SERS experiments. For excitation laser wavelengths in resonance with the absorption band of the target molecule, surface-enhanced resonance Raman scattering (SERRS) can result in higher total effective Raman cross sections.

Enhancement factors on the order of about 10^{10} to 10^{11} for Rhodamine 6G and other dyes adsorbed on colloidal silver and excited under molecular resonance conditions have been reported [2-4].

The large enhancement of the Raman scattering intensity has been explained by two mechanisms: the electromagnetic and chemical mechanisms. The electromagnetic mechanism attributed to the increase of the local electromagnetic field of the adsorbate because of the excitation of the surface plasmon on the metal surface. The chemical adsorption mechanism attributed to short distance effects due to the charge transfer between the metal and the adsorbed molecule [3].

The electromagnetic effect is dominant, the chemical effect contributing enhancement only on the order of one or two of magnitude [5]. The electromagnetic enhancement (EME) is dependent on the presence of the metal surface's roughness features, while the chemical enhancement (CE) involves changes to the adsorbate electronic states due to chemisorption of the analyte [6].

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Surface roughness or curvature is required for the excitation of surface plasmon by light. The electromagnetic field of the light at the surface can be greatly enhanced under conditions of surface plasmon excitation; the amplification of both the incident laser field and the scattered Raman field through their interaction with the surface constitutes the electromagnetic SERS mechanism.

Many versions of the electromagnetic theory for SERS mechanism have been developed to treat model systems such as isolated spheres, isolated ellipsoids, interacting spheres, interacting ellipsoids, randomly rough surfaces. We consider a simple model of a metal sphere in an external electric field. For a spherical particle whose radius is much smaller than the wavelength of light, the electric field is uniform across the particle and the electrostatic approximation is a good one. The field induced at the surface of the sphere is related to the applied, external field by the following equation:[5,6]

$$E_{induced} = \{[\varepsilon 1(\omega) - \varepsilon_2] / [\varepsilon_1(\omega) + 2\varepsilon_2]\} \, E_{laser}$$

where $e_1(w)$ is the complex, frequency-dependent dielectric function of the metal and e_2 is the relative permittivity of the ambient phase.

This function is resonant at the frequency for which $Re(e_1) = -2e_2$. Excitation of the surface plasmon greatly increases the local field experienced by a molecule adsorbed on the surface of the particle. The particle not only enhances the incident laser field but also the Raman scattered field.[5]

The structural and molecular identification power of SERS can be used for numerous interfacial systems, including electrochemical, modeled and actual biological systems, catalytic, in-situ and ambient analyses and other adsorbate-surface interactions. Due to the sensitivity of SERS, single-molecule detection experiments have been reported, as well.

In this paper, we report our experimental results of SERS measurement from a SERS substrate which was made of gold nanoparticle colloid using "coffee rings" method. The gold nanoparticle colloid was prepared by laser ablation in clean liquid environment without contamination. This method produced random substrates for SERS measurement. It is simple and feasible for the production of an efficient SERS substrate.

2. Experimental

Gold nanoparticles were prepared by laser ablation of gold plate in ethanol. The noble metal plate (99.9 % in purity) was placed in a glass cuvette filled with 10 ml ethanol. A Nd: YAG laser (Quanta Ray Pro 230,USA) was set in Q-switch mode to give the fundamental wavelength (1064 nm) in pulses with energy of about 80-100mJ, duration of 8 ns and repetition rate of 10Hz. The laser beam was focused on the metal plate by a lens having the focal length of 150mm. A small amount of the metal nanoparticles colloids was extracted for absorption measurement and TEM observation. The absorption spectrum was measured by a Shimadzu UV-2450 spectrometer. The TEM micrograph was taken by a JEM 1010-JEOL. The size of nanoparticles was determined by ImagieJ 1.37v software of Wayne Rasband (National institutes of Health, USA). The size distribution was obtained by measuring the diameter of more than 500 particles and using Origin 7.5 software.

Using synthesized gold nanoparticle colloid we studied to prepare SERS substrates. The gold nanoparticle colloid was dropped and left to dry on a silicon wafer by "coffee ring" method to form the rough surface. The silicon wafer was treated by H_2SO_4 acid for 2 hours, washed in deionised

water, then immersed in a solution of NH_4OH and finally sonicated in an ultrasonic bath for 30 minute. The SERS active substrate area is about $1cm^2$.

A Rohdamine 6G solution of 10^{-4} M concentration in ethanol was used as a test analyte to study SERS spectrum. Few droplets of the R6G solution were dropped and left to dry on the SERS substrate made of gold nanoparticle colloid on silicon wafer. R6G molecules will be absorbed onto the gold nanoparticles of the SERS substrate after some minutes. The surface morphology of SERS substrates was examined by a scanning electron microscopy SEM (JOEL-JSM5410LV). SERS spectra were observed by Micro-Raman spectrophotometer (Micro Raman LABRAM - 1B) using He-Ne laser (632.8nm) as a pump source.

3. Results and disscussion

Fig.1a shows absorption spectrum of gold nanoparticles produced in ethanol. The characteristic plasmon resonance absorption peak of gold nanoparticle colloid of around 520 nm appeared on the absorption spectrum. The TEM image and size distribution of gold nanoparticles were analyzed and given in Fig.1b. It is observed that the diameter of gold nanoparticles concentrate in a range from 5 to 20 nm and has the average size of 13 nm.
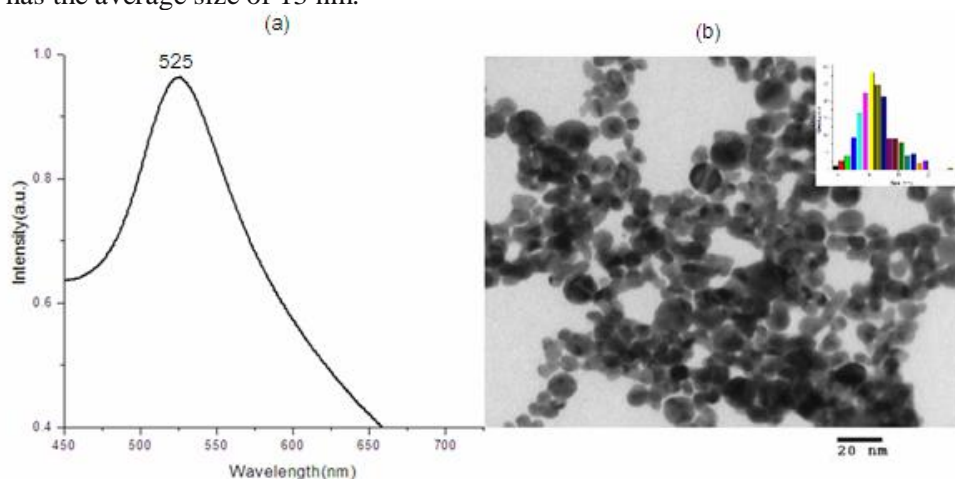

Fig. 1. Absorption spectra (a) and the electron micrograph and size distribution (b) of gold nanoparticles produced by laser ablation in ethanol.

SEM image of the surface including R6G molecules adsorbed on Au nanoparticle substrate was also observed. The result is shown in Fig.2.
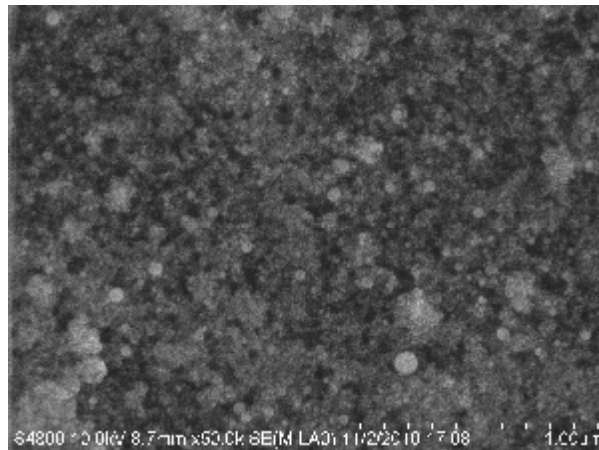
Fig. 2. Scanning electron micrographs of SERS substrates.

In order to examine the enhance effect of the SERS substrate samples we prepared and observed on 3 types of different samples: R6G on silica substrate without Au nanoparticle colloid (R6G/Si sample); Au nanoparticle colloid on silica substrate without R6G (Au/Si sample) and R6G on silica substrate with Au nanoparticle colloid (R6G/Au/Si sample). The Raman spectra were taken in three different positions of SERS substrate.

The Raman spectra of R6G/Si and Au/Si samples are shown in Fig.3. The spectra are quite similar for three random different positions of the sample.
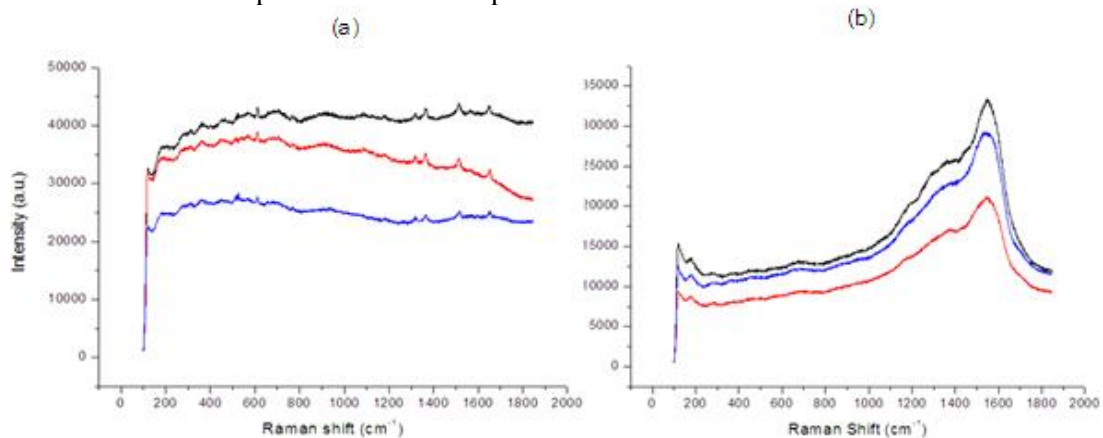

Fig. 3. Raman spectra of R6G/Si (a) and Au/Si samples (b) taken in three different positions of samples.

As shown in Fig.3. the Raman spectra of R6G/Si sample was so weak that quite undetected by even intense power of the excited laser. The spectra of Au/Si sample were taken to be reference for Raman spectra of R6G/Au/Si sample.

SERS spectra of R6G absorbed on gold colloid of SERS substrate (R6G/Au/Si sample) was measured and are shown in Fig.4.
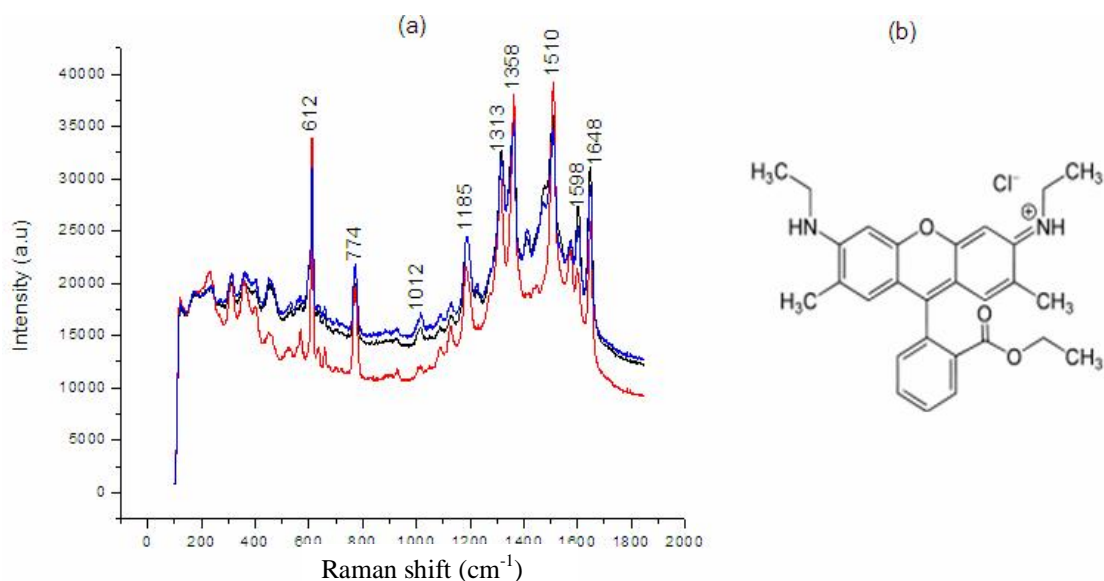
Fig. 4. SERS spectra of R6G absorbed on gold colloid taken in three different positions of SERS substrate (a) and formula of R6G molecule(b).

The regular Raman and SERS peaks for Rodamine 6G are assigned in Table 1. The differences between the regular Raman and SERS spectra can be explained by the gradient field and quadrupole effects [7].

Table 1. Raman peaks and the corresponding assignment in conventional and SER spectra
(for intensities s = strong; m= medium; w = weak)

	Regular Raman shift of R6G (cm-1)	Assignment	SER peaks (cm-1)
1	620m	$\delta(CCC)ip$	612
2	778m	$\delta(CH)op$	774
	1009m		1012
3	1198s	$\delta(CH)ip$	1185
4	1289ms	$\nu(COC)$	
5	1329s	$\nu(CC)^+$ $\nu(CN)$	1313
6	1360s	$\nu(CC)^+$ $\nu(CN)$	1358
7	1515s	$\nu(CC)$	1510
	1556s		
8	1569s	$\nu(COC)$	
	1606s		1598
9	1651s	$\nu(CC)$	1648

The SERS spectra of R6G are in good agreement with the published results of R6G Raman spectrum. Strong peaks at 1358 cm^{-1} ;1510 cm^{-1} and 1638cm^{-1} are assigned the C-C stretch. The peak at 620 cm^{-1} which is assigned to the C-C-C deformation in-plane vibration was experimentally observed at 612nm. The energy shift is explained by the plasmon-generated electric field [7] . The peak at 774 cm^{-1} and 1012 cm^{-1} are assigned to the C-H deformation band out-of-plane vibrations. The peak at 1185cm^{-1} indicates the C-H deformation in-plane vibration.

Comparing SER spectra of R6G, from samples with and without gold nanopalticle colloid we can conclude that SER signal was enhanced strongly by SERS substrate prepared by our procedure.

4. Conclusion

Using gold nanoparticle colloid prepared by laser ablation of gold plate in ethanol we produced successfully the substrates for SERS measurement. The Raman signal is strongly enhanced by our SERS substrate. The gold nanoparticles with rather spherical shape and average diameter of about 13 nm could be used to prepare SERS substrate. The experimental results showed advantages of laser ablation method which can produce metal nanoparticles in the clean liquids suitable for SERS studies. This simple and feasible method of SERS substrate preparation opens up the capacity to develop SERS spectroscopy in our laboratory.

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