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Fabrication of a high sensitive Ag-nanoparticle substrate and its application to the detection of toxic substances

Jinyu WANG[1], Yuan LIU[1], Zhen LI[2], Yan WANG[1], Jiqiang Wang[1], Tongyu LIU[2*], Tong SUN[3], and Kenneth T. V. GRATTAN[3]

[1] Key Laboratory of Optical Fiber Technology of Shandong Province, Qilu University of Technology (Shandong Academy of Sciences) Laser Institute, Jinan, 250014, China

[2] Shandong Micro-Sensor Photonics Ltd, Jinan, 250014, China

[3] School of Mathematics, Computer Science and Engineering, City University of London, London, EC1V 0HB, U.K.

E-mail: tongyu.liu@vip.iss-ms.com

Abstract. Surface Enhanced Raman Scattering (SERS) is typically observed with the substrate in a liquid medium and it has been proposed as a promising technique for detecting low levels of pollutants in liquids. A technique is presented for self-assembly to immobilize Ag nanoparticles (Ag-NPs), with diameters ranging from 100 to 800nm on a solid support. Experimental results have been obtained through experiments using Ag-NPs active substrates to detect Rhodamine 6G (R6G) and crystal violet in the deionized water. Further, the SERS spectrum and Raman spectrum of phoxim were also measured, showing the enhancement in the performance of the active substrate as a result.

1. Introduction

Food safety problem is a major human concern, with problems of additive abuse, fake and shoddy foods, as well as excessive pesticide residues, being seen daily and across the globe. Raman spectroscopy is a proven and effective technique for the detection and identification of unknown molecular species within a liquid medium. Raman scattering plays an important role in analytical science, such as in electrochemistry, biosensing and environmental analysis, for example. However, most molecular signatures, such as that from water, give a very weak Raman spectrum and hence this causes difficulties with signal detection.

Surface Enhanced Raman Spectroscopy (SERS) is a familiar technique for increasing the Raman signal emission and thus improving detection efficiency. When molecules are adsorbed onto active substrates, an enhanced Raman signal of the adsorbate is obtained, with up to 10^6 [1] greater signal intensity than would normally be observed. This phenomenon shapes the basis of Surface Enhanced Raman Spectroscopy as a valuable analytical technique. Metallic nanoparticles (MNPs) were used shortly after the discovery of the SERS effect and have become, as a result, the most studied class of substrates.

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Of the many different types of SERS active substrates, they can be classified into three main categories: (1) MNPs in suspension; [2,3] (2) MNPs immobilized on solid substrates; [4,5] and (3) Nanostructures fabricated directly on solid substrates, which includes nanolithography and template synthesis of nanostructures [6,7]. There are also many different techniques for self-assembly to immobilize metallic nanoparticles on a solid support. This paper will introduce a technique for self-assembly to immobilize Ag nanoparticles on a solid glass support and illustrate experimental results using Surface Enhanced Raman Spectroscopy for detecting important toxic substances, such as Rhodamine 6G, crystal violet and phoxim. The SERS spectrum of phoxim will also be compared with its Raman spectrum to emphasize the enhancement performance seen due to the use of the active substrate.

2. Substrate design and fabrication

2.1. Materials

All chemicals and reagents were commercially available and used as such. (3-Aminopropyl) trimethoxysilane (97%) (APTMS), L-Ascorbic acid (≥99.7%), Polyvinylpyrrolidone, Rhodamine 6G (98%, R6G) and Silver nitrate ($AgNO_3$) (≥99.8%) in analytical pure grade were purchased from Sigma-Aldrich. H_2O_2 (30%) and H_2SO_4 (98%) was obtained from Sinopharm Chenical Regent Co., Ltd. The deionized water used in all syntheses was filtered with a Millipore E-pure filtration system at >18 MΩcm. R6G and crystal violet stock solutions were prepared by dissolving them individually in the deionized water. All glassware used in the following procedures was cleaned with freshly prepared *aqua regia* (3:1 of HCl: HNO_3), rinsed thoroughly with tap water first and then deionized water and dried finally in an oven at 120°C, prior to use.

2.2. Experiment Details

Quartz plates (the substrates used) were washed with ethanol to clean them thoroughly, and then placed in an ultrasonic cleaner for about 10 minutes, after which they were rinsed thoroughly with deionized water. They were then immersed in a 30:70 (v/v) mixture of H_2O_2 (30%) and H_2SO_4 (concentrated) (Piranha Solution) for 30 min. After that, they were rinsed using an excess of distilled water, cleaned in an ultrasonic bath and then dried by using compressed nitrogen. These quartz plates were then modified by silanizing for 12 h in a 1% solution of APTMS in methanol. After that, they were washed with methanol and distilled water respectively and subsequently, dried by using compressed nitrogen. This procedure functionalizes the glass surface with polymerizable amino groups.

The following procedure was used to synthesize the seed solution. Firstly, Ascorbic Acid in aqueous solution (880mg, 1mol/L), Polyvinylpyrrolidone aqueous solution (222mg, 0.1mol/L), and $AgNO_3$ aqueous solution (170mg, 0.1mol/L) were prepared. Secondly, 2ml $AgNO_3$ aqueous solution blended with 20ml Polyvinylpyrrolidone aqueous solution was poured into a conical bottle, stirred using a magnetic mixer, then 78ml deionized water was added into the solution. Lastly, 2ml Ascorbic acid aqueous solution was poured into the mixture solution quickly, and it was noticed that the solution turned into grey immediately. A few minutes later, the solution became dark grey - this indicated that the nanoparticles had been obtained. The solution was then centrifuged twice at the rate of 1000r/min for 10 minutes with the supermatant replaced by deionized water.

The final procedure was to deposit the nanoparticles. To do so, the quartz plates that had been prepared were placed at the bottom of a beaker, and then the uniformly mixed seed solution was poured into the beaker. The beaker was sealed with a preservative film and then left for 12 hours to allow the deposition to happen. This procedure forms a layer of Ag nanoparticles on the surface of the quartz plates. Following this, the Ag active substrate must be stored under vacuum, or the Ag nanoparticle will be oxidized quickly in the air and not be usable.

3. Results and Discussion

3.1. SEM Measurement

A scanning electron microscope (SEM) was used to obtain the SEM images to observe the surface morphology of the Ag nanoparticles (at 5 kV operating accelerating voltage). Figure 1 also shows a typical SEM image of the Ag-NPs formed. As shown in Figure 1, the particle sizes of Ag-NPs are 100nm to 800 nm and it can be seen that some Ag-NPs are overlapping, but overall the particles are isotropic in shape.

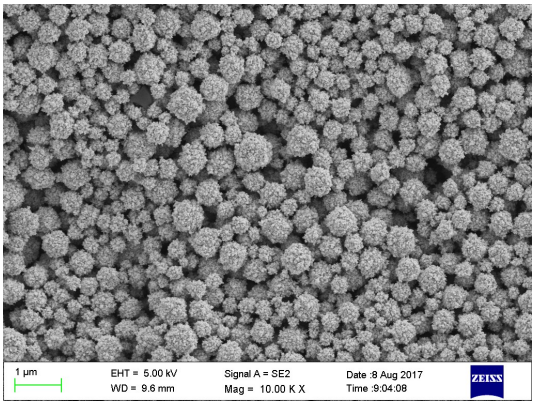

Figure 1. SEM images of the Ag-NPs substrate prepared.

3.2. Raman Spectra Measurements

A Raman spectrometer (nVia Raman Microscope, Renishaw, UK) with a 785 nm laser and a 1024 x 400 pixels CCD (Andor detector) was used to observe the Raman spectra produced. The laser beam was focused by a 100× objective onto the Ag-NPs active substrate which absorbed the sample to be measured. Raman signals were collected by the same objective and coupled into the Raman spectrometer. The wavenumber of the scanned wavelength range was from 200cm^{-1} to 2000cm^{-1} and the integral time used was 10s.

For the liquid samples, the Ag-NPs active substrate was mixed thoroughly with R6G or crystal violet solution of known concentration. When the solution became a film on the substrate, the Ag-NPs active substrate was taken to the Raman spectrometer to obtain the SERS spectra. Figure 2 shows the SERS spectra of 10^{-5}M and 10^{-6}M concentrations of R6G absorbed on the Ag-NPs active substrate, excited by light from a 785nm laser (with 2.5mW power). The spectra are very similar to those reported in the literature [8], except for a 10cm^{-1} shift. Figure 3 shows the SERS spectra of different concentrations of crystal violet absorbed on the Ag-NPs active substrate, excited again by light from the 785nm laser (with 0.25mW power used).

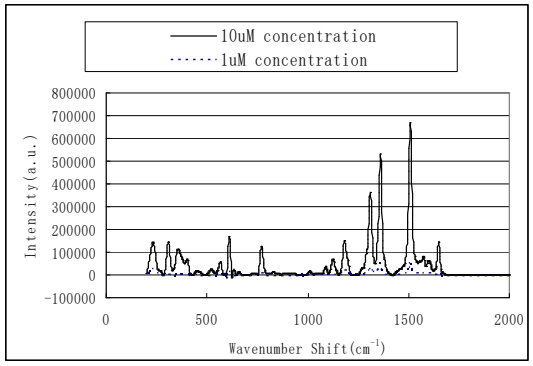

Figure 2. SERS spectra of different concentrations of R6G.

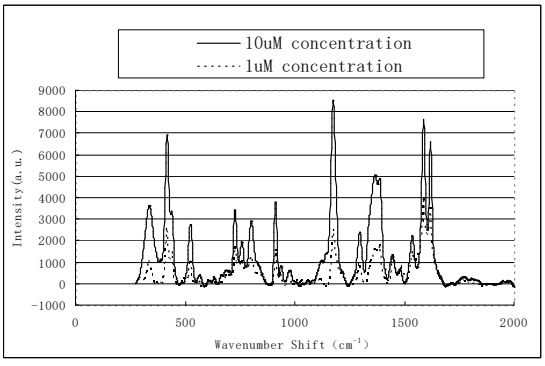

Figure 3. SERS spectra of different concentrations of crystal violet.

A 40% concentration of phoxim was also measured using the Ag-NPs active substrate. Figure 4 shows the SERS spectrum of this phoxim, excited again by use of the 785nm laser (with 2.5mW power) and 10s integral time. The Raman spectrum of this phoxim was detected by the QEPro65 spectrometer with the 785nm laser and an InPhotonics Raman Probe. Figure 5 shows the Raman spectrum of this phoxim, excited also by the 785nm laser (with 200mW power) and 1s integral time. As can be seen from Figures 4 and 5, the spectral intensity of the SERS spectrum is much higher then that of the Raman spectrum of this phoxim The above shows the presence of the Ag-NPs active substrate playing a key role in this SERS spectrum.

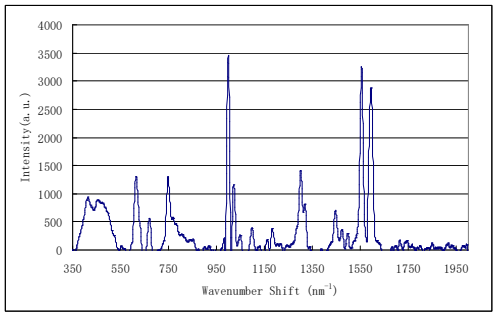

Figure 4. SERS spectrum of phoxim.

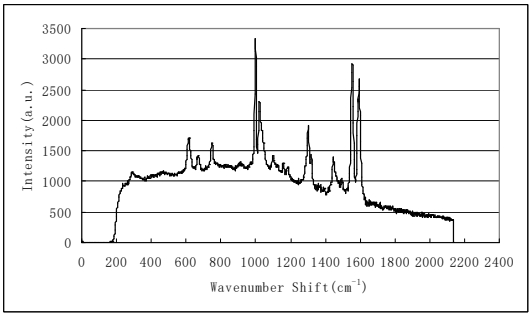

Figure 5. Raman spectrum of phoxim solution

4. Conclusion

In summary, a high-yield synthesis of Ag nanospheres with complex surface morphology which are formed by the agglomeration of small Ag nanoparticles has been proposed. The SERS spectra of R6G and crystal violet in deionized water have been measured when combined with the use of this Ag-NPs substrate. This SERS-active substrate plays an important role in molecular detection – however the SERS measurement method is more complex and off-line. As optical fibers provide greater flexibility, ease of sampling, and remote sensing capability, the combination of SERS and optical fibres makes a real-time, compact, flexible, reliable method feasible. Work is continuing to fabricate an Ag-NPs substrate on an optical fibre and to measure its enhancement properties using a simple Raman spectrum system, looking towards the goal of a portable, online SERS detection system.

Acknowledgments

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