Synthesis of silver–platinum nanoferns substrates used in surface-enhanced Raman spectroscopy sensors to detect creatinine

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Abstract
Creatinine is one of the most commonly used bio markers of renal function. This paper reports a study on detection of creatinine using silver–platinum (AgPt) nanoferns substrates to fabricate a surface-enhanced Raman spectroscopy (SERS) sensor. The AgPt nanoferns were synthesized by liquid phase deposition (LPD) where the morphology structures and thickness of the AgPt nanoferns were controlled by varying the concentration of formic acid which was acting as the reducing agent. We have obtained four different nanoferns structures and thicknesses. This study showed that the AgPt nanoferns structure synthesized with 40 mM formic acid give the highest Raman peak intensity for a 0.05 M creatinine sample.

Keywords: AgPt nanoferns, SERS sensor, creatinine
Classification numbers: 4.00, 4.02, 4.10, 5.00

1. Introduction
Surface-enhanced Raman spectroscopy (SERS) is a highly sensitive optical technique that has been developed from conventional Raman spectroscopy (RS) and has been widely used for decades. Conventional RS is one of the spectrometric techniques used to detect diseases [1]. However, due to the weak Raman scattering signal caused by the small cross section of light scattered by the molecules, SERS has been developed. SERS enhances the Raman peak intensities of detected molecules. It is highly selective and sensitive which allows detection of a single molecule in a sample at a very low concentration [2]. The enhancement in SERS is triggered by two enhancement mechanisms which are either electromagnetic or chemical [3]. Electromagnetic enhancement occurs when there are localized-surface plasmon resonance (LSPR) effects from the rough surface of a nanostructured metal like gold, copper and silver as SERS substrates. Meanwhile, the chemical enhancement involves the adsorption of molecule on a metal surface which will change the polarizability of the electrons on the surface. Due to the enhancement mechanisms of SERS, choosing SERS substrates to be used is important in order to enhance the Raman peak intensities of detected molecules.

Gold nanoparticles (AuNPs) have been used as SERS substrates in many studies. Spherical gold nanoparticles of various sizes and conditions are able to enhance the Raman signal of 4-aminothiophenol [4]. The spherical AuNPs were synthesized by seed-mediated growth technique. Gold nanorods that were prepared by seed-mediated method are effective as SERS substrates in detection of rhodamine 6G (R6G) [5, 6].
Silver nanoparticles (AgNPs) have also been used as SERS substrates as they give more enhancement of Raman scattering signal compared to that of AuNPs. Triangular silver nanoparticles are used as SERS substrates as they have sharp edges which help to enhance the Raman signal for detected molecules [7, 8]. Silver nanowell arrays prepared by a wet chemical reduction method were also effective as a SERS sensing platform [9]. Recently, bimetallic nanostructures have been increasing as SERS substrates. Since single metal nanostructures have been proven to enhance the Raman signal, bimetallic nanostructures are also being studied. Bimetallics of silver–platinum (AgPt) core-shell that were synthesized by seed-mediated growth method have been shown to enhance the Raman intensities of pyridine due to the plasmonic effect of the bimetallic nanoparticles formed [10]. Adenine molecules have been successfully detected by AgPt bimetallic nanoparticles where the Raman intensities of the adenine was enhanced [11]. We report the synthesis of AgPt nanoferns substrates using a facile liquid-phase deposition (LPD) method as shown in previous study [12]. Silver–platinum (AgPt) nanoferns thin films were prepared on a cleaned ITO surface by a liquid phase deposition (LPD) method. In a typical method, the colloidal AgPt was firstly synthesized by simultaneously mixing 1 mM potassium hexachloroplatinate (IV), 0.2 mM silver nitrate, 10 mM sodium dodecyl sulfate and 5 mM formic acid in deionized water. The mixture was subjected to a sonication treatment and the final color of the solution was milky-white. This colloidal AgPt was placed in a beaker on a hot plate and the cleaned ITO was then inserted into the vial. The colloidal dispersion was stirred at 400 rpm at 40 °C for 30 min. The synthesis reaction was completed after the milky-white solution changed to a colorless solution. The ITO was taken out and washed with copious amount of deionized water before being dried under the flow of nitrogen gas. A uniform black thin film was observed on the ITO surface. Next, we studied variation of formic acid concentrations and its effect on the AgPt nanoferns grown on the ITO surface. The four concentrations of formic acid used were 5 mM, 20 mM, 40 mM and 100 mM. The effect of different formic acid concentrations will be observed by determining the distributions and coverage of AgPt nanoferns formed on the ITO surfaces. These thin films were used as SERS substrates to detect creatinine using a home-made SERS sensor. Creatinine samples with 0.05 M were prepared by diluting creatinine powder in deionized water. The mixture was dissolved with sonication treatment for 1 min. After that, 0.06 ml creatinine was dropped on the ITO substrate and AgPt thin film surfaces. The detection of creatinine was studied by comparing Raman spectra of creatinine on ITO surfaces.

2. Experimental

The chemical used are potassium hexachloroplatinate (IV) (reagent grade, ≥ 95%), silver nitrate (ACS reagent, ≥ 99%), sodium dodecyl sulfate (ACS reagent, ≥ 99%), formic acid (reagent grade, ≥ 95%) and creatinine (anhydrous, ≥ 98%). All chemicals were purchased from Sigma-Aldrich and used as received without further purification.

Silver–platinum (AgPt) nanoferns thin films were prepared on a cleaned ITO surface by a liquid phase deposition (LPD) method. In a typical method, the colloidal AgPt was firstly synthesized by simultaneously mixing 1 mM potassium hexachloroplatinate (IV), 0.2 mM silver nitrate, 10 mM sodium dodecyl sulfate and 5 mM formic acid in deionized water. The mixture was subjected to a sonication treatment and the final color of the solution was milky-white. This colloidal AgPt was placed in a beaker on a hot plate and the cleaned ITO was then inserted into the vial. The colloidal dispersion was stirred at 400 rpm at 40 °C for 30 min. The synthesis reaction was completed after the milky-white solution changed to a colorless solution. The ITO was taken out and washed with copious amount of deionized water before being dried under the flow of nitrogen gas. A uniform black thin film was observed on the ITO surface. Next, we studied variation of formic acid concentrations and its effect on the AgPt nanoferns grown on the ITO surface. The synthesis steps for the AgPt are repeated to prepare different AgPt nanoferns thin films. The four concentrations of formic acid used were 5 mM, 20 mM, 40 mM and 100 mM. The effect of different formic acid concentrations will be observed by determining the distributions and coverage of AgPt nanoferns formed on the ITO surfaces.
and AgPt thin films surfaces. The change in Raman intensity of each AgPt thin films was observed where creatinine on ITO surface was the reference spectrum. The SERS system comprises a light source, Raman probe, sensor chamber, and spectrometer. The wavelength of the laser light is 532 nm of wavelength and integration time is 10 s with 5 scans.

The morphology of the AgPt thin films was characterized using field-emission scanning electron microscopy (LEO SUPRA 55VP FESEM). Meanwhile, the optical absorbance spectra of the films were recorded using UV–Vis spectrometer (Hitachi U-3900H) and the Raman spectra of creatinine sample were recorded by QEPr0-65 spectrometer (Ocean Optic) with 532 nm laser source wavelength.

3. Results and discussion

Silver–platinum (AgPt) nanofern thin films were successfully prepared by LPD. Figure 1 shows FESEM images of AgPt structure grown on an ITO surface, that were synthesized with four various concentrations of formic acid ranging from 5 mM, 20 mM, 40 mM and 100 mM. The surfaces show heights of 0.63 µm, 1.18 µm, 1.59 µm and 0.90 µm, respectively. It was observed that the structures of AgPt thin film were compromised of layers of pyramidal shapes which resemble nanoferns. The film covered almost all the surface of the ITO substrate. It can be seen that the AgPt particles of figure 1(a) did not have a nanoferns morphology. AgPt nanoferns were successfully grown in figure 1(c). Under this conditions, the AgPt was high in density as it covered almost all of the ITO surface. However, the AgPt nanoferns started to shrink and decrease in density in figure 1(d). From the FESEM images, we can see that once it reached the optimum concentration of formic acid at 40 mM, the growth of AgPt nanoferns started to distort when the concentration of formic acid was further increased.

Figure 2 shows the LSPR absorption spectra of the AgPt thin films for the different AgPt nanofern structures prepared. The broad regions at 350 nm to 470 nm were due to the plasmonic effect of Ag particles. The presence of Pt particles in the AgPt nanoferns thin films lowered the absorbance of Ag particles as they replaced and covered the Ag particles [13]. The reduction of Ag caused the Pt to receive electrons from Ag which lowered the absorbance spectra of Ag [14].

The synthesized AgPt nanofern thin films were used as SERS substrates for detection of 0.05 M creatinine. Figure 3 shows the Raman spectra of creatinine without and with AgPt thin film of 40 mM formic acid taken with 532 nm laser excitation. The Raman intensities of creatinine were enhanced as the percentage of silver in the
thin films increased. The composition of silver for figure 4(c) was 7.45% which higher than that of figure 4(a), (b) and (d) which were 2.2%, 3.4% and 2.7%, respectively. The surface with a low composition of silver will have high composition of platinum which will inhibit the intensity of the Raman signal.

4. Conclusion

We have demonstrated the synthesis of AgPt nanoferns substrates by liquid-phase deposition by varying the concentration of its reducing agent, formic acid. Different concentrations of formic acid will produce different surface profiles of AgPt nanoferns. The optimum concentration was 40 mM. The AgPt nanoferns formed were successfully used as a SERS substrate where they were able to enhance the Raman scattering signal of creatinine molecules.

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