



EFFECT OF CURRENT DENSITY ON MORPHOLOGY AND SURFACE - ENHANCED RAMAN SCATTERING PROPERTIES OF SILVER NANOPARTICLES ARRAYS FABRICATED BY ELECTROCHEMICAL DEPOSITION

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Abstract:

Surface-enhanced Raman scattering (SERS) is an analytical technique that allows the detection of trace amounts of organic and biological molecules. In this technique, the SERS substrate, where the Raman scattering signal of the analyte molecules is to be enhanced, plays a particularly important role. One of the most commonly used SERS substrates is the SERS substrate made of silver nanoparticles (AgNPs) immobilized on a solid substrate. Typically AgNPs arrays are fabricated by electroless deposition, in this report we present the fabrication of AgNPs arrays on a silicon surface by electrochemical deposition method. Results showed that this method allows the creation of an array of silver nanoparticles which are relatively uniform in size, morphology, as well as the distance between the particles. Moreover, the size and the density of the AgNPs can be controlled by changing the electrochemical current density. To test the performance of the SERS substrate, AgNPs arrays were used as SERS substrates for detecting traces of crystal violet (CV). The results showed that the intensity of the SERS signal depends strongly on the size of the AgNPs, and the distance between them. With optimal AgNPs arrays, we have recorded a SERS spectrum of CV at concentrations below 0.1 ppb.



ẢNH HƯỞNG CỦA MẬT ĐỘ DÒNG ĐIỆN LÊN HÌNH THÁI VÀ TÍNH CHẤT TÁN XẠ RAMAN TĂNG CƯỜNG BỀ MẶT CỦA CÁC MẢNG HẠT NANO BẠC CHẾ TẠO BẰNG LẮNG ĐỘNG ĐIỆN HÓA

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Tóm tắt

Tán xạ Raman tăng cường bề mặt (SERS) là một kỹ thuật phân tích cho phép phát hiện lượng vết của các phân tử hữu cơ và sinh học. Trong kỹ thuật này, để SERS, nơi mà tín hiệu tán xạ Raman được tăng cường, đóng vai trò đặc biệt quan trọng. Một trong những loại đế SERS được sử dụng phổ biến nhất là các hạt nano bạc (AgNPs) gắn trên một đế rắn. Thông thường, các mảng AgNPs được chế tạo bằng phương pháp lắng đọng không điện, trong báo cáo này chúng tôi trình bày việc chế tạo các mảng AgNPs trên bề mặt silic bằng phương pháp lắng đọng điện hóa. Kết quả cho thấy, phương pháp này cho phép tạo ra mảng hạt nano bạc đồng đều về kích thước, hình thái cũng như khoảng cách giữa các hạt. Hơn thế nữa, kích thước và khoảng cách giữa các hạt có thể được điều khiển bằng sự thay đổi mật độ dòng điện hóa. Để kiểm tra hiệu suất của các đế SERS, các mảng hạt AgNPs được sử dụng là đế SERS để phát hiện tinh thể tím (CV). Các kết quả cho thấy cường độ của tín hiệu SERS phụ thuộc mạnh vào kích thước của AgNPs và khoảng cách giữa chúng. Với các mảng hạt AgNPs tối ưu, chúng tôi đã ghi nhận được phổ SERS của CV ở nồng độ dưới 0,1 ppb.

1. Introductions

Surface-enhanced Raman spectroscopy (SERS) is recognized as a highly surface-sensitive and powerful analytical technique, which not only provides a spectral fingerprint of molecules in a non-destructive manner, but also achieves ultra-trace detection or even single molecule level [1]. Recently, Surface-enhanced Raman scattering

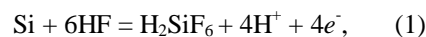
(SERS) as a powerful analytical tool has been shown to have wide potential applications in biochemistry, chemical production, food safety and environmental monitoring [2–6]. In SERS technique, the SERS substrate, where the Raman scattering of the analyte molecules is to be enhanced, plays a particularly important role.

Typically, the SERS substrates made from the noble metals in the nanometer-scale such as nanoparticles, nanorods, nanodendrites...[3, 4, 7] and SERS effect is determined primarily by size, shape and gap distance of these nanostructures. Because in fact, there are two kinds of enhancement mechanisms for SERS. One is the chemical enhancement caused by the charge transfer between the metal surface and the adsorbed analyte molecules [8]. The other is the local electromagnetic (EM) enhancement that originates from the excitation of plasmon on the surface of metals [8–11]. Usually, the local EM enhancement is much higher than the chemical enhancement, and much more attention is paid to the structures that offer obvious local EM enhancements. Specifically, under appropriate circumstances, SERS enhancements as large as 10^{14} can be achieved [11], in which at least 8–10 orders of magnitude can arise from the EM effect, while the enhancement factor due to the chemical effect is only 10^1 – 10^2 times [13, 11]. The intensity of local EM field can be promoted by two kinds of nanostructures on the SERS substrates. One is a sharp tip with high curvature that acts as a ‘lightning rod’, and the other is a slit formed between neighboring metal nanoparticles that serve as a nanogap [14–16]. The regions of highly enhanced local EM field are often called ‘hot spots’. The sharp tips and nanogaps usually are the main hot spots, and they play a decisive role in the enhancement of the Raman signal. Besides the requirement of enhancing the Raman signal strength, the structure of SERS substrates have to be a uniform and repeated in the different fabrication times to be used for quantitative analysis. The silver nanoparticles (AgNPs) arrays on a flat silicon surface is one of the SERS substrates, which promises to meet all of requirements mentioned above. In addition, the creation of AgNPs arrays on silicon substrates is quite simple.

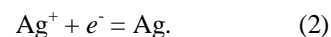
Typically, AgNPs arrays on a silicon surface are fabricated by electroless deposition in the solution of silver nitrate (AgNO_3) and hydrofluoric acid (HF) [7, 17]. The electroless deposition of silver onto silicon in an aqueous solution containing silver

ions (Ag^+) and HF is based on an electrochemical redox reaction in which both anodic and cathodic processes occur simultaneously at the silicon surface [18]. Electrochemical reactions are illustrated in the following equations:

anodic:



cathodic:



In the reactions above e^- denotes electron (with a negative charge). H_2SiF_6 is a soluble compound, so the reaction (1) is the reaction of the Si removing by etching. Meanwhile the reaction (2) is the reaction of the reduction of ionic silver to atomic silver on the silicon surface. From the reaction (1), (2) may find that the silver nanoparticles will be formed on the silicon surface at locations where silicon was etched. However, the distribution of these positions on the surface of the silicon substrate is not uniform because the etching process began randomly on the surface of the wafer. This result led to the uneven of silver nanoparticles on the surface of the silicon substrate after the fabrication process.

In this report we present the fabrication of AgNPs arrays on a flat silicon surface by electrochemical deposition method. This process have been carried out in an ethanol solution of AgNO_3 and HF by the constant current mode. By this method, AgNPs arrays has been created with the uniformity in size, morphology and density of the particles. Influence mechanism of the electrochemical current density on the morphology of AgNP arrays was also discussed. To evaluate the possibility of enhanced Raman scattering, after that fabricated AgNPs arrays were used as SERS substrates for detecting traces of crystal violet (CV). The chemical formula of CV is $\text{C}_{25}\text{H}_{30}\text{N}_3\text{Cl}$, it is a triphenylmethane dyes that is used quite a lot in the paper, printing and textile industry. CV is also used extensively as a fungicide and antiprotozoal agent in the fish industry throughout the world [19]. However, this dye has generated

much concern regarding its use, due to its reported toxic effects. CV recently has been reported to cause carcinogenesis, mutagenesis, chromosomal fractures and respiratory toxicity to animals exposed to it [19].

2. Experimental

AgNPs arrays have been fabricated by electrodeposition at 17°C on the flat surface of silicon substrates, using an ethanol solution of AgNO₃ and HF. Silicon was used the boron-doped p-type single crystalline (100) with resistivity of 22 Ω.cm. The reagents used were of the analytical reagent grade with concentrations as follows: AgNO₃ is 99.8%, HF is 40%, ethanol is 99.7%. The electrodeposition of AgNPs was carried out under the constant current mode using a typical electrodeposition set-up consisting of a current source with a platinum grid anode and a silicon cathode, the current densities were changed in range of 0.1-1.2 mA/cm². The two electrodes were placed parallel to each other and separated by a distance of 2 cm in a teflon container. Prior to electrodeposition, aluminum was evaporated on the back of the Si wafer to create an ohmic contact, this process allowed the Si wafer to be used as an electrode. The electrodeposition time was 4 min. The solution used was an ethanol solution containing 0.1 mM of AgNO₃ and 0.14 M of HF. During fabrication, electrochemical solution was stirred at a rate of 50 cycles/min. The 0.1 mM concentration of AgNO₃ was used, because in another our study [7] it was found that this concentration is the most suitable for the fabrication AgNPs arrays on silicon substrate by the electroless deposition method.

The structure and morphology of representative AgNPs arrays on Si samples were examined by scanning electron microscopy (SEM) using a S-4800 field emission scanning electron microscope (Hitachi, Japan). The SERS measurements of CV were performed by dripping 50 µl of aqueous CV solution with different concentrations onto the

AgNPs arrays surface. The spreading area is 1×1 cm². After CV dripping, samples were let stand in air at room temperature until dry. Raman spectra were recorded only when the samples were dried. Raman spectra were recorded with a Jobin–Yvon LabRam Raman microscope with input laser light of 632.8 nm wavelength.

3. Results and discussion

The SEM images in Fig. 1 show the morphology of the surface of AgNPs arrays after the deposition process in the ethanol solution containing 0.1 mM of AgNO₃ and 0.14 M of HF for 4 min. Fig. 1a is the surface morphology of the samples were fabricated by chemical deposition, sample with the best morphology when AgNPs arrays are fabricated by electroless deposition, it shows that the size of the silver nanoparticles (gray-white areas) are not uniform with diameter of particles in the range of 30-60 nm, the particle density is relatively sparse and the distribution of the particles is not uniform. When the sample was fabricated by electrochemical deposited with the current density of 0.1 mA/cm², immediately the size of the particles becomes more uniform, the diameter of the particle is about 35 nm (Fig. 1b). At current density of 0.3 mA/cm², the size and the density of silver nanoparticles increased (Fig. 1c), higher-magnification SEM images (inset of Fig. 1c) showed that the size of nanoparticles were very uniform with the diameter of nanoparticles is 45 nm and the distances between the particles are from 1 to 10 nm. When the current density is further increased, the size of the particles also increases and the nanoparticles start to stick together. At current density of 0.5 mA/cm², the diameter of nanoparticles is 60 nm (Fig. 1d), with current density of 0.7 mA/cm², the diameter of nanoparticles is 80 nm (Fig. 1e). SEM image of the sample is deposited with the current density of 1.2 mA/cm² (Fig. 1f) shows that the size of the particles increased to 120 nm, and this time the particles piled up to form a multi-layer structure.

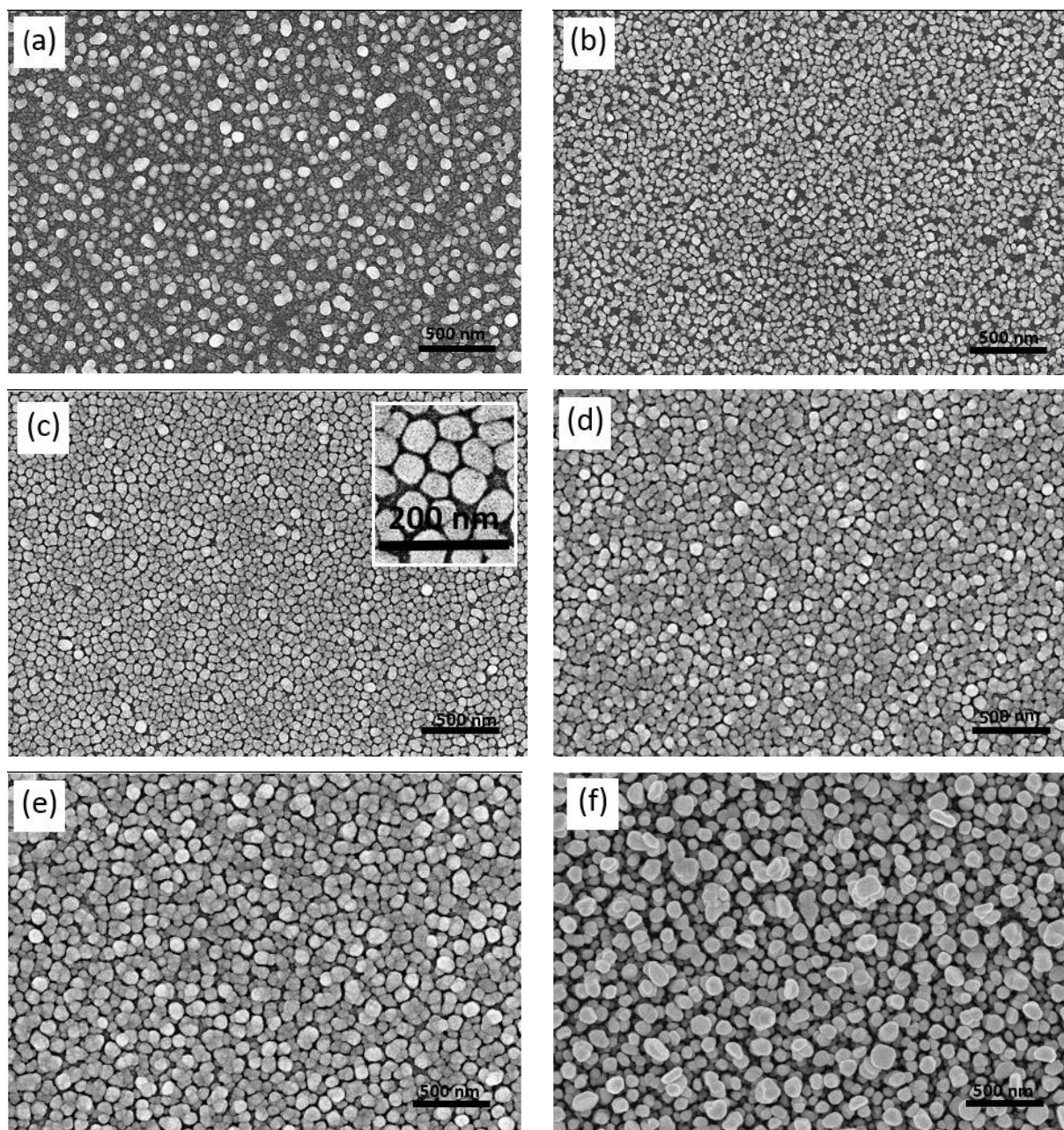


Fig. 1. SEM images of AgNPs arrays on the flat surface of Si substrate after electroless deposition (a), electrochemical deposition (b, c, d, e and f) in the ethanol solution containing 0.1 mM of AgNO_3 and 1.4 M of HF with current densities 0.1, 0.3, 0.5, 0.7 and 1.2 mA/cm^2 , respectively

To explain these results, we first reiterate that the reduction of ionic silver to atomic silver on the silicon surface is shown by equation 2. This means that the silver atoms forming depends on the encounter between ionic silver and electron. In electroless deposition process, electron for the reduction of ionic silver is removed from the reaction 1 (silicon corrosion reaction). And as mentioned above, this process will produce silver nanoparticles with sizes and uneven density. This result is illustrated in Fig. 1a. With electrochemical deposition process, electrons for the reduction of ionic silver was taken from a constant current source. Thus the electrons will be ejected the flat

silicon surface evenly. Therefore, this process will produce silver nanoparticles with uniform size and density. Obviously, when the current density increases, the electron density which is sprayed to the surface also increases, which leads to more uniform density of particles but it also increases the size of the silver nanoparticles. The results in Fig. 1b-f view have confirmed this hypothesis. In addition, it should also mention the role of HF, ethanol and stirring for the formation of silver nanoparticles. Here, HF will dissolve silicon oxide produced during the deposition process, ethanol and the stirring will make the process of diffusion of ionic silver in solution to a silicon surface was more rapid.

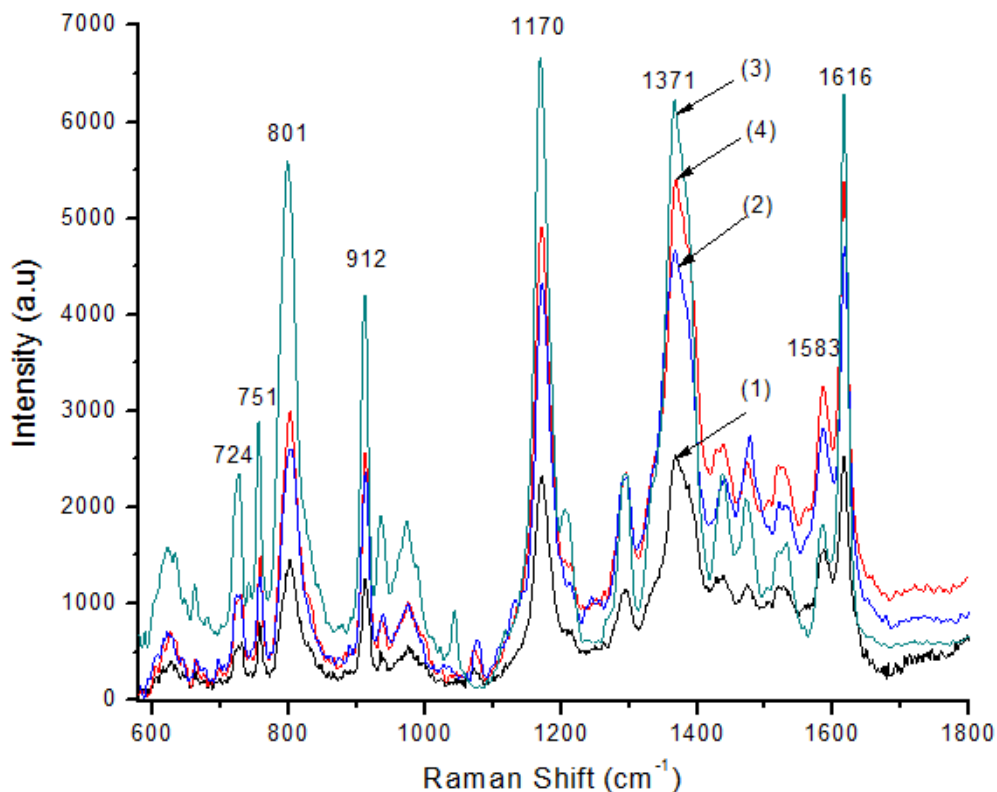


Fig. 2. SERS spectra recorded in the same conditions of CV with 10 ppb concentration dripped onto AgNPs arrays, which have been manufactured for the same time period (4 min) in the same solution (0.1 mM of AgNO_3 and 1.4 M of HF) by (1) electroless deposition and (2, 3, 4) electrodeposition with current densities 0.1, 0.3 and 0.5 mA/cm^2 , respectively

After fabrication, the AgNPs arrays substrates prepared at different current densities are tested for SERS activity using CV dye as a probe molecule with-out adding any external chemical enhancer. Fig. 2 shows the SERS spectra of $50 \mu\text{l}$ of 10 ppb aqueous CV solution dripped on different AgNPs arrays substrates (as shown in the figure caption), the water used was deionized water. As previously reported [17], all well-separated and strong peaks in Fig. 2 are the Raman peaks of the CV molecule. Especially, signals observed at 1616 and 1583 cm^{-1} are attributed to the C-phenyl in-plane antisymmetric stretching mode; signals at 1371 cm^{-1} come from C-N, Phenyl-C-phenyl antisymmetric stretching mode; the peak assigned to C-phenyl, C-H in-plane antisymmetric stretching mode appeared at 1170 cm^{-1} ; one of strong peak at 912 cm^{-1} is related to the phenyl ring breathing mode; Another strong peak at 801 cm^{-1} is contributed of Phenyl-H out-of-plane antisymmetric bending mode; A small peak at 724

cm^{-1} is related to C-N-C symmetric stretching mode. Fig. 2 shows clearly that the intensity of the SERS spectrum of samples fabricated by electrochemical deposition (curve (2-4) in Fig. 2) is much stronger than that of sample fabricated by electroless deposition (curve (1) in Fig. 2). The strongest intensity sample fabricated by electrochemical deposition is stronger about three times than that of fabricated by electroless deposition. Moreover, the peak intensity of the SERS spectra changed largely with the change of AgNPs size and density, which were depended on electrochemical current density. The strongest peak intensities were obtained from the substrate prepared with the current density of 0.3 mA/cm^2 (SEM image of sample is Fig. 1c).

The influence of the size and density of silver nanoparticles on the Raman intensity can be explained by SERS enhancement mechanism. As mentioned in the introduction, the nanogaps play a decisive role in the enhancement of the Raman

signal of AgNPs arrays, for all arrays, the enhancement factors (EF) increases with increasing of nanogap density and decreasing of nanogap size. Nanogaps are created when the distance between the nanoparticles is nano size [9], therefore, the sample with the smallest particles and highest

density will make the highest enhancement factor. According to this theory, and the SEM images in Figure 1, the sample which is deposited by current density of 3 mA/cm^2 will have the highest enhancement factor. And in fact, this has been confirmed by the SERS spectrum in Figure 2.

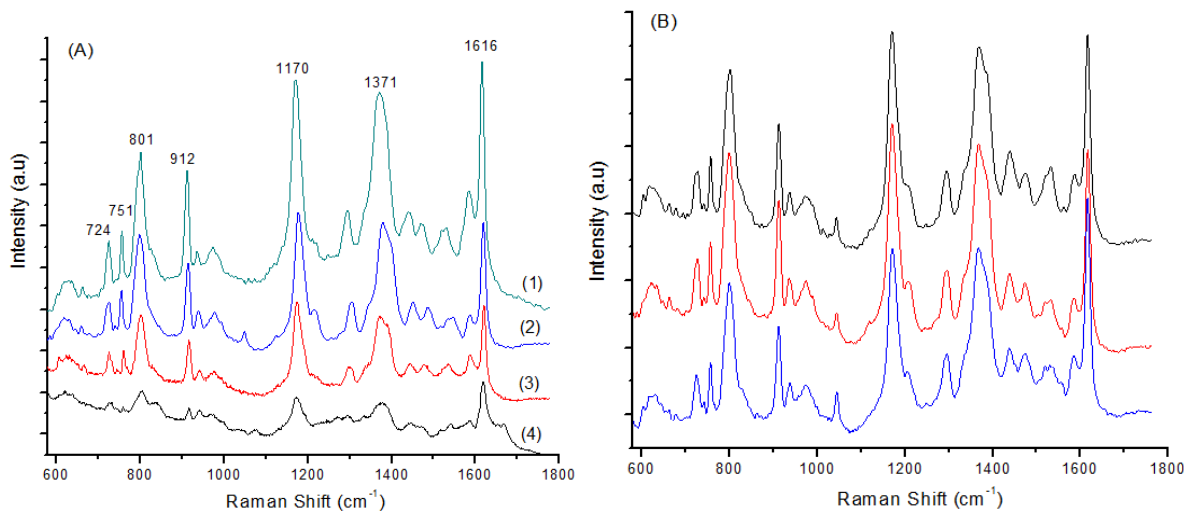


Fig. 3. SERS spectra of CV with different concentrations (A): (1) 100, (2) 10, (3) 1, (4) 0.1 ppb dripped onto AgNPs arrays and SERS spectra of CV with 10 ppb concentrations (B) dripped onto AgNPs arrays measured at three different point, AgNPs arrays have been fabricated with current density of 0.3 mA/cm^2

From the results obtained above, the samples fabricated with current densities 0.3 mA/cm^2 were used as SERS substrates to find out the detection limit of fabricated AgNPs arrays substrates, SERS spectra of substrates covered with different concentrations of CV were recorded. The SERS spectra of different CV concentrations are presented in Fig. 3A, in which the curves (1), (2), (3) and (4) are corresponding to SERS spectra of the aqueous solutions containing 100, 10, 1 and 0.1 ppb CV, respectively. We can easily see the intensity of the Raman peaks decreasing with the CV concentration in the solution dripped onto the substrate. In the curve (4) all Raman peaks of CV molecule still appeared. Thus, we can conclude the detection limit for CV molecules of our AgNPs arrays substrate is as low as 0.1 ppb.

Besides, to evaluate the reproducibility, SERS spectra were recorded at different points on a substrate and different substrates fabricated under identical conditions. The Fig. 3B shows SERS spectra of CV with 10 ppb concentrations dripped onto AgNPs arrays measured at three different point, the substrate was fabricated with current

density of 0.3 mA/cm^2 . The recorded spectra showed that the spectrum at different points may overlap very closely. This result have been repeated for the SERS spectra taken at different substrate, which were fabricated by electrochemical deposition under identical conditions. The superposition of the SERS spectrum along with the SEM images indicated the good uniformity of fabricated AgNPs arrays. These results above indicate good reproducibility and stability of the AgNPs arrays substrates, which were fabricated by electrochemical deposition. Thus, the AgNPs arrays substrates fabricated by electrochemical deposition can be used for quantitative analysis.

4. Conclusions

In conclusion, the AgNPs arrays deposited on silicon have been manufactured by electrodeposition, using the ethanol solution of AgNO_3 and HF, and after that they have been used as SERS-active substrates to detect trace amounts of CV, a triphenylmethane dyes used is used for the light industry and the fishing industry. The AgNPs arrays were also deposited on silicon by electroless deposition in same solution to compare. The results showed that the electrodeposited AgNPs array have much

better ramification. Specifically, the density of the nanoparticles becomes thicker and particles arranged together in a better order. The size of particles becomes smaller, the particles are almost of the same size and evenly spaced. Corresponding to the improvement of AgNPs morphology is the improvement of the intensity and resolution of the SERS spectrum of CV, when the AgNPs with improved morphology were used as SERS substrates. As a result, the Raman intensity of the optimal SERS substrates prepared by electrodeposited AgNPs was three times higher than that of sample fabricated by electroless deposition. And they were able to detect CV with concentration below 0.1 ppb.

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