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SURFACE - ENHANCED RAMAN SCATTERING FROM A LAYER OF SILVER NANOPARTICLES

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ABSTRACT

We studied to prepare silver nanoparticle substrate for Surface-Enhance Raman Scattering (SERS). Silver nanoparticles were produced by laser ablation of silver plate in ethanol. The average size of silver nanoparticles is 15nm. The silver nanoparticle colloid was allowed to dry on a silicon wafer to prepare SERS substrate. Using the silver nanoparticle substrates we could obtain SERS spectrum of Rhodamine 6G molecules adsorbed on silver 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, silver nanoparticle*

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 [2,3,4].

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 (EM) 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]

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,

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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 $\varepsilon_1(\omega)$ is the complex, frequency-dependent dielectric function of the metal and ε_2 is the relative permittivity of the ambient phase.

This function is resonant at the frequency for which Re (ε_1) = -2ε_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 RS 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 made of silver nanoparticles prepared by "coffee rings" method. The silver 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.

EXPERIMENTAL

We prepared silver nanoparticles by laser ablation of silver 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 silver nanoparticle colloid we studied to prepare SERS substrates. The silver 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 before by H_2SO_4 acid for a period of 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 silver nanoparticle colloid on silicon wafer. R6G molecules will be absorbed onto the silver 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)

RESULTS AND DISCUSSION

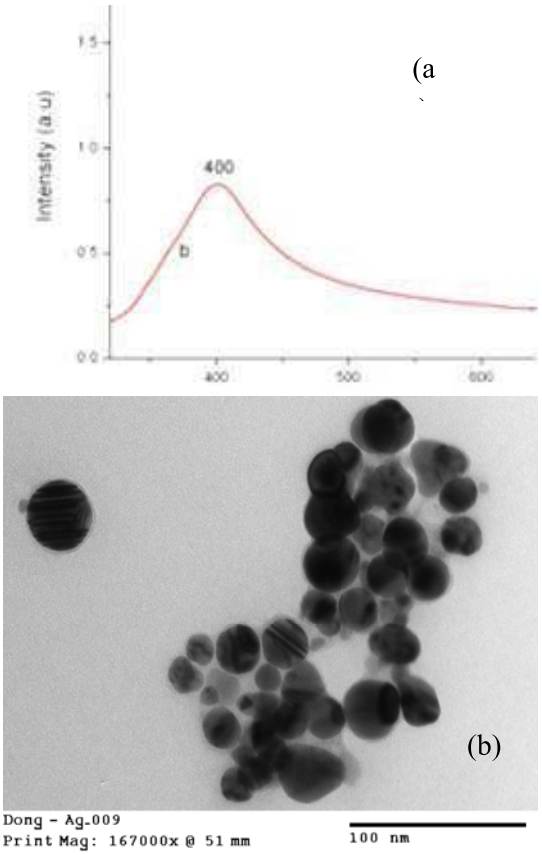


Fig.1. *Absorption spectra (a) and the electron micrograph (b) and size distribution (c) of silver nanoparticles produced by laser ablation in ethanol*

Fig.1a shows absorption spectrum of silver nanoparticles produced in ethanol. The characteristic plasmon resonance absorption peak of silver nanoparticle colloid of around 400 nm appeared on the absorption spectrum. The TEM image and size distribution of silver nanoparticles were analyzed and given in Fig.2b. It is observed that the diameter of silver nanoparticles concentrate in a range from 5 to 20 nm and has the average size is 15 nm.

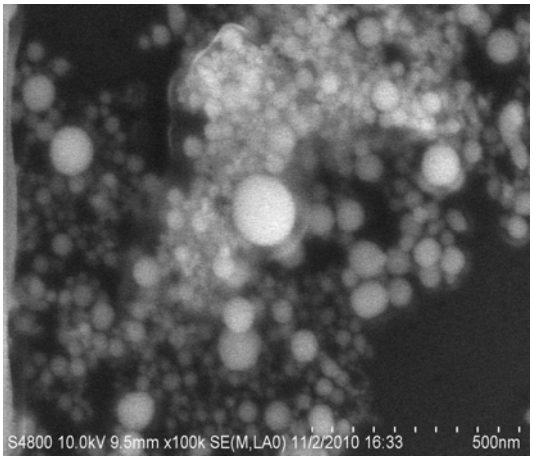


Fig.2. *Scanning electron micrographs of SERS substrates*

SEM image of the surface including R6G molecules adsorbed on Ag nanoparticle substrate was also observed. The result was shown in Fig.2.

In order to examine the enhance effect of the SERS substrate samples we prepared and observed 2 types of different samples: R6G on silica substrate without Ag nanoparticle colloid (R6G/Si sample); R6G on silica substrate with Ag nanoparticle colloid (R6G/Ag/Si sample). Spectra of the three samples were excited by a He-Ne laser (632.8nm) and measured by Micro Raman Spectrophotometer (LABRAM - 1B). The spectra were taken in three different positions of SERS substrate.

We first measured Raman spectra of R6G/Si. The results are shown in Fig.3.

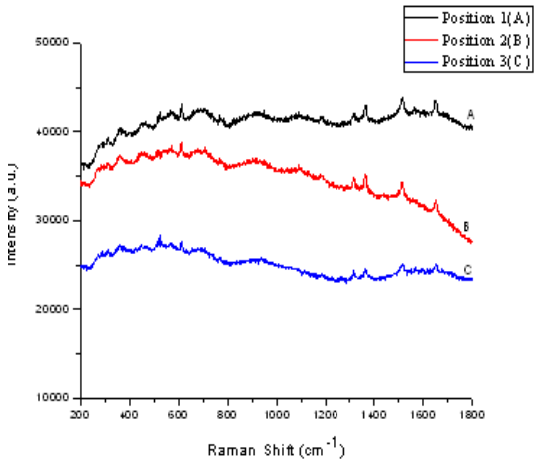
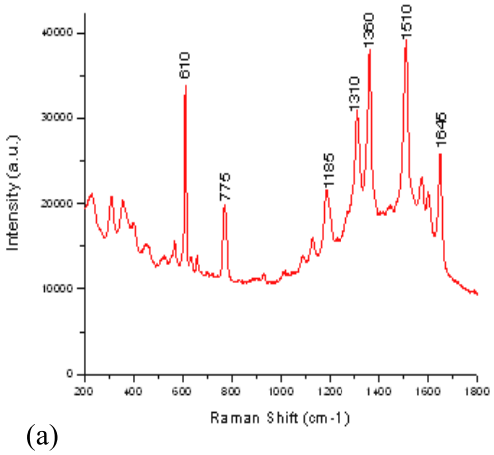
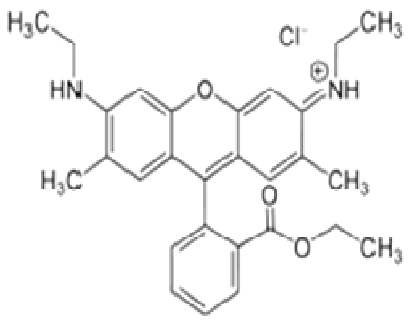


Fig.3. *Raman spectra of R6G/Si taken in three different positions of samples*

And then, SERS spectra of R6G absorbed on silver colloid of SERS substrate was measured and shown in Fig.4.



(a)



(b)

Fig.4. *SERS spectra of R6G absorbed on silver 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 SERS spectra*

(for intensities s = strong; m= medium; w = weak)

	Regular Raman shift of R6G (cm^{-1})	**Assignment**	**SERS peaks (cm^{-1})**
1	620m	δ(CCC)ip	610
2	778m	δ(CH)op	775
3	1198s	δ(CH)ip	1185
4	1329s	$\nu(CC)^{+}$ ν(CN)	1310
5	1360s	$\nu(CC)^{+}$ ν(CN)	1360
6	1515s	ν(CC)	1510
7	1651s	ν(CC)	1645

The SERS spectra of R6G are in good agrement with the published results of R6G Raman spectrum. Strong peaks at 1360 cm^{-1} ;1510 cm^{-1} and 1645cm^{-1} are assigned the C-C stretch. The peak at 610 cm^{-1} assigned to the C-C-C deformation in-plane vibration was experimentally observed at 620 cm^{-1}. It is explained by the plasmon-generated electric field [7] . The peak at 775 cm^{-1} are assigned the C-H deformation band out-of-plane vibrations. The peak at 1185cm^{-1} indicate the C-H deformation in-plane vibration.

Comparing SERS spectra of R6G, from samples with and without silver nanoparticle colloid we can conclude that SER signal was enhanced strongly by SERS substrate prepared by our procedure. Raman spectra of R6G was so weak that quite undetected by even more intense power of the excited laser.

CONCLUSION

Using silver nanoparticle colloid prepared by laser ablation of silver plate in ethanol we produced successfully the substrates for

SERS measurement. The Raman signal is strongly enhanced by our SERS substrate. The silver 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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TÓM TẮT

TÁN XẠ RAMAN TĂNG CƯỜNG BỀ MẶT TỪ ĐƠN LỚP HẠT NANO BẠC

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Chúng tôi nghiên cứu chế tạo chất nền là các hạt hạt nano bạc sử dụng cho tán xạ Raman tăng cường bề mặt (SERS). Hạt nano bạc được chế tạo bằng phương pháp ăn mòn laser trong ethanol. Kích thước trung bình của hạt nano bạc chế tạo được là 15 nm. Dung dịch các hạt keo nano bạc được nhỏ và làm khô trên một đế silic để làm chất nền SERS. Sử dụng các hạt nano bạc làm chất nền chúng tôi có được phổ SERS của các phân tử Rhodamine 6G hấp thụ trên các hạt nano bạc. Phổ Raman của Rhodamine 6G được tăng cường mạnh bởi chất nền SERS. Kết quả này cho thấy các hạt nano bạc tạo ra bằng phương pháp ăn mòn laser trong chất lỏng tinh khiết có thể sử dụng làm chất nền SERS để phát hiện phân tử trong phòng thí nghiệm.

Từ khóa: *Plasmon bề mặt, cộng hưởng, ăn mòn laser, tán xạ Raman, hạt nano bạc*

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