Flexible and ultrasensitive surface-enhanced Raman scattering substrates for the pesticide detection

Runhua Wang¹², Jia Zhu², Guanzhou Lin² and Wengang Wu¹²*

¹ Shenzhen Graduate School of Peking University, Shenzhen, P. R. China
² National Key Laboratory of Science and Technology on Micro/Nano Fabrication, Institute of Microelectronics, Peking University, Beijing, P. R. China

* Corresponding Author’s Email: wuwg@pku.edu.cn

Abstract. In this paper, a simplified method for preparing surface-enhanced Raman scattering (SERS) substrates with spin-coating is reported. The green chemical synthesis of Ag nanoparticles (NPs) is environmentally friendly without complex instruments. The Ag NPs are coated on a polydimethylsiloxane (PDMS) film by spin coating for detecting pesticides. By this method, we can get the substrate with high sensitivity. The results showed that the substrate has a strong SERS signal even the concentration of thiram (pesticide) is down to 10⁻⁹ M. Compared with the allowed residue dose in food security (10⁻⁵ M), the detection limit of thiram is lower. On the other hand, PDMS has the advantage of flexibility and transparency, it can meet the demands of the detection of analytes on irregular objects.

1. Introduction

With decades of development and accumulation, surface-enhanced Raman scattering (SERS) is considered to be a very valuable method of information analysis [1]. The spectral signal obtained by the test can reflect the characteristics of the substance and will not cause damage to the sample [2]. It has made a lot of progress to facilitate the wide utilization of SERS in many fields, such as pesticide and molecular detection [3].

Only a small portion of precious and alkali metals can get the SERS spectra, including silver, gold, platinum and other metals [4]. In many synthesis methods of nanoparticles, metal colloid is the first widely used SERS substrate because of simple preparation, low cost and strong signal enhancement. On the one hand, compared with gold and copper, silver has a higher surface plasmon efficiency. On the other hand, silver SPR can cover all wavelengths in the visible region by designing reasonable nanostructures. Moreover, silver costs less than gold.

The common SERS substrates are mainly made of rigid materials such as silicon and glass wafer. As an applied substrate, due to its informality, rigidity, brittleness and other characteristics, it has the disadvantages of complex preparation, expensive processing and other defects [5]. As a transparent, flexible polymeric material, PDMS has a variety of uses such as optics and SERS substrates [6].

Various pesticides play an important role in protecting crops from pests and diseases in daily production [7]. However, with the increase of pesticide varieties and dosage in agriculture, pesticide residues pose a growing threat to human health [8]. Therefore, the problem of pesticide residues has attracted extensive attention and needs further study.
Hence, a practical and applied SERS substrate was prepared on a large scale of Ag NPs modified PDMS by spin coating. In addition to the advantages of low cost for Ag NPs-decorated PDMS, the modified Tollens method to synthesis Ag NPs does not cause damage to the environment. Furthermore, the results indicate that the detection limits for R6G and thiram are $10^{-10}$ M and $10^{-9}$ M.

2. Experiment

2.1. Characterizations
The surface of the PDMS was treated by the BD-20AC laboratory corona processor (Electro-Technic Products Inc., Chicago, IL, USA). The SERS substrates were prepared by spin-coating silver colloid on treated PDMS film with KW-4A Spin Coater (Chinese Academy of Sciences, China). The Raman spectrum is obtained by a reflection Raman microscope and a spectrometer (Renishaw, Gloucestershire, UK). The integral time of spectrum collection for measurement is set to 5s. Five points were detected on the substrate and their mean values were taken for analysis.

2.2. Synthesis of Ag NPs
The silver nitrate (99.9%) was dissolved in the deionized water to prepare AgNO$_3$ solution (0.05 mol/l, 10 ml) and the ammonia solution (25% w/w) was continuously dripped into the AgNO$_3$ solution under magnetic stirring until a clear colorless solution was obtained. After that, add 4 μl of the Tollens solution to the solution of D-glucose (0.2 mol/l, 40 ml) every half hour and repeat 10-15 times.

2.3. Preparation of SERS substrate
PDMS film was made by mixing the prepolymer and curing agent at the ratio of 10:1 for 1.5 hours at 65 °C. Then it was cut into 1cm $\times$ 1cm size and treated by O$_2$ plasma for 30 s. Finally, about 0.5 ml of the Ag NPs solution was dropped into the PDMS films and rotated at 500 r/min for 18 seconds by KW-4A Spin Coater. After evaporation, the fabricated substrates can be used for SERS detection of the analyte. The fabricated substrates and test process are shown in figure 1.

![Figure 1. The diagram of test and the prepared substrate.](image)

3. Analysis and Discussion

3.1. UV-Vis absorption spectrum of Ag NPs
The improved Tollens method is high-efficiency and environmentally friendly. Because of the excess glucose, the silver ion is completely reduced. As can be seen from figure 2, by analysing the absorption spectrum of silver particles under the UV-Vis absorption spectrum, Ag NPs have a high absorption peak at 415nm. It shows that Ag NPs is close to sphere in shape, which could be used as SERS substrate.
3.2. Substrate performance
Rhodamine 6G (R6G, 99%) is a standard probe used to measure the quality of SERS substrates. Herein, we prepared various concentrations of R6G to investigate the substrate performance. During the measurement, the laser was focused on the interface between the droplets and the SERS substrate. When the solution drips on the substrate, glucose is dissolved by water, exposing Ag NPs to contact with the substance, thus generating an enhanced SERS signal. As can be seen from figure 3, the detected peaks were the same as previously reported [9]. It can be observed that the substrate showed excellent sensitivity and could be clearly identified at $10^{-10}$ M.

![Figure 2. UV-visible absorption spectrum of Ag NPs.](image)

**Figure 2.** UV-visible absorption spectrum of Ag NPs.

In order to measure the reproducibility of SERS substrate, we measure the intensities of R6G at concentration of $10^{-9}$ M at 5 spots on the same substrate. It can be seen from the figure 4 that the substrates have good signal uniformity.

![Figure 3. SERS spectra of R6G with different concentrations.](image)

**Figure 3.** SERS spectra of R6G with different concentrations.
3.3. Application for thiram detection
Due to the overuse of pesticides such as thiram, the residues in agricultural products directly threaten the health of people and arouses strong public concern. We measured different concentrations of thiram, as shown in figure 5, and the results are consistent with previous reports [10]. As can been seen, the detection limit of thiram is $10^{-9}$ M, which is below residue limits of thiram ($2 \times 10^{-5}$ M).

In addition, owing to PDMS’s good flexibility and transparency, such SERS substrates has potential for practical applications on irregular objects in the future.

4. Conclusions
In summary, we demonstrated SERS substrate based on PDMS film coated with Ag NPs, which exhibited high SERS signal enhancement. Synthesis of Ag NPs is high-efficiency and environmentally friendly. The PDMS film modified Ag NPs by spin coating. On the other hand, the oxidation of silver is prevented by the coating of glucose. Furthermore, the substrates reveal strong signal when the concentration of thiram is $10^{-9}$ M, lower than the Chinese national standard ($2 \times 10^{-5}$ M). Because of the
flexibility and transparency of PDMS, SERS substrate based on PDMS is an ideal choice to detect ultra-low concentration analytes on irregular surfaces, which makes it widely used in flexible sensors.

**Acknowledgments**

This study was supported by the National Natural Science Foundation of China (Grant No. 61474006) and the National Basic Research Program of China (973 Program, Grant No.2015CB352100). Thanks to the Electron Microscopy Laboratory of Peking University, and the School of Earth and Space Science of Peking University for using their equipment.

**References**

[1] Fleischmann M, Hendra P J and McQuillan A J 1974 *Chem. Phys. Lett.* 26 163
[2] Ando J, Fujita K, Smith N I and Kawata S 2011 *Nano Lett.* 11 5344
[3] Zhang L 2013 *Appl. Surf. Sci.* 270 292
[4] Zeman E J and Schatz G C J o P C 1987 91 634
[5] Fu E, Liang T, Houghtaling J, Ramachandran S, Ramsey S A, Lutz B and Yager P J A c 2011 83 7941
[6] Guan N, Dai X, Messanvi A, Zhang H, Yan J, Gautier E, Bougerol C, Julien F H, Durand C and Eymery J J A p 2016 3 597
[7] Fodjo E K, Riaz S, Li D-W, Qu L-L, Marius N P, Albert T and Long Y-T J A M 2012 4 3785
[8] Daruich J, Zirulnik F and Gimenez M a S a J E r 2001 85 226
[9] Lin D, Wu Z, Li S, Zhao W, Ma C, Wang J, Jiang Z, Zhong Z, Zheng Y and Yang X J A n 2017 11 1478
[10] Kang J-S, Hwang S-Y, Lee C-J and Lee M-S J B o t K C S 2002 23 1604