2D-ARRRAYS OF CU NANODISKS ON ANODIC ALUMINUM OXIDE (AAO) TEMPLATE FOR SERS APPLICATIONS

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Abstract. *Copper nanodisks (Cu NDs) of 50 nm were prepared on square-inch anodic aluminum oxide substrates by sputtering method. The samples were annealed at 450ºC, then the walls of AAO substrates were lift off in a solution of acid phosphoric. The 2D arrays of Cu NDs were fabricated in high quality. Morphology of the substrates were observed by scanning electron microscopy. Surface plasmon resonance absorption was observed with different peaks in the range of 400-1400nm wavelengths that means the substrate is promising for SERS application. To demonstrate, we observed Raman spectrum of Rhodamine 6G using the enhancement effect of the substrate.*

Keyword: Cu nanodisk, SERS

I. INTRODUCTION

In recent decades, chemical analysis of food achieves continuous advances with significant improvements in automation, sensitivity and accuracy. Two widely used analytical instruments are gas chromatography (GC) and high-performance liquid chromatography (HPLC). They are often combined with UV-visible spectrophotometry, nuclear magnetic resonance and mass spectrometry to identify the molecular characteristics of specific peaks [1]. The disadvantages of those method are time-consuming, the need to be analyzed in the laboratory. It is essential to develop simple, portable, rapid and sensitive methods for food analysis, especially for food safety.

Infrared and Raman spectroscopy have been developed since the early 20th century. They are rapid and nondestructive tools to identify raw materials and for quality inspection [2]. The conventional Raman spectroscopy has been used to characterize food components [3]. The surface-enhanced Raman scattering (SERS) was discovered in 1974 [4]: the weak Raman scattering signals are greatly enhanced using noble metal nanostructures. Two proposed explanation for the enhancement mechanism is electromagnetic and chemical enhancement. The large electromagnetic field is induced by the excitation of localized surface plasmon resonance [5] [6]. The probability of a Raman transition is increased when molecules are absorbed onto roughened surfaces. Recently, major applications of SERS in food science are detection of chemical and microbial hazards. The development of SERS application has progressed thanks to the increasing availability of suitable nanostructured SERS substrates. This article will focus on a particular nanostructured SERS substrate: 2D-arrays Cu nanodisks on anodic aluminum oxide (AAO) substrate.

II. EXPERIMENTAL

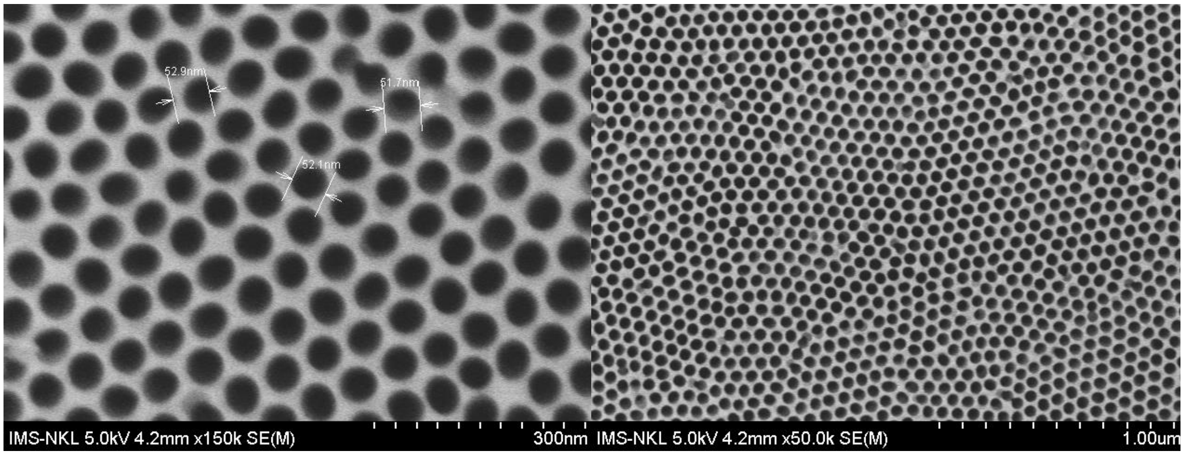
AAO templates with the 50 nm – diameter pores were fabricated using the method given in the previous literature [7]. In sum, the AAO templates were prepared by two steps of anodization. Firstly, aluminium foil (5N) pieces (2 x 2 inches) were cleaned by organic solvent and DI water. They were electro-polished in a solution of alcohol and acid phosphoric during 2 minutes at 20 V and 7 ºC to obtain a mirror-like surface. The first anodization was carried out in a solution of oxalic acid 0.3 M for 90 minutes at the temperature of 10 ºC. The anodically aluminium oxides were completely stripped by a solution of H_3PO_4 and CrO_3 for 30 minutes at 65ºC. The second anodization was carried out in the solution of oxalic acid 0.3 M at 10ºC for 1 minute. Then, the templates were immersed in the solution of H_3PO_4 0.1 M at 30ºC to widen the pores.

To create the 2D-array of Cu nanodisks on the AAO template, the idea was to sputter a copper layer on top of the template, and then remove the pore wall. Copper was filled into the nanopores of the template using RF sputtering technique under a pressure of 0.6 Pa and a power of 20 W for 15 minutes. Then, in order to fortify Cu on the substrate, it was annealed for 30 minutes at 450ºC. The walls of the substrate were removed by a solution of H_3PO_4 0.5 M during 30 minutes.

We observed the morphologies of the fabricated Cu nanodisks by scanning electron microscope SEM Hitachi S-4800. The absorption spectra of Cu nanodisk 2D-arrays were recorded by the equipment Shimadzu-UV2600. To demonstrate the SERS effect of the fabricated substrate, we recorded the Raman scattering spectra of Rhodamine 6G (Rh6G) on the glass substrate, and on the 2D-array Cu nanodisks upon the AAO substrates with the excitation source of 532nm using the equipment Labspec 6.

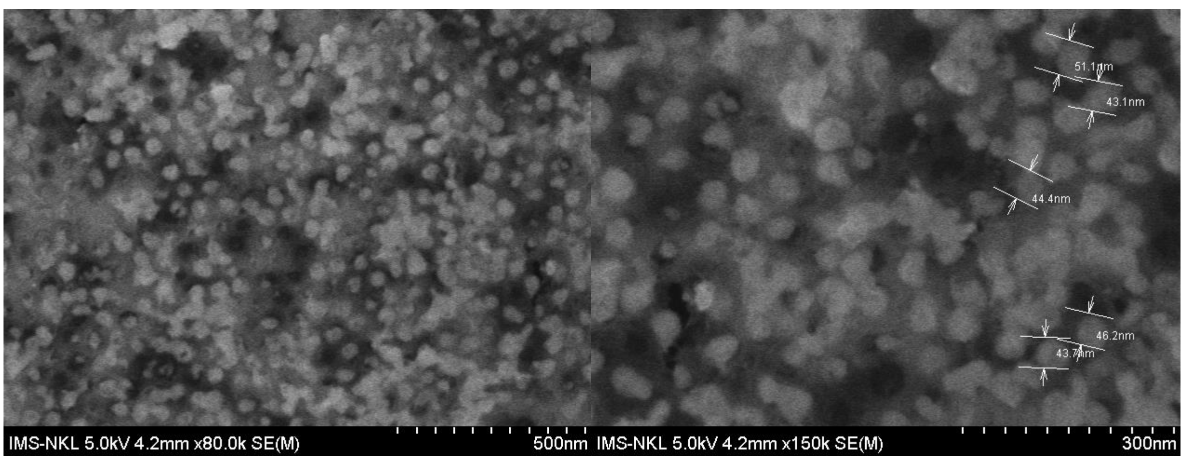
III. RESULTS AND DISCUSSION

Figure 1 shows the SEM image of the AAO template. The morphologies of the surface is shown very nice. The diameter of pores is about 50 nm and the wall thickness is roughly 15 nm. This AAO template was used to prepare Cu nanodisk with diameters and inter-space following the AAO template. It is shown in figure 2 the SEM image of the 2D array of copper after sputtering Cu into the pores and the surface of the AAO templates, annealing and removing the AAO pore walls. The thickness of the Cu nanodisks was adjusted by sputtering time. It was determined sputtering time 15 minutes to obtain a good quality of Cu layer. The Cu-filled AAO template was annealed at 450ºC for 30 minutes in open air to solidify Cu on Al_2O_3 and easily remove the pore walls while remaing Cu nanodisks. The size of Cu nanodisks is shown in the figure 2b that is comprehensive with the pore size of the AAO templates. The 2D-array of Cu nanodisks forms "hot-spots' and induce the enhancement of the electromagnetic field, hence promising for SERS application. In this case, the plasmon resonance is presented for moderate Cu nanodisk size.



a) b)

Figure 1: SEM images of the orignial AAO template showing the diameter of the pores



a) b)

Figure 2: SEM images of the Cu nanodisk 2D array on the AAO template

The absorption spectra of the fabricated substrate is shown in figure 3. The surface plasmonic resonance peaking at 1320nm, 860nm, 633nm and 490nm were observed. It is mentioned in the literature that the closer Cu nanodisks interact stronger and so, making more red-shift of the peaks [8]. The fabricated 2D array of high density copper nanodisks creates “hot-spots” to induce huge enhancement of the EM field making it suitable for SERS application.

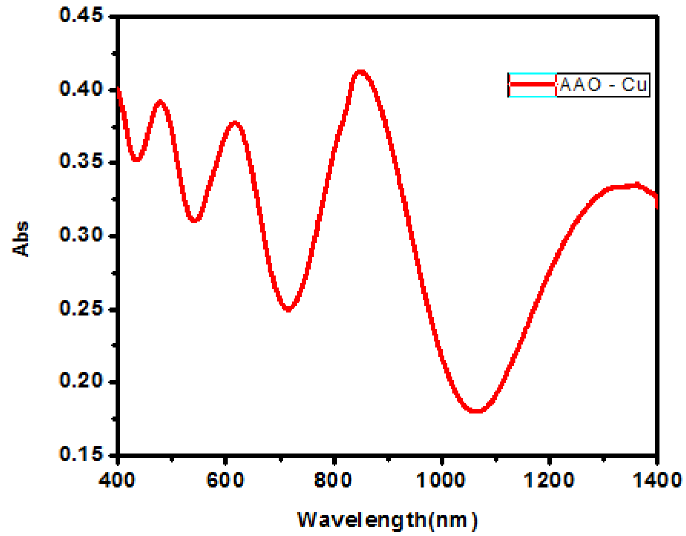


Figure 3: Absorption spectra of the AAO-Cu template

To test the enhancement effects of the fabricated substrate, we measured the Raman scattering spectrum for Rhodamin 6G loaded on the glass substrate and the fabricated SERS substrate. Figure 4 shows the spectra for comparison. The choice of 532nm laser excitation is suitable with the surface plasmon of the 2D array of Cu nanodisks. The Raman scattering spectra indicate the peaks corresponding to the normal vibrations of molecular groups of Rh6G. The enhancement factor is about 40 times. The results show the possibility of using the fabricated substrate for detection of pesticides, disease pathogens and herbicides. It should be mentioned that the fabricated Cu 2D array is very stable and we can have multiple use after cleaning by ultrasonic.

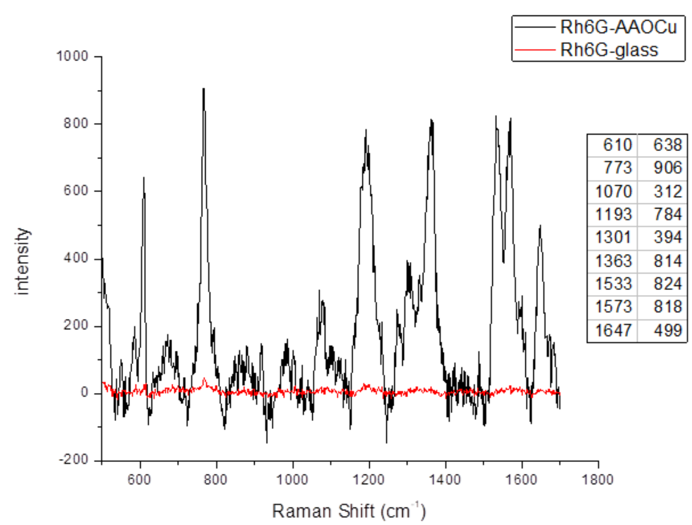


Figure 4: Raman scattering spectra of Rh6G loading on the AAO-Cu template and the glass substrate

IV. CONCLUSION

2D arrays of Cu nanodisks were fabricated in high quality by sputtering Cu onto AAO template and removing the pore wall of the template. The fabricated 2D array of Cu nanodisks showed different surface plasmon resonance peaks in the spectral range from 400 nm to 1400 nm. That is promising for SERS application. To demonstrate the enhancement effect of the fabricated SERS substrate, we recorded the Raman scattering spectra of Rh6G loaded on the AAO-Cu template and the glass substrate. One can use the method described in this paper to fabricate 2D arrays of other metals or alloys.

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