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Effect of surface density silver nanoplate films toward surface-enhanced Raman scattering enhancement for bisphenol A detection

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Abstract. This paper reports a study on surface-enhanced Raman scattering (SERS) phenomenon of triangular silver nanoplate (NP) films towards bisphenol A (BPA) detection. The NP films were prepared using self-assembly technique with four different immersion times; 1 hour, 2 hours, 5 hours, and 8 hours. The SERS measurement was studied by observing the changes in Raman spectra of BPA after BPA absorbed on the NP films. It was found that the Raman intensity of BPA peaks was enhanced by using the prepared SERS substrates. This is clearly indicated that these SERS silver substrates are suitable to sense industrial chemical and potentially used as SERS detector. However, the rate of SERS enhancement is depended on the distribution of NP on the substrate surface.

1. Introduction

Bisphenol A (BPA) is an organic chemical that is used domestically by the manufacturing plant to produce polycarbonate plastic [1], stabilizer in polyvinyl chloride, epoxy coating, and antioxidant [2]. The use of BPA could negatively impact human health, harm to the environment, flora, and fauna. However, prevention in the production of BPA for human consumption is still very difficult to do because of its importance in everyday life. Therefore, monitoring techniques on BPA chemical need to be done so that our future generations will live in a clean environment and not suffer from chronic diseases such as cancer.

Recently, surface-enhanced Raman scattering measurement was rapidly developed in sensor technology especially for monitoring contamination of environment and food, in medical and crime. SERS sensor is an important measurement technique in chemistry and biology fields due to it can directly detect a specific molecule precisely. For instance, SERS was studied for detection of melamine in dairy products [3], pesticides [4], kidney disease diagnosis [5], cancer and diabetes [6], forensic analysis for blood classes [7], urea [8], and human semen [9].

SERS phenomenon occurs when the signal from the Raman spectrum of a specific molecule near the defined metal surface was amplified by a factor of 10^3 and above [10]. This phenomenon is due to a result from plasmonic effect of the metal nanoparticles [11]. Before doing SERS measurement, analyte was mixed with nanometal colloidal or absorbed on a deposited nanometal substrates which


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are called SERS substrates. Nanometal elements that are commonly used to get a good plasmonic effect are gold and silver. However, nanosilver has attracted attention in SERS due to low synthesis preparation cost, sharp and high plasmon resonance curve, and strong SERS effect [12].

In this paper, we attempt to study the detection of BPA molecule on four SERS substrate using self-build SERS sensor system. These SERS substrates were prepared with various immersion times to obtain different morphologies on substrate surface. It was observed that the distribution of NP on the surface will be affected by the sensitivity of the sensor towards BPA detection. The result of this work suggested that NP films can be used as a good indicator for an industrial chemical detection.

2. Experiment

Silver triangular nanoplate (NP) substrates were prepared by depositing silver nanoplate on the quartz surface from a colloidal using self-assembly technique. This preparation was described in a previous report [13]. Normal grade quartz substrates without special specification have been purchased from Latech Scientific Supply (Kuala Lumpur, Malaysia) and cut to size 1.2×1.2 cm. Quartz substrate has been chosen because it does not have a Raman spectrum and suitable for implementing in the use of surface-enhanced Raman scattering (SERS). In the study of NP film formation, the experiment was conducted by varying the immersion time of the quartz surface in the colloidal NP for 1 hour, 2 hours, 5 hours, and 8 hours to obtain different film morphologies. The films were labeled as S1, S2, S5, and S8 for 1 hour, 2 hours, 5 hours, and 8 hours of immersion time process respectively.

Bisphenol A (BPA) was supplied by Sigma Aldrich (Kuala Lumpur, Malaysia) with purity of 99.9% and was used without further purification. BPA solution was prepared by dissolving it in ethanol with eight different concentrations, namely 0.001 M, 0.005 M, 0.01 M, 0.025 M, 0.05 M, 0.1 M, 0.5 M, and 1.0 M. In this study, SERS substrate was prepared by depositing BPA solution onto S1, S2, S5, and S8 surface. These substrates were prepared by dropping 0.02 ml of BPA solution and allowed to dry at room temperature for 5 minutes. After that, the SERS substrates were measured to study the presence of BPA molecule on the surface using home-made SERS sensor. Raman spectra of a bare quartz, BPA on quartz surface, NP films were recorded as reference spectra.

Basic characterizations were performed on the NP films to study the change in morphologies of the film's surface. The S1, S2, S5, and S8 were characterized using field emission scanning electron microscopy (FESEM) (Zeiss Supra 55-VP, Selangor, Malaysia) and optical absorbance (Shimadzu UV-160A, Selangor, Malaysia). The SERS measurement was recorded using a self-build SERS sensor system with a 785 nm excitation laser wavelength with 10 seconds integration time.

3. Results and discussion

Triangular silver NP films were simply prepared on a quartz surface using self-assembly technique with four different immersion times which were varied from 1 hour to 8 hours. FESEM was employed to study the successful attachment of the NP on the surface as presented in figure 1. Silver NP particles were starting to attach on the surface toward increasing immersion time after exposing the surface into the colloidal silver NP for 1 hour. The distribution of the NP attachment on the quartz surface was subsequently increasing towards the longer immersion time of the surface into the colloidal. Hence, the calculated of NP distribution on the surface for S1, S2, S5, and S8 are 60, 113, 209, and 430 counts/μm respectively. Besides, the FESEM images showed that the triangular-shape NP on the surface was maintained with the increasing of the immersion times. The average size of the triangular NP on the surface is from 18 nm to 25 nm. These images also revealed the deposited nanoplates particles were well organized on the surface without overlapping each other and formed monolayer films on the surface. The high coverage of the nanoplates with slightly overlapping each plate was obtained after exposing the surface for eight hours into the colloidal.

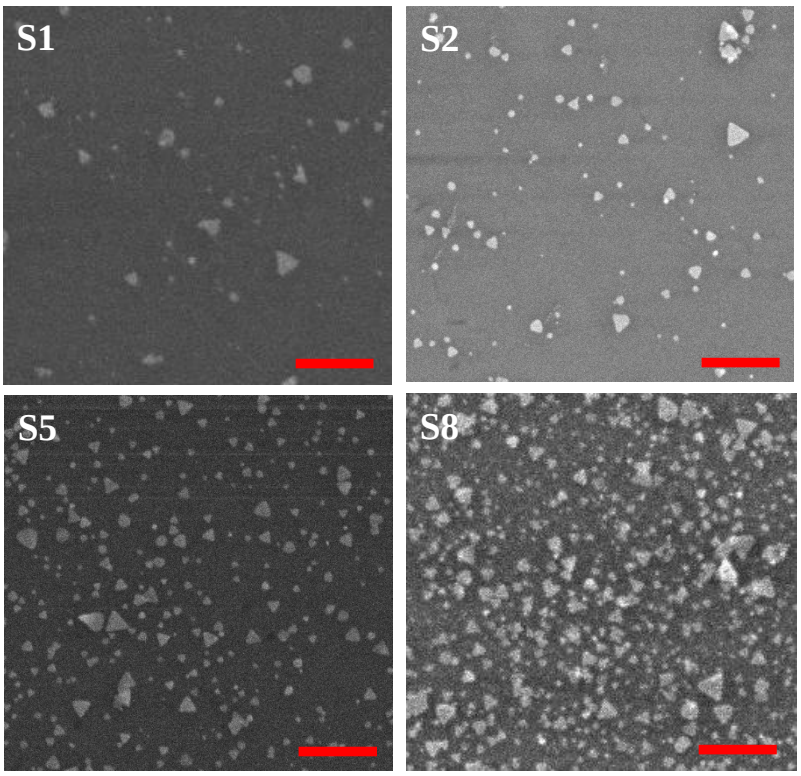

Figure 1. FESEM images of the triangular silver NP on the quartz surface. Scale bars are 100 nm.

Optical spectroscopy has been used to study surface plasmon resonance properties of the triangular silver NP. Figure 2 shows typical absorbance spectra of the NP for S1, S2, S5, and S8. It was found that the triangular silver NP has two absorbance peaks at 330 nm and 640 nm with an absence of a shoulder at 440 nm. A weak intensity of 330 nm peaks was existed due to the small percentage of deposited quasi-sphere on the surface. Meanwhile, an intense broad surface plasmon at 640 nm peak and the shoulder are attributed to Localized Surface Plasmon Resonance (LSPR) and Transverse Surface Plasmon Resonance (TSPR) respectively. The shoulder situated at 440 nm also refers to the successful formation of anisotropic nanoparticles. The intensity of LSPR and TSPR were generally increased with the increase of the immersion times, which is corresponding to the increase of the NP distribution on the surface. However, the position peaks of the absorbance did not have significant changes for S1, S2, S5, and S8.

These four NP films were carried out to sense BPA molecule using SERS sensor. BPA solution at 0.5 M of concentration was dropped on a bare quartz surface as a reference spectrum and dropped on the each NP films. BPA was then let dry under room temperature for 5 minutes. SERS sensor was measured by capturing the Raman spectra of 0.5 M BPA concentration on the bare quartz substrate and on the S1, S2, S5, and S8 as shown in figure 3. Raman spectra were also recorded for bare quartz and the NP substrates without BPA molecule but no Raman peaks existed. Based on the Raman spectra in figure 3, BPA has exhibited seven major Raman peaks at 642 cm^{-1}, 819 cm^{-1}, 832 cm^{-1}, 1114 cm^{-1}, 1183 cm^{-1}, 1600 cm^{-1}, 1614 cm^{-1} [14]. These Raman peaks were enhanced when the BPA molecule absorbed on S1, S2, S5, and S8, clearly demonstrated as a result from plasmonic effect of the triangular silver NP which referred to SERS phenomenon. The intensity of SERS signal was increasing towards increasing of thin films NP distribution on the surface except for S5 and S8 but the Raman peaks position of BPA molecule remain.

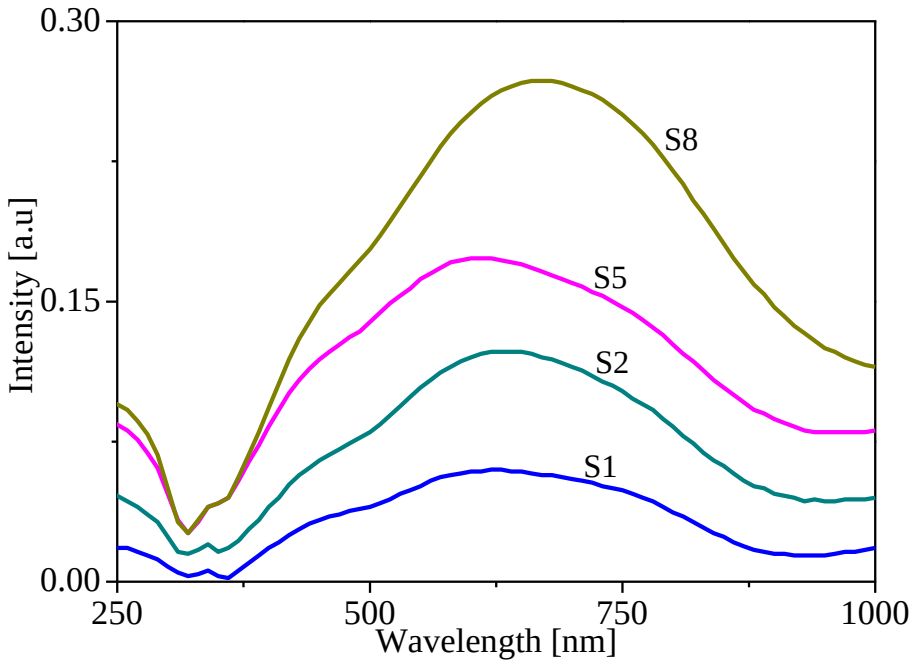

Figure 2. Optical absorbance of the triangular silver NP films.

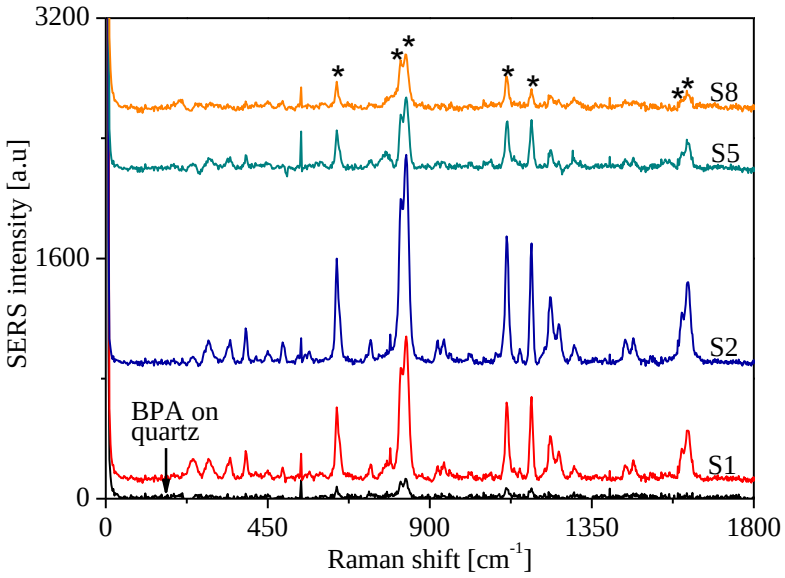

Figure 3. SERS spectra of BPA molecule on the bare quartz and on the NP films surface. BPA peaks are represented as stars.

Referring to SERS analysis in figure 3, it was found that the different morphologies of NP films have given different performance towards bisphenol A detection. Here, we study the sensitivity of the NP films as a SERS substrates towards detection of BPA molecule by calculating the Enhancement Factor (EF). This EF calculation was reported previously in [15]. The analysis of EF values for 642 cm^{-1} peaks and distribution of surface density of each film were arranged in table 1.

The EF value for BPA peaks at 642 cm^{-1} for S1 is 1.04×10^{3} which demonstrated that S1 has been giving a good sensitivity to sense BPA molecule. S2 has shown more sensitivity by increasing EF

value and distribution of NP on the surface. However, the EF value of S5 and S8 was decreasing with increasing NP distribution on the surface, indicating that S5 and S8 are less sensitive than S1 and S2 towards BPA detection.

Table 1. Enhancement factors of 642 cm^{-1} peaks using four SERS substrates.

SERS substrate	Enhancement factor [EF]	Distribution [count/μm] (based on FESEM images)
S1	1.04×10^3	60
S2	1.52×10^3	113
S5	5.53×10^2	209
S8	3.87×10^2	430

To explain why high distribution surface gave low EF value, we need to refer to absorption spectra and morphology images of S1, S2, S5, and S8. NP structure has obtained two oscillation modes after the NP particles irradiated by electromagnetic wave, namely localized oscillation which is horizontal to the surface and transverse oscillation which is vertical to the surface. As shown in figure 2, SERS substrate has high distribution and will produce high-intensity absorbance of localized mode.

In SERS mechanism, electromagnetic wave that irradiated on NP will be absorbed and transferred to analyte molecule and then Raman intensity signal will be enhanced. However, induce oscillation mode on NP that contributes to the energy transfer is transverse mode. At the same time, localized oscillation mode interacted with same oscillation mode from the nearest neighbouring nanoplate. As the result, localized oscillation mode is not contributed to the enhancement of intensity Raman signal. Therefore, closer nanoplate arrangement in the film surface gives lower EF value.

Generally, in previous research, EF value increased with rough surface or dense nanometal distribution [16]. However, EF and distribution density relationship is contradicted for metal materials which have a thin thickness or monolayer film such as NP film [17].

4. Conclusion

Study on using NP substrates in SERS sensor successfully detected BPA molecule using four SERS substrates namely S1, S2, S5, and S8. S2 substrate has shown optimum SERS substrates with highest sensitivity of EF value, i.e. 1.52×10^3. Density surface distribution of nanoplates substrates determined EF value and lowest detection limit of BPA concentrations. The low-density distribution of nanoplates on the surface gave high EF value. Hence, the NP substrates are potential to be used as SERS substrates to detect BPA for monitoring the food, water, and environmental quality.

Acknowledgments

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