



Conference Paper

Application of Gold Nanoseeds in Surface-Enhanced Raman Spectroscopy for Detection of Urea

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Abstract

This paper reports a study to detect urea by a homemade surface-enhanced Raman Spectroscopy (SERS) sensor using gold-nanoseeds (AuNS). The nanoseeds were prepared by the first of two steps of the seed-mediated technique where the sizes of the nanoseeds were controlled through the heat treatment periods. It was demonstrated that gold-nanoseeds (AuNS) with the averages sizes of 15-20 nm can be utilized to enhance the Raman peaks intensities of urea. The enhancement intensities of the Raman peaks are linear with the urea concentrations where the lowest urea concentration that was detected using AuNS from this study is 0.0901 g/L.

Keywords: surface-enhanced Raman spectroscopy (SERS), gold-nanoseeds (AuNS), urea, chemical sensors

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1. Introduction

High level of urea in blood or in urine may indicate renal failure. Most methods used to determine urea are based on indirect chemical process such as enzymatic and chemical assays [1]. Enzymatic methods use the urea-metabolizing enzyme urease, which degrades urea into ammonia. The produced ammonia is measured by a pH indicator [2]. Meanwhile, chemical assays used particular chemicals to form colored product [3]. All of these methods are time consuming and may have byproducts from the chemical reactions that interfere in the measurement result. It is a great interest to use a direct spectrometric determination of urea. Raman Spectroscopy (RS) technique is one of the possible techniques where urea is able to produce a specific Raman shift spectrum. However, due to the limitations of RS such as weak Raman signal and small cross section of Raman scattering, surface-enhanced Raman spectroscopy (SERS) has been developed [4]. SERS is an optical sensor system that highly sensitive as compared to normal RS which allows the detection of single molecule even at low concentration of sample [5]. The enhancement in SERS is provided by the localized-surface plasmon resonance (LSPR) of nanostructured metals such as gold, silver, copper and platinum.

This paper reports the application of gold nanoparticles to enhance Raman shift spectrum of urea using a homemade SERS sensor system. The nanoparticles were prepared using a simple of seed-mediated technique.

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2. Experimental

Gold(III) chloride trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) (99.9%), trisodiumcitrate ($\text{C}_6\text{H}_5\text{Na}_3\text{O}_7$), sodium borohydride (NaBH_4) and urea powder were purchased from Sigma Aldrich and used without further purification. Gold nanoseeds (AuNS) were prepared by the first of two steps of the seed-mediated technique where 0.5 mL of 0.01 M $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, 0.01 M $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7$ and 0.1 M cooled NaBH_4 were mixed in deionized water. The colloidal of gold-nanoseeds were heated using microwave for 10s, 30s and 60s respectively and characterized using Uv-Vis Spectrometer (Hitachi U- 3900H), particle size analyzer (PSA) and field- emission scanning electron microscopy (LEO SUPRA 55VP FESEM). Urea solutions in pure water of four different concentrations ranging from 0.1M to 2.0 M were prepared and then mixed with the colloidal of AuNS. The SERS substrates were prepared by dropping the pure urea or the mixed urea-AuNS solutions onto cleaned quartz substrates and left to dry at the room temperature. The detection of urea was studied by recording Raman spectra of the prepared SERS substrates using a homemade SERS sensor system that consists of a laser as light source (523nm), a fiber probe, a spectrometer QPro-60 (Ocean Optics) and a sensor chamber.

3. Results and Discussion

Figure 1 shows the FESEM images of gold- nanoseeds (AuNS) thin films on ITO substrates that were prepared with variation of heat treatment periods. The AuNS have quasi-spherical shaped with average diameter as measured by the particle size analyzer were 8, 11, 15 and 20 nm corresponding to 0, 10s, 30s and 60s heat treatment periods respectively. Hence, we may have variation of the nanoseeds sizes through heat treatment periods of the colloidal. In the next discussion, we refer the localized-surface plasmon resonance (LSPR) based on the nanoseeds sizes.

Figure 2 shows the LSPR absorption spectra of colloidal gold- nanoseeds samples with variation of the particles sizes. Each sample has one LSPR peak ranging from 503 nm to 512 nm according to the increasing sizes of nanoseeds respectively. The intensities of peaks are increasing with the nanoseeds sizes. This results is agreed with the previous research [6].

Figure 3 shows the Raman spectra of urea samples excited with 532 nm laser light. The concentration of urea used is 0.5 M. The samples are pure urea and urea mixed with AuNS of different sizes. The Raman spectrum of the pure urea has two sharp peaks at 548 cm^{-1} and 1012 cm^{-1} , and a small broad peak at 1181 cm^{-1} . It is observed that two samples, urea mixed with 15 nm and 20 nm AuNS are able to enhance the Raman peaks intensities. Meanwhile for the other two samples, 8 nm and 11 nm AuNS, the samples are not able to enhance the Raman scattering signal. This means that the samples with small size of AuNS and low LSPR peaks are not able to assist urea molecules to produce the Raman scattering signal because smaller nanoparticles will have less surface area and low conductivity of electron for oscillation. Thus, less light is absorbed by the surface which weakens its electromagnetic field and reduces the

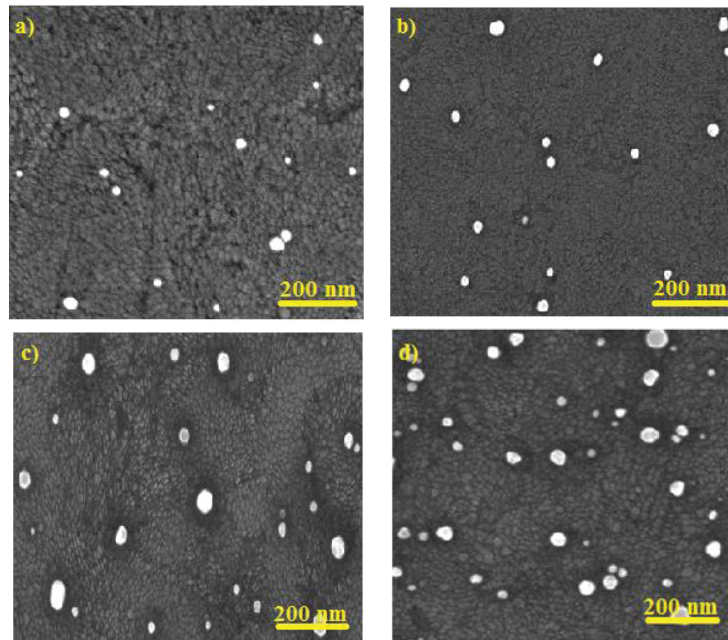


Figure 1: FESEM images of gold-nanoseeds prepared at different heat treatment periods: (a) 0, (b) 10, (c) 30 and (d) 60s.

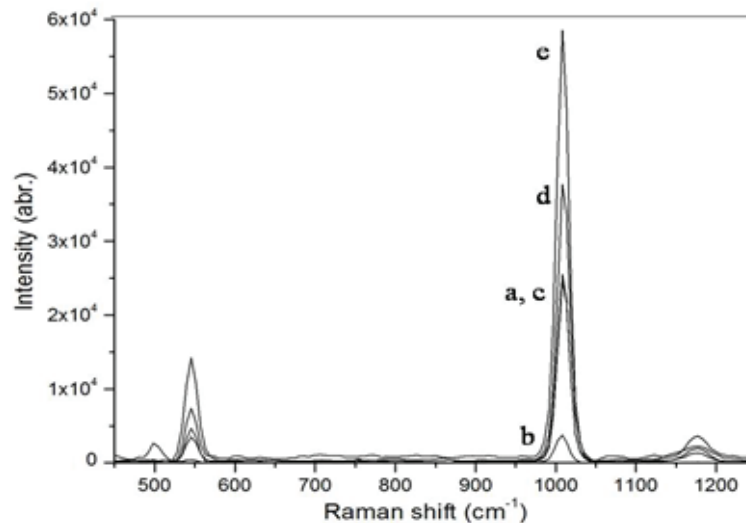


Figure 2: Absorption spectra of the localized- surface plasmon resonance (LSPR) of colloidal gold-nanoseeds with variation of the nanoseeds sizes: (a) 8 nm, (b) 11 nm, (c) 15 nm, and (d) 20 nm.

signal of Raman scattering [7]. From these results, we may concluded that the effective sizes of the AuNS to enhance the Raman scattering are about 15-20 nm.

Figure 4 shows the SERS spectra of urea samples with variation of urea concentrations; 0.1M, 0.5M, 1.0M and 2.0M. The size of AuNS used in this measurement is 15 nm. It was observed that the enhancement intensities of the Raman peaks are linear with urea concentrations. The linearity correlation coefficients (r) are 0.968 and 0.996 for peaks at 548 cm^{-1} and 1012 cm^{-1} respectively (Figure 5). The lowest urea concentration that was detected using AuNS from this study is 0.1 M which is 0.0901 g/L. The AuNS used in this study were prepared using a simple technique that involves

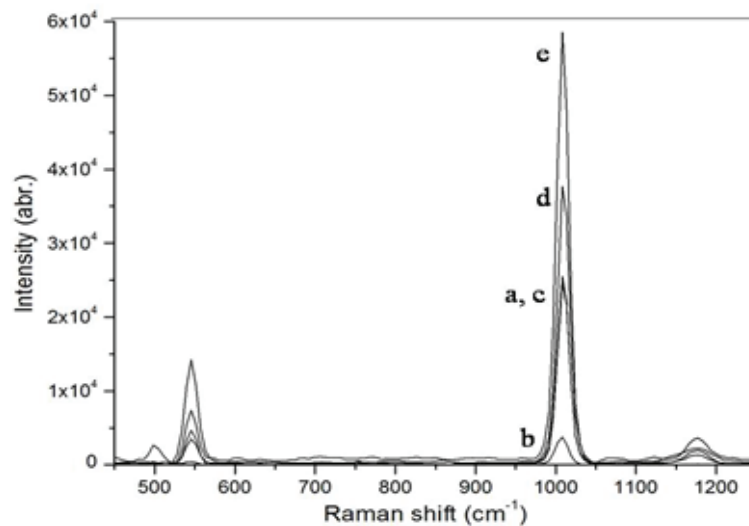


Figure 3: SERS spectra of urea samples taken with 532 nm excitation. (a) 0.5M urea, and 0.5M urea mixed with (b) 8 nm (c) 11 nm (d) 20 nm (e) 15 nm AuNS.

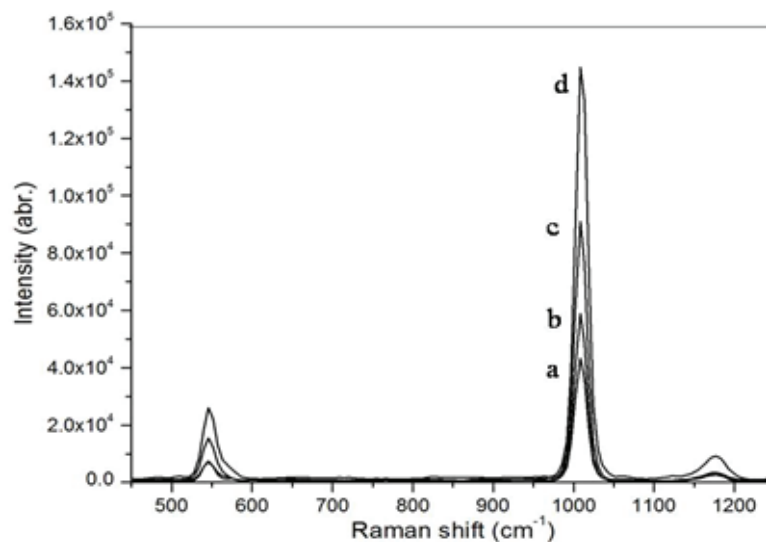


Figure 4: SERS spectra of 15nm gold-nanoseeds for variation concentrations of urea: (a) 0.1 M, (b) 0.5 M, (c) 1.0 M and (d) 2.0 M.

only the seeding process. Hence, to improve the sensing sensitivity of the SERS system, we have to prepare gold nanoparticles using a complete process of the seed-mediated growth technique.

4. Conclusion

We have demonstrated that gold-nanoseeds (AuNS) with the averages sizes of 15-20 nm can be utilized to enhance the Raman intensity of urea. The nanoseeds were

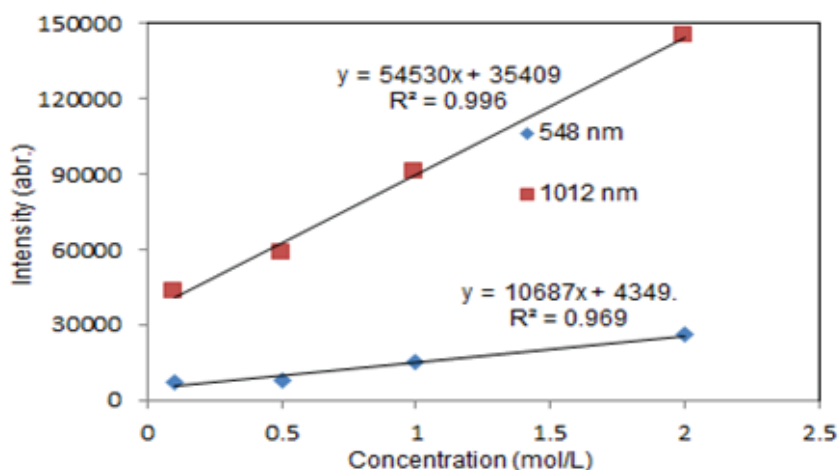


Figure 5: Linearity correlation of 15 nm gold- nanoseeds for variation concentrations (M) of urea: (a) 0.1, (b) 0.5, (c) 1.0 and (d) 2.0.

prepared by the first step of the seed-mediated technique where their sizes were controlled by the heat treatment. Using our homemade surface-enhanced Raman spectroscopy (SERS) sensor we are able to detect the urea concentration as low as 0.0901 g/L in seeding state of gold.

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