

Ag Nanoparticle-Modified Silver Nanorods for Surface Enhanced Raman Scattering

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Abstract—In recent years, surface-enhanced Raman scattering (SERS) technology has been very popular in some fields. The key point is to prepare active substrates. In our paper, rhodamine 6G was detected with silver nanorod arrays (AgNR), silver sols (AgNP), and Ag nanoparticle-modified silver nanorods (AgNP@AgNR). The detection limits of AgNR, AgNP, and AgNP@AgNR were detected as 1.0×10^{-7} M, 1.0×10^{-6} M and 5.0×10^{-8} M. At the same time, the same trace of R6G was detected with three types of substrates and found that the SERS signal acquired from the AgNP@AgNR is the strongest.

Keywords—surface enhanced Raman spectroscopy; composite substrate; silver nanoparticles; silver nano array

I. INTRODUCTION

Due to the good SERS effect of precious metal materials, nano-sized substrates of some metals have been widely prepared. The precious metal sol-gel method is one of the commonly used methods for preparing surface-enhanced Raman scattering (SERS) substrates. For example, Wu *et al.* successfully synthesized flower-like silver nanoparticles for the detection of carmine by a simple aqueous nitrate reduction reaction in the presence of polyvinylpyrrolidone (PVP) surfactants [1]. Colloidal materials have poor stability and are easy to agglomerate, so it is a trend to develop solid substrates. In recent years, oblique angle deposition (OAD) has been recognized as a stable and effective method for the fabrication of nanostructures [2, 3]. During the fabrication process, the deposition angle of the nanostructure substrate was successfully prepared exceeds 75° relative to the substrate normal, which is consistent with the cosine rule based on OAD's atomic self-shading effect. Under the high temperature vacuum condition, the raw material turns into a gas and deposits on the substrate [4]. Moreover, the substrates fabricated by OAD have already been applied to many applications such as environmental monitoring, food safety and biological testing. Among the base structures prepared by OAD, one is silver nanorod arrays (AgNR). In order to further improve the detection ability of silver nanoparticles and silver Nano array for substances, we attempted to prepare a new SERS substrate. With the comparison of the SERS performance of silver nanoparticles, silver Nano array and

composite substrates, which provides guidance for the potential development and application of SERS composite substrates.

II. EXPERIMENTAL SECTION

A. Technology road-map

Firstly, the AgNR substrate was prepared by physical vapor deposition. Secondly, AgNP was prepared by using sodium citrate and silver nitrate through a chemical reduction method. Finally a new assembled substrate was prepared through AgNP modified AgNR method (AgNP@AgNR). It can be clearly seen from Fig. 1.

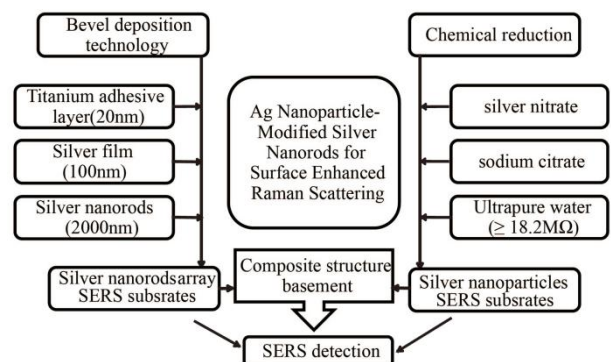


Fig. 1. Flow chart of SERS detection based on silver nanoparticles modified silver nano arrays.

B. Materials

Silver (99.999%) and titanium (99.995%) pellets were purchased from Kurt J. Lesker Co., Ltd. (USA). Silver nitrate, sodium citrate, rhodamine 6G (R6G), citric acid, ultrapure water (≥ 18.2 MΩ) was used in all experiments.

C. Preparation of AgNP

The colloidal dispersion of AgNP was prepared as follow [5, 6]. 0.018 g of silver nitrate was added into a beaker of 100 mL of pure water, and placed on a heating apparatus until boiling. 0.02 g of sodium citrate was added to 2 ml of water and stir well, the solution was added dropwise to the micro-boiled silver nitrate solution along the beaker by using a plastic

dropper. AgNP was kept boiling for about 20 minutes and was cooled to room temperature for 12 hours before we used. Silver nanoparticles with a particle size of 60 to 80 nm were obtained.

D. Fabrication of AgNR

AgNR substrates were fabricated in an e-beam deposition system (DE500, DE Technology Inc., Beijing, China) [7]. The specific preparation process is as follows: Firstly, the glass slices were cut into $1 \times 1 \text{ cm}^2$, then put it into the alcohol for 5 minutes. After repeating the cleaning process three times, the glass sheet was blown dry with nitrogen and fixed on the sample stage in the deposition chamber. When the pressure of the deposition chamber was less than 5.0×10^{-7} Torr, the 20 nm titanium film and the 100 nm silver film were deposited at 0.2 nm/s and 0.3 nm/s. Finally, the sample table was rotated about the axis so that the surface of the sample table was perpendicular to the direction of steam incidence of 86° , continue to deposit 2000 nm silver at a rate of 0.3 nm/s. The deposition thickness and rate were monitored by a quartz crystal microbalance (QCM) facing directly toward the vapor direction.

E. SERS measurements

SERS spectra were recorded using a portable Raman spectrometer (proramana-l-785A2, Enwave Optonics, Irvine, CA) with a 785 nm excitation wavelength. During SERS measurements, a laser beam diameter of 85 nm was vertically projected onto the sample. Specific testing process is as follows, 2 μL of different concentrations of R6G solution were applied to the AgNR substrate surface, and allowed to dry under ambient conditions. Then SERS spectra were taken from the substrate with a laser power of 30 mW and an integration time of 10 s. At least five random sampling locations were measured from each drop. When using AgNP detection, different concentrations of R6G and AgNP need to be mixed into a cuvette and place it in a sample cell for Raman detection. Laser power and integration time are the same as AgNR detection. When testing with an assembly substrate, R6G and AgNP first necessary to be mixed. 2 μL of different concentrations of mixed solution were applied to the AgNR substrate surface, and allowed to dry under ambient conditions. At least five random sampling locations were measured from each drop.

All of the SERS spectra were plotted using Origin 8.5 (Origin Lab, Northampton, MA). The raw spectra obtained from the Raman analyzer were used without further processing unless otherwise specified. Spectra analysis, including subtracting the baseline and fitting peaks, were performed using GRAMS/AI spectroscopy software suite (Thermo Fisher Scientific, Waltham, MA).

III. RESULTS AND DISCUSSION

A. Comparison of detection limits of three substrate

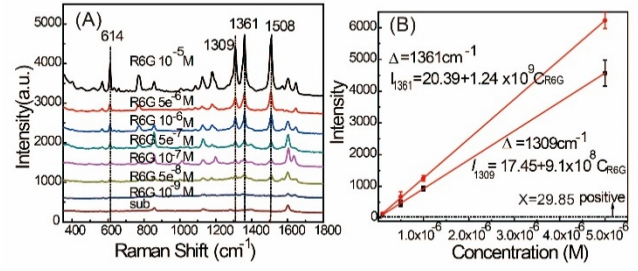


Fig. 2. (A) SERS spectra of R6G under different concentrations adsorbed onto a silver nano array. (B) The relationship between characteristic peaks of R6G and concentration. The average intensity was plotted and the error bars represent the standard deviation values.

1) The limit of AgNR detection

Fig.2A illustrates SERS spectra obtained from six different concentrations of R6G adsorbed on a silver nano array. With the increase of the concentration of the analytes, the peak intensity of R6G increased significantly. The spectra reveal that an R6G concentration as low as 1.0×10^{-7} M still exhibits an observable SERS signal. Fig. 2B showed that intensity of the SERS peak at 1310 cm^{-1} and 1361 cm^{-1} was linearly dependent on the concentration of the R6G, $I_{1309} = 17.45 + 9.1 \times 10^8 C_{R6G}$ and $I_{1361} = 20.39 + 1.24 \times 10^9 C_{R6G}$. The detection limit (LOD) was 1.0×10^{-7} M by 3σ method (σ is the mean square root of the noise signal, which was determined by standard deviation of the spectral intensity at a spectral region at the range of $1700\text{--}1800 \text{ cm}^{-1}$).

2) The limit of AgNP detection

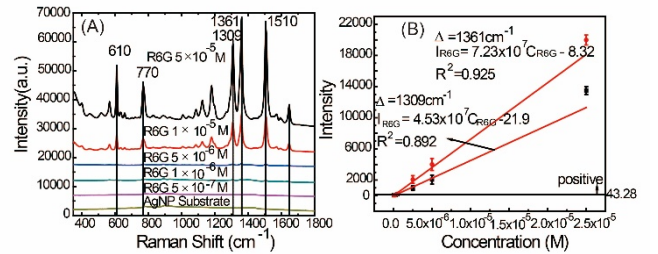


Fig. 3. (A) SERS spectra of the different R6G concentrations adsorbed onto silver nanoparticles. (B) shows the peaks of two characteristic peaks of R6G 1310 cm^{-1} and 1361 cm^{-1} . The average intensity was plotted and the error bars represent the standard deviation values.

Fig. 3A shows enhanced signals of six different concentrations of R6G in silver nanoparticles. Spectra showed that R6G concentrations as low as 1.0×10^{-6} M still exhibit an observable SERS signal. Fig. 3B plots the intensities of SERS peak at 1309 cm^{-1} and 1361 cm^{-1} versus the C_{R6G} : $I_{1309} = 4.53 \times 10^7 C_{R6G} - 21.9$ and $I_{1361} = 7.23 \times 10^7 C_{R6G} - 8.32$. Based on these results, the detection limit (LOD) was of R6G was 1.0×10^{-6} M by 3σ method (σ is the mean square root of the noise signal, which was determined by standard deviation of the spectral intensity at a spectral region at the range of $1700\text{--}1800 \text{ cm}^{-1}$).

3) The limit of Composite Substrate detection

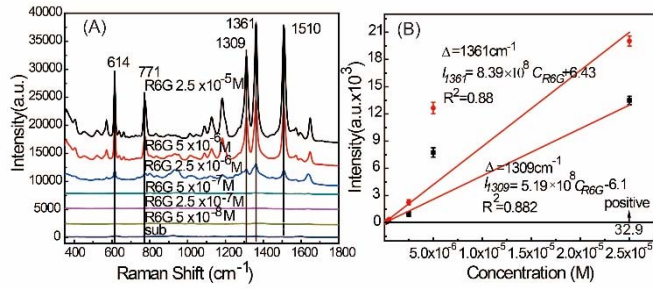


Fig. 4. (A) SERS spectra of on the different R6G concentrations adsorbed onto AgNP@AgNR. (B) shows the peaks of two characteristic peaks of R6G 1310 cm^{-1} and 1361 cm^{-1} . The average intensity was plotted and the error bars represent the standard deviation values.

Fig. 4A shows the enhanced signal of six different concentrations of R6G in a composite substrate. The spectrum shows that R6G concentrations as low as 5.0×10^{-8} M still show an observable SERS signal. Fig. 4B depicts a fitted curve equation for two characteristic peaks at 1309 cm^{-1} and 1361 cm^{-1} for R6G: $I_{1309} = 5.19 \times 10^8 C_{R6G} - 6.1$ and $I_{1361} = 8.39 \times 10^8 C_{R6G} + 6.43$. For the peaks of 1309 cm^{-1} and 1361 cm^{-1} in SERS signals of different concentrations of R6G, the intensity of these peaks were stronger than 3σ at the lowest concentration (1.0×10^{-7}) in our experiment when silver Nano arrays are used as substrates. So the detection limits of the AgNR determined to be 1.0×10^{-7} M. And when AgNP are used as substrates, the detection limit of the substrates was 10^{-6} M obtained from Fig. 3B. Besides, Fig. 4 B clearly reveals that the detection limit of the AgNP@AgNR substrate can be 5.0×10^{-8} M using R6G as a probe molecule.

B. The same amount of sample detection

For the comparisons of the performance of the three substrates, 2 μL of 5.0×10^{-6} M R6G were adsorbed, respectively, on each of the three substrates, using the same procedure described for the substrate detection limit.

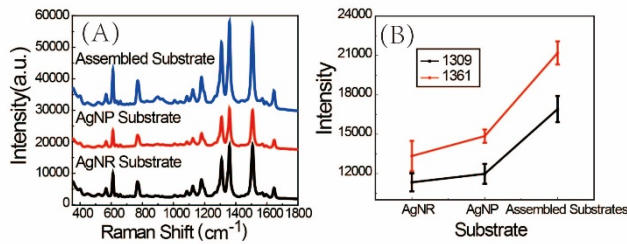


Fig. 5. (A) SERS spectra of R6G with a concentration of 10^{-5} M adsorbed on the three kinds of substrates. (B) The average intensity was plotted and the error bars represent the standard deviation values.

The same concentration of R6G was used as the probe molecule, the enhanced signal measured by the portable Raman

spectrometer is different. From Fig. 5, it can be clearly seen that the R6G signal measured by the composite substrate is the strongest, so we get the Ag nanoparticle-modified silver nanorods have the best performance of composite substrate. We suspect that the combination of AgNP and AgNR increases the surface area of the substrate in contact with the sample molecules and increases the number of hot spots, resulting in the highest SERS signal of the assembled substrate when compared to the other two substrates.

IV. CONCLUSIONS

In this study, AgNR, AgNP, and AgNP@AgNR substrates were prepared and they were separately subjected to SERS detection. Using different concentrations of R6G as probing molecules, the detection limits of AgNR, AgNP, and AgNP@AgNR were detected as 1.0×10^{-7} M, 1.0×10^{-6} M and 5.0×10^{-8} M. By comparison, the detection limit of the composite substrate was higher than that of the silver gel, which is better than the detection limit of the silver Nano array substrate. At the same time, when three kinds of substrates were used to measure the same sample with the same concentration, the signals collected from the assembled substrate were stronger.

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