Optimum growth time in AgPt nanofern preparation for enhancement of surface-enhanced Raman scattering intensity

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Abstract
Surface-enhanced Raman scattering (SERS) is a phenomenon where the signal of the Raman spectrum of an analyte increased due to a plasmonic effect of metal nanoparticles. This phenomenon is potentially be implemented in biosensor application to detect the presence of a molecule in blood and urine. This paper reports a study on bimetallic thin film of argentum-platinum (AgPt) nanoferns as a SERS substrate for detection of creatinine. Nanofern-shaped AgPt was prepared directly on ITO surface using liquid phase deposition technique. The growth time of the AgPt preparation was varied from 5 to 60 min to study the effect of growth time towards deposition of AgPt nanofern on the surface. This sensitivity of SERS measurement was studied by comparing the Raman spectra of creatinine on ITO surface and creatinine on AgPt surface. We observed that the sensitivity of the spectroscopy system towards creatinine molecule detection is dependent on the morphology structures of AgPt substrate.

Keywords: AgPt, nanofern, surface-enhanced Raman scattering
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1. Introduction

Raman spectroscopy is a powerful technique in analyzing chemical content in complex biological samples. This technique based on an optical system that uses an inelastic light scattering to produce a spectrum of the detected molecules of the material. The Raman spectrum for each molecule material is unique. Thus, Raman spectroscopic technique provides accurate molecular detection without requiring complex processes. However, detection using this Raman spectroscopy is limited because Raman signals from the inelastic light scattering are very weak [1]. In 1974, three scientists from Southampton University, Fleischmann, Hendra and McQuillan, accidentally detected a strong Raman signal from pyridine deposited on a rough silver substrate surface [2]. The enhancement of this Raman signal has identified as a result of the plasmonic effect of metal nanostructures which known as surface-enhanced Raman scattering (SERS) phenomenon [3]. The amplification of this Raman signal allows a molecule to be detected although the molecular concentration is low. Zhou’s group have used the SERS technique and successfully detected polychlorinated biphenyls molecules; a type of chemical found in pesticides at 5 μl−1 of concentration [4]. The sensitivity of this SERS technique is highly dependent on a SERS substrate used [5–7]. This SERS substrate is made up of thin films of metal elements, usually gold, argentum and copper deposited on the surface of glass, quartz or indium-titanium oxide (ITO) substrate. The surface morphology of the film made to form a coarse nanostructure, since the surface of the metal may thus have a high plasmonic effect. The plasmonic effect of the metal element is the result of the reaction between the laser beam and the free electrons found on the metal surface. Therefore, SERS substrate with sharp-pointed morphological structure has a higher density of free electrons than rod and plate structure, thereby enhancing Raman spectral signal when the reaction occurs. Cui’s group has established a powerful SERS measurement using AuPt multibranched nanoparticle substrate to produce an enormous SERS enhancement [8]. In this report, we attempted to study the variation of growth time during the preparation of AgPt towards the formation of AgPt nanofern-structured on the surface. The AgPt thin films subsequently implemented as SERS substrate to detect creatinine molecule using home-made SERS sensor system. The result of this study suggested that the optimum growth time formed the high electrochemical surface area by giving higher SERS intensity.

2. Experimental

2.1. Materials

Chemicals used in the synthesis of silver-platinum (AgPt) nanofern are potassium hexachloroplatinate (IV), silver nitrate, sodium dodecyl sulfate and formic acid. These chemicals were purchased from Sigma-Aldrich and used without further purification. Substrate for AgPt nanofern deposition is ITO on a glass that was procured from Merk Balzers. The ITO layer thickness is 40 ± 1.0 nm and electrical resistance is 100 Ω × m−2 and the size of ITO is 1.5 × 1.5 cm2.

2.2. Preparation of AgPt nanofern thin film

The silver-platinum nanofern thin film was prepared using a liquid phase deposition technique as described in the previous report [9]. In the typical preparation of AgPt nanofern film, the synthesis solution consists of potassium hexachloroplatinate (IV), silver nitrate (AgNO3), sodium dodecyl sulfate and formic acid was mixing in deionized water. After that, the ITO substrate vertically immersed in the vial’s solution and then stirred under 400 rpm at 40 °C for 5 min. After that, the AgPt nanofern directly deposited on ITO surface and the substrate rinsed with copious amounts of deionized water. Finally, the AgPt substrate heated at 200 °C for 1 h before using in SERS measurement. The growth time was varied from 5 min to 60 min to study the effect of growth time towards the growth of AgPt nanofern on the ITO surface. The samples were labeled as T5, T15, T30, T45 and T60 for 5 min, 15 min, 30 min, 45 min and 60 min of growth time, respectively. These morphology and optical properties of the samples were characterized using FESEM and UV-Vis.

2.3. Detection of creatinine

The sensitivity of AgPt films as SERS substrates was studied to detect creatinine using a home-made sensor [10]. This home-made sensor was built by combining optical components such as a diode laser with 785 nm of wavelength, a duplex fiber optic with Raman optical probe and Raman spectrophotometer. Creatinine powder was purchased from Sigma Aldrich and used without any purification process. Creatinine was prepared in solution with 1.0 M concentration by mixing in deionized water. After that, the solution was dropped on each AgPt thin film surface and dried under ambient temperature prior to test a SERS measurement.

3. Results and discussion

Silver-platinum nanofern thin film was prepared on an ITO surface using liquid phase deposition technique. In typical nanofern formation during the growth process, a yellowish growth solution was changed to a grey color. This process has interpreted as successfully deposited of AgPt nanofern particles on ITO surface after a homogenous and transparent grey layer film was formed on the surface. Figure 1 showed the deposition of AgPt nanofern on the ITO substrate surface with different growth times at 5 min to 60 min. The thin films were labeled as T5, T15, T30, T45 and T60 for 5 min, 15 min, 30 min, 45 min and 60 min of growth time respectively. Various growth time during the deposition process on the ITO surface was expected to change the morphology and structure of AgPt nanofern on the surface. The morphology of the AgPt nanofern deposition has observed by field emission scanning electron microscope (FESEM) at 3 keV and 5 × 103 magnification. At the same time, we characterized the films using cross-section
and energy dispersive x-ray spectroscopy (EDX) on the same AgPt film samples. The results of Ag and Pt compositions and thickness of the films from EDX and cross-section characterizations were illustrated in table 1, respectively.

Based on the FESEM images, it can vividly see that the AgPt particles have deposited on the surface after the ITO surface

| Samples | Ag composition (%) | Pt composition (%) | Thickness (μm) |
|---------|--------------------|--------------------|---------------|
| T5      | 6.25               | 93.75              | 0.55          |
| T15     | 4.80               | 95.20              | 0.85          |
| T30     | 3.34               | 96.66              | 0.95          |
| T45     | 3.87               | 96.13              | 1.07          |
| T60     | 4.69               | 95.31              | 0.87          |

Figure 1. FESEM images of AgPt with different growth times of 5 min to 60 min.

Figure 2. Optical absorbance of AgPt thin films.
immersed in the solution for 5 min. The nanofern structure has not formed yet, but small clusters were starting to grow on the surface. The AgPt particles are covered nearly 70% on the surface with the measured thickness of grown particles is $0.55 \mu m$. After 15 min deposition, the AgPt particles have covered the surface almost 80% and the clusters were grown to upwards direction with measured thickness is $0.85 \mu m$. Then, the nanofern-shaped AgPt particles were started to form and vertically grow with sharp leaves after 30 min deposition with $0.95 \mu m$ of the nanofern thickness. Referred to the image, we also observed that the branch of nanofern obtained from a combination of overlapping of nanopyramid. This AgPt nanofern has grown and covered almost 90% to 95% on the surface after the deposition time was increased by 45 min and 60 min during the synthesis. The average film thickness for T45 and T60 is $1.07 \mu m$ and $0.87 \mu m$, respectively. Table 1 has presented EDX result for a composition of Ag and Pt elements and the thickness for the AgPt thin film with different growth time. Referred to the result, we can see that increasing of the growth time will decrease the Ag and Pt elements on the formation of AgPt bimetal system. The composition analysis has presented that the percentage composition of Ag element on the ITO surface has decreased and Pt element has increased with the increase of growth time. Meanwhile, the composition of Pt element generally increased at first 5 min to 30 min and decreasing after 45 min and 60 min of growth time.

The effect of different growth time towards the morphology of AgPt thin film surface can observe from the absorbance spectra that illustrated in figure 2. The AgPt thin film presented a good plasmon property by exhibiting three absorbance peaks situated at 321 nm, 436 nm and 676 nm. The absorbance intensity of the thin films with different growth time has changed although the peaks position remains. It found that the absorbance intensity of AgPt thin films has increased with the increase of the growth time except after 45 min. Based on the absorbance of the thin films, T30 has revealed the highest absorbance intensity for peaks situated at 321 nm, 436 nm and 676 nm. Additionally, these absorbance intensities of the AgPt thin films considerably agreed with the composition analysis and thickness result of AgPt thin film.

The sensitivity of SERS substrate towards analyte detection has observed by comparing the intensity of Raman spectrum of the analyte adsorbed on a metal surface and without metal surface. Hence we dropped 1.0 M creatinine solution on the ITO substrate surface and AgPt thin film surfaces to study the performance AgPt thin film as SERS substrate in creatinine detection. Figure 3 showed Raman spectrum for creatinine in ITO as reference spectrum and Raman spectrum of creatinine on T30 surface. Based on the Raman spectra, the home-made SERS sensor has successfully detected four Raman peaks of creatinine at 610, 678, 839 and 900 cm$^{-1}$ on ITO and T30 [11]. It was found that an enhanced Raman signal of creatinine molecule has exhibited after this molecule placed on T30 surface. We could say that the plasmonic effect from AgPt has induced the magnetic field of photon and enhanced the vibration properties of creatinine molecule [12]. The increasing of Raman signal of creatinine named as SERS phenomena.

The detection experiment continued by dropping the same concentration of creatinine solution on different AgPt thin film surfaces namely T5, T15, T45 and T60 surface. The SERS spectra of creatinine on AgPt surfaces were recorded and plotted in figure 4. It found that the SERS sensor has sensed the four main Raman peaks of creatinine molecule by using AgPt nanofern substrates. Interestingly, these AgPt substrates have presented as a good candidate as SERS substrates by exhibiting an enhancement on Raman intensity of creatinine after creatinine placed on AgPt nanofern surfaces. However, the SERS intensity for each surface has shown different intensities with peaks position remains. Referred to SERS spectra in figure 4, the SERS intensity was increased from T5 to T30 but decreasing for T45 and T60. It found that T30 surface is high sensitive substrate by enhancing the four Raman peaks of creatinine molecule compared with other SERS substrates. Based on the SERS intensity, it can be summarized that T30 has the optimum structure to use as a SERS substrate and for further study in biomolecule detection.
4. Conclusion

In this paper we have successfully studied the variation of growth times during AgPt preparation to form AgPt nanofern-shaped on the ITO substrate surface as a SERS substrate to detect creatinine. The result demonstrated that sensitivity of SERS measurement towards creatinine detection depends on morphology and composition of Ag and Pt elements on the surface of the thin films. These AgPt thin films have shown as good SERS substrates by exhibiting the enhancement at each Raman peaks of creatinine molecule after creatinine placed on the AgPt surfaces. In this future work, these AgPt thin films potentially implemented in monitoring environmental pollution, food quality, security and medical application.

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