

FABRICATION OF SILVER NANODENDRITES ON COPPER FOR DETECTING RHODAMINE 6G IN CHILI POWDER USING SURFACE-ENHANCED RAMAN SPECTROSCOPY

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Abstract. *Surface-enhanced Raman spectroscopy (SERS) is increasingly used as an effective method for detecting traces of contaminants in a variety of specimens. To maximize the performance of SERS, it is most important to have a substrate with high SERS activity. In this work, a low-cost SERS substrate was fabricated by chemically depositing silver nanodendrites (AgNDs) onto the surface of a copper (Cu) plate. The results showed that, after deposition, an array of fern-like AgNDs was formed on the Cu surface. The density of these AgNDs is relatively thick and they are evenly distributed over the entire surface of the Cu plate. The prepared AgNDs were applied as SERS substrates for detection of Rhodamine 6G (R6G) in water and chili powder. The results showed that, using the prepared AgNDs substrates, R6G with concentrations as low as 10^{-11} M in water and 10^{-10} M (0.05 ppb) in chili powder could be detected. This result opens great prospects for the application of SERS substrates based on AgNDs in the analysis of contaminants in food.*

Keywords: SERS, silver nanodendrites, Rhodamine 6G, chili powder, chemical deposition.

Classification numbers: 33.20.Fb; 78.30.-j; 81.07.-b; 81.15.-z; 82.80.Gk.

I. INTRODUCTION

In recent years, surface-enhanced Raman spectroscopy (SERS) has shown great potential in detecting and identifying target molecules at low concentrations and has received considerable

research interest. SERS is a molecular spectroscopy technique in which the Raman signals of molecules are greatly enhanced when they are adsorbed on surfaces of metal nanostructures [1, 2]. The surfaces of metal nanostructures used to enhance the Raman signal of the target molecules are called SERS substrates. As is well known, the SERS enhancement factor is determined primarily by the morphological properties of the SERS substrate. It has been found that the substrates with many sharp tips and nanogaps would be able to provide high Raman signal enhancement [3–5]. Hence, various metal structures with such characteristics have been synthesized, among which silver nanodendrites (AgNDs) receive much attention due to the abundant existence of sharp tips, nanoparticle junctions and nanogaps between neighboring metal nanoparticles [6, 7].

Recently, many methods have been reported to fabricate the AgNDs [6, 8–10]. However, most of these methods have been reported to require high temperature, microwave or surfactants, etc. In this paper, we present a simple and low-cost method to fabricate AgNDs on the surface of a copper (Cu) plate (AgNDs/Cu) based on chemical deposition using an aqueous solution of AgNO_3 . Cu is one of the most commonly used substrates to reduce silver ions to form silver nanostructures due to its higher standard reduction potential, which makes the reaction process easy to control and no copper oxides exist in the final products [7]. There have been a few reports presenting the fabrication of AgNDs on Cu using chemical deposition method. Specifically, Zhang *et al.* have synthesized silver dendrites with the length of about 3 – 8 μm on Cu rod [11]. Yang *et al.* have fabricated the single-crystalline dendrite with a length of about 20 μm by reducing silver ions in AgNO_3 solution on Cu mesh [12]. By immersing the Cu plate in an aqueous solution of AgNO_3 , we obtained an array of fern-like AgNDs on the Cu surface. These AgNDs/Cu samples were used as SERS substrates for Rhodamine 6G (R6G) analysis in water and chili powder. In fact, because of its intensive color and low cost, R6G is widely used as a colorant in the textiles and food processing industries [13, 14]. Experts have recommended that R6G is a toxic chemical, it affects internal organs including the liver and kidneys and can cause cancer. Therefore, the detection of R6G in food becomes essential for public health and food safety. Regarding the use of SERS to detect R6G in food, Wei *et al.* used Ag-coated cellophane substrates to analyze R6G in water and in chili powder. The detection limit they reached for detection of R6G in water and chili powder was 10^{-11} M and 10^{-10} M, respectively [14]. The SERS results showed that, using the prepared AgNDs/Cu substrates, R6G with concentrations as low as 10^{-11} M in water and 10^{-10} M (0.05 ppb) in chili powder could be detected. This result opens great prospects for the application of SERS substrates based on AgNDs.

II. EXPERIMENT

AgNDs have been chemically deposited at 20°C onto the surface of Cu by immersing Cu plate into an aqueous solution of AgNO_3 . AgNO_3 used was analytical grade with 99.8% purity. Deionized water was used throughout the fabrication process. Deposition process of AgNDs on Cu was performed as follows. First, the Cu plate (99.9%) with a size of $6 \times 6 \text{ mm}^2$ was washed with acetone and H_2SO_4 (1%) to wash off grease. After rinsing with deionized water, the Cu plate was soaked in an aqueous solution containing 5 mM AgNO_3 for 30 min at 20°C to produce AgNDs on Cu surfaces. The structure and morphology of the fabricated AgNDs were investigated by S-4800 Field Emission Scanning Electron Microscope (Hitachi, Japan).

R6G (in the form of powder with 95% purity) was purchased from Energy Chemical Ltd. (China). For SERS measurements, R6G powder was dissolved with water to form stock solution

with a concentration of 10^{-2} M. The stock solution was then diluted with water to obtain concentrations from 10^{-7} M to 10^{-11} M. The chili powder extracts containing R6G were prepared as follows. Firstly, 2 g of chili powder were accurately weighed out, put into a beaker and vigorously mixed with 20 mL of acetonitrile. After that, the mixture was spiked with R6G at a concentration of 10^{-5} M (~ 5 ppm). The mixture was then added by 4g MgSO_4 and 1g NaCl. After a centrifugation step (4500 rpm for 10 min), the supernatant was transferred to centrifuge tube containing 1200 mg MgSO_4 and 400 mg Graphitized Carbon Black (GCB). Finally, the resulting extracts were diluted with R6G-free chili powder extract solution to obtain concentrations from 10^{-6} M (0.5 ppm) to 10^{-10} M (0.05 ppb) for SERS analysis. The extracts spiked with R6G were kept at refrigerator temperature before further use. The blank sample was R6G-free chili powder extract.

To perform SERS measurements, 25 μl of R6G in water solution or chili powder extracts containing R6G with different concentrations was dripped on the AgNDs/Cu substrate. The samples were then allowed to dry naturally in air at room temperature. The Raman spectra were measured at room temperature using a portable Raman spectrometer (model BWS475-785H produced by B&W Tek Inc., USA) with a 785 nm excitation laser.

III. RESULTS AND DISCUSSION

The surface morphology of the Cu plate after chemical deposition of AgNDs in the aqueous solution containing 5 mM AgNO_3 for 30 min at 20°C is showed by SEM images with different magnifications in Fig. 1a and 1b. We can see that after the fabrication, an array of fern-like AgNDs was formed on the Cu surface. The obtained AgNDs are distributed evenly on the surface of Cu and well branched. Specifically, an AgND has one main stem and many short side branches growing along the sides of the main stem. The main stem diameter is around 100-150 nm and their length is in the range of 10-20 micrometers. The short branches are about a few micrometers length. In particular, these sub-branches can also become the main stem for other branches to grow on either side (Fig. 1a). As a result, the AgNDs become a multi-level branching structure with many hotspots to enhance Raman scattering. Scanning electron microscopy (SEM) image with lower magnification shows that the density of AgNDs formed on Cu surface is quite thick and consists of many overlapping layers (Fig. 1b). The XRD pattern of the AgNDs layer formed on the Cu surface after the deposition process shows (111), (200) and (220) peaks of the face-centered cubic silver crystal (Fig. 1c). The strong and sharp diffraction peaks indicate that silver is well crystallized. No peak of Cu was recorded. This is probably due to the fact that the AgNDs layers are relatively thick and completely cover the Cu surface.

To investigate the SERS activity of the fabricated AgNDs/Cu substrates, they were used as SERS substrates in the detection of R6G in water. Fig. 2 shows the SERS spectra of R6G diluted in water at different concentrations ranging from 10^{-11} M to 10^{-7} M which has been dripped on the fabricated AgNDs/Cu substrate. First, it can be seen that all main peaks recorded are the peaks at 612 cm^{-1} , 775 cm^{-1} , 1184 cm^{-1} , 1311 cm^{-1} , 1362 cm^{-1} , 1511 cm^{-1} and 1650 cm^{-1} . According to the published works, these peaks are the Raman characteristic peaks of R6G [13–16]. Specifically, the peak at 612 cm^{-1} is attributed to the C-C-C ring in-plane. The peak at 775 cm^{-1} represents the out-of-plane vibration of C-H. The peak at 1184 cm^{-1} is corresponding to in-plane vibration of C-H bonds. The peaks at 1311 cm^{-1} , 1362 cm^{-1} , 1511 cm^{-1} and 1650 cm^{-1} are related to aromatic C-C stretching vibration mode [14]. We could also observe that the intensity

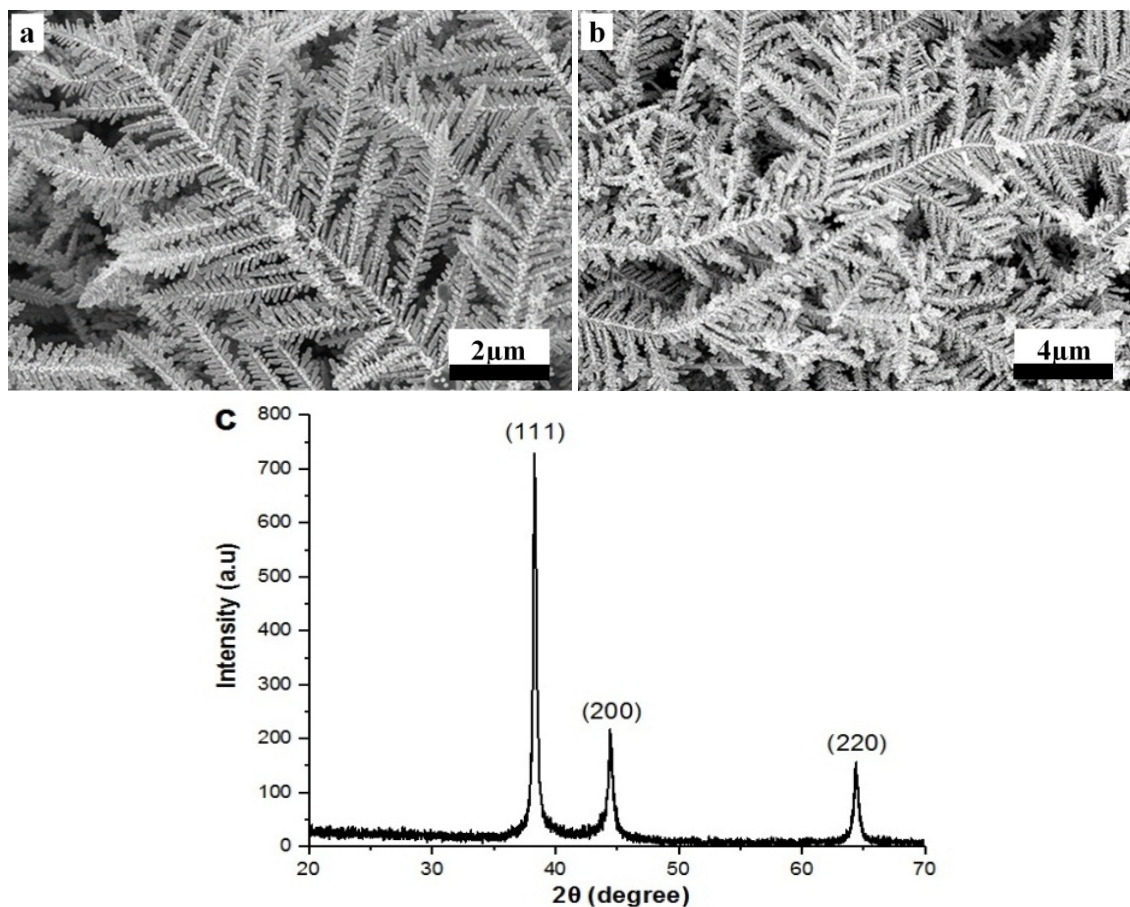


Fig. 1. SEM images with different magnifications (a, b) and XRD pattern (c) of the AgNDs that has been chemically deposited on Cu plate in 5 mM AgNO₃ aqueous solution for 30 min at 20°C.

of the characteristic peaks of R6G decreased steadily as the concentration of R6G in the analytical solution decreased. It can be seen that by using the AgNDs/Cu as SERS substrate, we can detect R6G in water with concentrations lower than 10⁻¹¹ M. It is quite comparable to the other author's results reported recently [13–16].

Next, we have estimated the Raman enhancement factor (REF) of AgNDs/Cu substrate using the following equation [17]

$$REF = \frac{I_{SERS}C_{RS}}{I_{RS}C_{SERS}}$$

where I_{SERS} and I_{RS} are the Raman intensity of a characteristic band of R6G adsorbed on the SERS and non-SERS substrate (a glass plate), respectively. C_{SERS} is the concentration of R6G on AgNDs/Cu substrate (10⁻¹¹ M) and C_{RS} is the concentration of R6G on the non-SERS substrate (10⁻³ M). The band at 1511 cm⁻¹ was chosen to calculate the REF because it is a single peak and

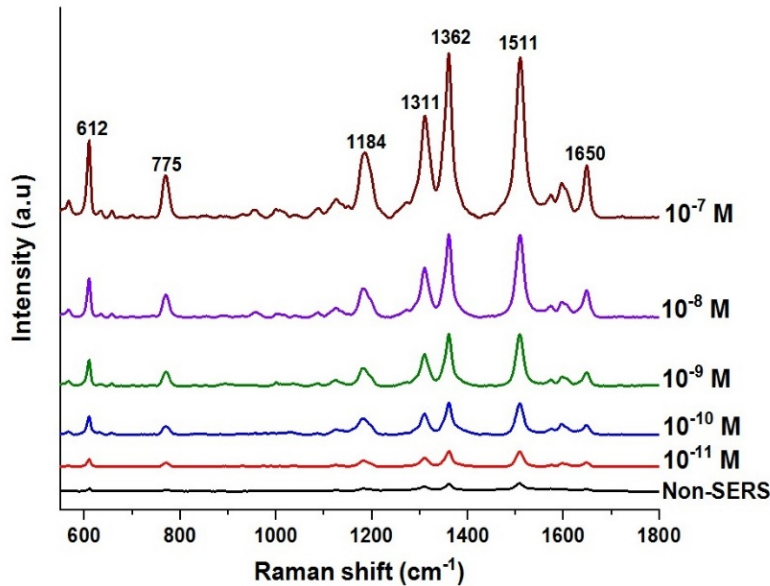


Fig. 2. SERS spectra of R6G at different concentrations in the range of 10^{-7} M to 10^{-11} M which have been dripped onto AgNDs/Cu substrate and Raman spectrum of 10^{-3} M R6G on a non-SERS substrate (glass plate).

has strong intensity, so when the R6G concentration decreases, it is still clearly visible. The intensity of 1511 cm^{-1} band of R6G with the concentration of 10^{-3} M on the glass plate is about 377 in arbitrary unit (a.u.). The intensity of R6G with the concentration of 10^{-11} M on the AgND/Cu is about 900 in a.u. The REF of AgNDs/Si is estimated to be 2.4×10^8 .

To investigate the uniformity of our SERS substrates, SERS spectra of R6G with the concentration of 10^{-10} M from three random positions on the AgNDs/Cu substrate were recorded. The obtained results are shown in Fig. 3. It can be seen that SERS spectra obtained on these three spots are overlapping well. The intensities of all Raman peaks of these three SERS spectra are approximately equal. This result shows good uniformity of AgNDs/Cu substrates.

The AgNDs/Cu substrate was also used to detect R6G in chili powder. Fig. 4 shows the SERS spectra of R6G-free chili powder extract (the blank sample) and chili powder extracts containing R6G with different concentrations which have been dripped onto AgNDs/Cu substrate. First, it can be seen that the SERS spectrum of R6G-free chili powder presents the main peaks at 730 cm^{-1} , 1157 cm^{-1} and 1520 cm^{-1} which did not coincide with characteristic peaks of R6G. The similar result was observed by Wei et al. [14]. In addition, the SERS spectra of R6G doped chili powder extracts clearly showed the Raman characteristic peaks of R6G at 612 cm^{-1} , 775 cm^{-1} , 1184 cm^{-1} , 1311 cm^{-1} , 1362 cm^{-1} , 1511 cm^{-1} and 1650 cm^{-1} . In Fig. 4, it can be seen that the intensity of the main peaks of R6G decreases regularly as the concentration of R6G in chili powder extracts decreases. When the concentration of R6G in the chili powder extracts drops to 10^{-10} M (0.05 ppb), characteristic peaks of R6G can still be observed on the obtained SERS spectrum. This proves that, with AgNDs/Cu substrate, we can determine R6G in chili powder with the concentrations as low as 10^{-10} M (0.05 ppb).

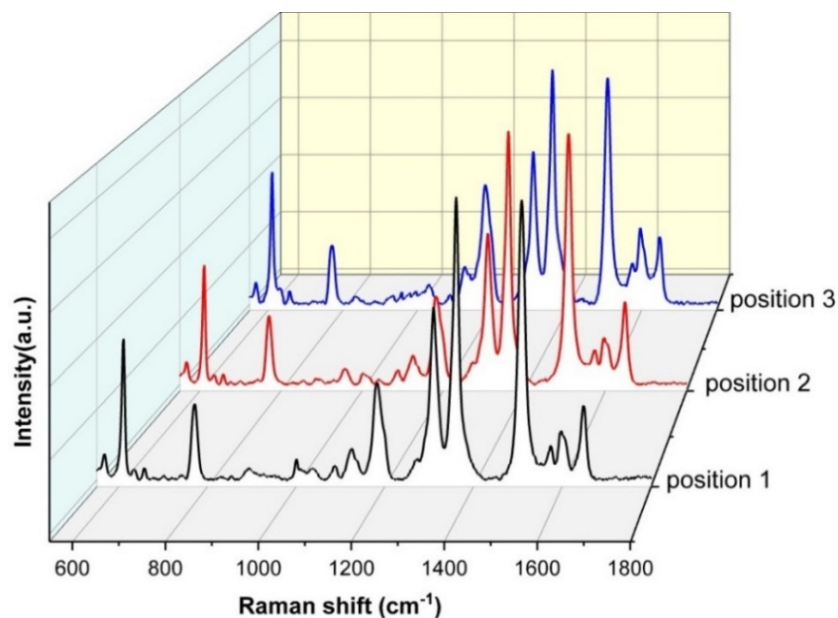


Fig. 3. SERS spectra of 10^{-10} M R6G which were obtained from 3 different positions on a AgNDs/Cu substrate.

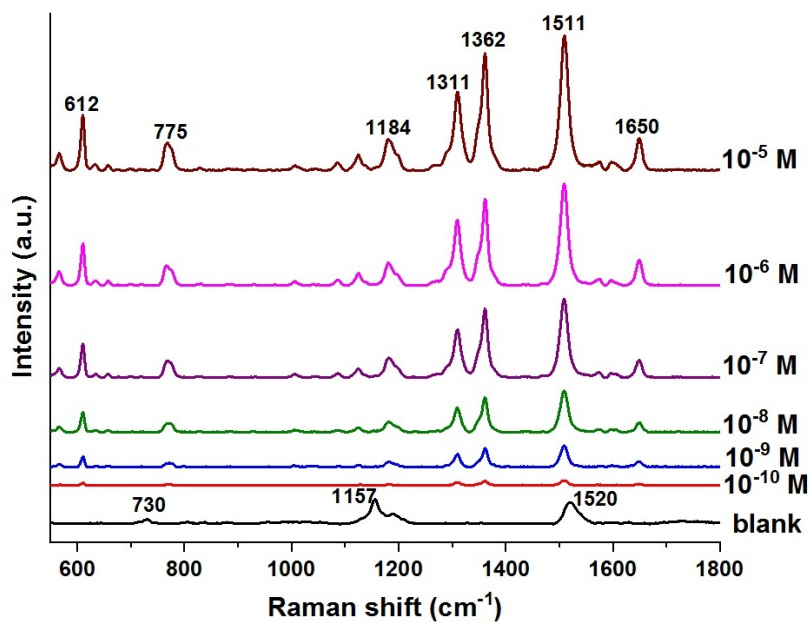


Fig. 4. SERS spectra of chili powder extract (the blank sample) and chili powder extracts containing different concentrations of R6G which have been dripped onto AgNDs/Cu substrate.

IV. CONCLUSION

By chemical deposition method using the aqueous solution of AgNO_3 , we have succeeded in fabricating the fern-like AgNDs on Cu surface. Fabricated AgNDs/Cu samples have been used as SERS substrates for detection traces of R6G in water and in chili powder. The results showed that by using the AgNDs/Cu substrates, R6G can be detected with the concentration as low as 10^{-11} M in water and 10^{-10} M (0.05 ppb) in chili powder. This demonstrates the applicability of such prepared AgNDs as a substrate with high SERS activity.

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