

Study on Detection of Pigment Amaranth Based on Surface-enhanced Raman Scattering

Qi Zou, Yue Yao, Wen Wang, Jingwen Li, Changchun Yan, Caiqin Han*

Jiangsu Key Laboratory of Advanced Laser Materials and Devices
School of Physics and Electronic Engineering, Jiangsu Normal University
Xuzhou, China

*hancq@jsnu.edu.cn

Abstract—Amaranth is a synthetic pigment widely used in daily use. In this paper, silver nanorods (AgNR) array substrates were prepared by oblique angle deposition (OAD) to detect the amaranth in water based on surface-enhanced Raman spectroscopy (SERS) rapidly and quantitatively. The theoretical spectrum and their characteristic peaks were simulated by density functional theory (DFT). The results showed that the main characteristic peaks of amaranth were located at 1345 cm^{-1} and 1361 cm^{-1} . The signal intensity of amaranth increased linearly with the concentration in the range of $1\text{ mg/L} \sim 100\text{ mg/L}$, and the detection limit was 1 mg/L .

Keywords—surface enhanced Raman Spectroscopy; silver nanorod; synthetic pigments

I. INTRODUCTION

With the development of science and technology, more and more synthetic chemical additives are frequently added to daily necessities. Although it has bright colors and rich flavors, long-term excessive consumption will cause serious harm to human health. Amaranth (AM, E110) may cause allergies, diarrhea and other symptoms in the mouthwash of daily necessities. When the intake is too large, it will cause damage to the kidneys and liver [1]. At present, the commonly detection methods of AM are ultra-high performance liquid chromatography, thin layer chromatography, polarography, near infrared spectroscopy and spectrophotometry, etc [2-4]. However, these methods have high requirements for sample size and sample representativeness. And it also needs to have good knowledge of chemical analysis and laboratory conditions. Therefore, there is an urgent need for a rapid and reliable detection method for monitoring the addition of synthetic pigments.

Surface-enhanced Raman spectroscopy (SERS) technology has the advantages of high sensitivity, good selectivity, low cost, small sample size, and rapid analysis results, etc. It has been widely used in biology, chemical sensor, disease diagnosis and environmental detection [5-6]. Metal and oxide nanomaterials and structures prepared by oblique angle deposition have high efficiency and stability. It has high application value in the field of biological and chemical sensors [7-8]. Yue Yao et al used a highly reproducible AgNR array prepared by OAD to detect the Allura Red (AR) in candy by SERS. By using SERS substrate, the relative standard deviation (RSD) is 5.7% and 11.0%. The detection limit of AR is 0.05 mol/L and the linear range is $0.8 \sim 100\text{ mol/L}$. [9]

In this paper, the synthetic pigment AM was studied by AgNR array substrates based on SERS technique. DFT was used to determine the characteristic peaks and vibration assignments. SERS characteristic spectrum, intensity versus AM concentration and the detection limits were obtained. It provides a new rapid and sensitive method for the detection of synthetic pigment in daily necessities.

II. MATERIALS AND METHODS

Materials

Silver (99.999%) and titanium (99.995%) pellets were purchased from Kurt J. Lesker Co., Ltd. (USA). AM ($\geq 99.9\%$) is purchased from Chinese Medicines Group Chemical Reagent Co., Ltd (Beijing, China). Ethyl acetate ($\geq 99.5\%$) and ethanol ($\geq 99.7\%$) were purchased from Bailinway Technology Co., Ltd (Beijing, China). Ultra-pure water ($\geq 18.2\text{ M}\Omega$) was obtained from laboratory.

Preparation of AgNR substrate

The AgNR substrate was prepared by an electron beam evaporation deposition system (DE500, DE Technology Inc.). Firstly, the glass piece was cut to a size of $1 \times 1\text{ cm}^2$, soaked in alcohol and washed three times with an ultrasonic cleaner for 5 minutes each time. Then, at the pressure of 10^{-5} Pa , the samples were evaporated at the rates of 0.2 nm/s and 0.3 nm/s for 20 nm and 100 nm titanium and silver film respectively, and the sample vapor was incident to the surface of the sample stage. Finally, the sample stage is rotated around the axis, the normal line of the surface of the sample is 86° with the incident direction of steam, and the silver film is deposited at 2000 nm. The evaporation rate and the film thickness during the experiment were read and controlled by quartz crystal microbalance (QCM). The surface morphology of AgNR substrate was observed by a field emission scanning electron microscope (SEM, SU8010, Hitachi).

Preparation of AM

In order to determine the SERS intensity versus concentration calibration curve and the limit of detection of AM, standard solution was prepared by secondary deionized water into different concentrations. The concentration of the prepared AM standard solution was 1 mg/L , 5 mg/L , 10 mg/L , 20 mg/L , 30 mg/L , 50 mg/L , 80 mg/L and 100 mg/L respectively.

SERS signal acquisition and processing

A portable Raman spectrometer (ProRaman-L-785A2, Enwave Optonics, Irvine, CA) a 785 nm diode laser was used to collect SERS signals. The specific detection process was: 2 μL of the solution was dropped onto the surface of the substrate and dried naturally. The Raman spectrometer was used to detect it. The laser power was selected to be 30 mw, the integration time was 10 s, and the spectra of 9 positions within the sample area were randomly scanned. In order to compare and confirm the characteristic peaks of AM, the powder was also detected by Raman spectroscopy. The laser power was 100 mw and the integral time was 10s.

Density Functional Theory Calculations

The theoretical Raman spectrum of AM and the corresponding vibrational modes of the characteristic peaks were calculated by Gaussian 09W software package. The calculation of DFT is based on the three parameter exchange function of Becke (B3) and the dynamic correlation functions of Lee Yang and Parry. The molecular structure of AM was optimized using the B3LYP function in conjunction with a modest 6-311g (d) basis set.

III. RESULTS AND DISCUSSION

Characterization of AgNR Array Substrates

Fig. 1a shows the schematic diagram of the diagonal deposition system. Fig. 1b is the top view SEM image of the AgNR array substrate tilted in the same direction with good uniformity in a large area. The results show that the length of AgNR is $L = 918 \pm 82$ nm. In the manufacturing process, the incident angle of steam and the supporting surface are set at a large angle of 86° , but the final AgNR array angle is about 73° , which is consistent with the cosine law of shadow deposition. The diameter of nanorods and the distance between the rods are about 100 nm and 150 nm.

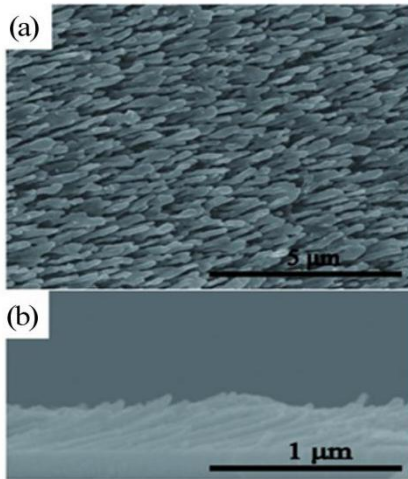


Fig. 1. (a) Top view and (b) cross-section SEM images of the AgNR array substrate fabricated by OAD.

SERS spectrum of AM

The SERS spectra of AM solution were scanned by a portable Raman spectrometer. All the spectra were normalized and the corresponding peaks were compared. The experimental

results show that the peaks of AM are mainly located at 1176 cm^{-1} , 1229 cm^{-1} , 1345 cm^{-1} and 1361 cm^{-1} . Fig.2 shows the optimized molecular structure, theoretical spectrum and SERS spectrum of AM. By comparison, it can be found that the main peak positions of AM are completely coincident, and only a few peaks are slightly different in relative intensity, which may be due to the selection of algorithms in DFT simulation and the sensitivity of spectrometers in practical applications. Table 1 shows the vibrational modes of AM molecules. It can be seen from the table that the most typical peaks appear around 1345 cm^{-1} and 1361 cm^{-1} , which are attributed to $\text{C}_3\text{-C}_4$ stretching vibration and $\text{C}_{25}\text{-H}_{29}$ wagging. Other characteristic peaks, such as 739 cm^{-1} , 937 cm^{-1} , 1176 cm^{-1} , and 1433 cm^{-1} , are due to different types and ranges of C-H wagging. In addition, the peaks at 1512 cm^{-1} and 1570 cm^{-1} are caused by $\text{N}_{17}\text{-N}_{18}$ stretching and ring asymmetric stretching.

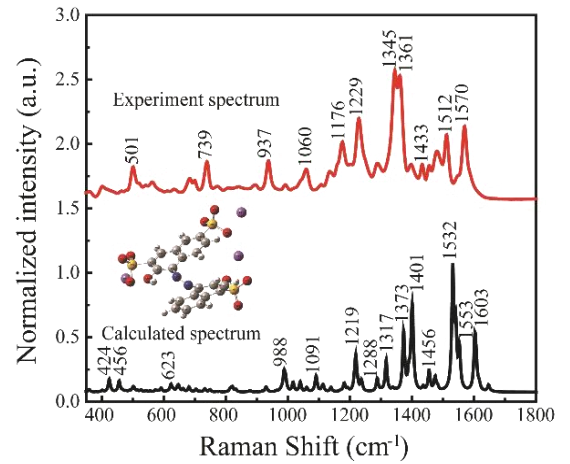


Fig. 2. The optimized structure of AM molecular; The Raman spectrum calculated by DFT and SERS spectra of AM. (All the spectra were normalized by the highest peak in each spectrum).

TABLE. 1. BAND ASSIGNMENTS FOR THE DFT-RAMAN AND SERS SPECTRA OF AM.

DFT (cm^{-1})	SERS (cm^{-1})	Vibrational modes
526	501	$\text{O}_{40}\text{-S}_{35}\text{-O}_{39}$ scissoring
770	739	C-H rocking
963	937	C-H rocking
1181	1060	$\text{O}_{39}\text{-S}_{35}\text{-O}_{41}$ asymmetric stretching
1193	1176	C-H wagging
1237	1229	$\text{O}_{45}\text{-S}_{46}$ wagging
1373	1345	$\text{C}_3\text{-C}_4$ stretching
1390	1361	$\text{C}_{25}\text{-H}_{29}$ wagging
1456	1433	C-H wagging
1532	1512	$\text{N}_{17}\text{-N}_{18}$ stretching
1603	1570	Ring asymmetric stretching

In order to quantitatively analyze the performance of AgNR array substrates, SERS spectra of different concentrations of AM solution were measured. As shown in Fig. 3a, the SERS intensity of AM was significantly increased with the increase of the analyte concentration. In addition, Fig. 3b shows a linear relationship between SERS intensity and AM concentration in

the range of 1 ~ 100 mg/L at 1343 cm^{-1} . The linear relationship is $I_{1343} = 88.59C_{AM} + 291.8$. Using the 3σ method (σ is the root mean square value of the noise signal, in the spectral region: 1700 to 1800 cm^{-1} , σ is determined by the standard deviation of the spectral intensity, $3\sigma = 284.7$), the LOD is 1 mg/L.

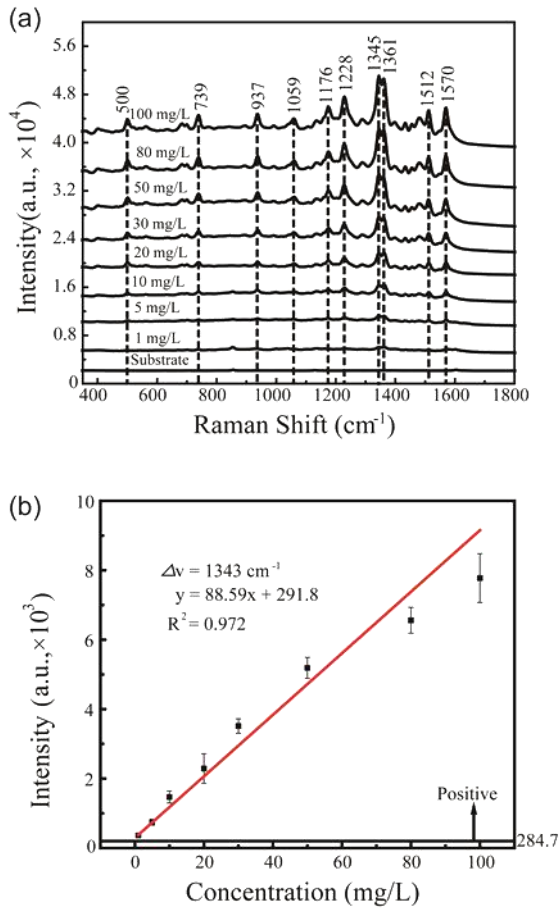


Fig.3. (a) SERS spectra of AM at different concentrations. (b) Characteristic peaks intensity of AM are offset for clarification. The average intensity were plotted and the error bars represent the standard deviation values.

IV. CONCLUSIONS

AgNR array substrate which has a good SERS enhancement prepared by OAD technology was used to detect the AM signal. The characteristic peak positions of AM were determined by DFT simulations, which were mainly located at

1345 cm^{-1} and 1361 cm^{-1} . The SERS detection of AM exhibits a linear relationship in the range of 1 ~ 100 mg/L and the detection limit was 1 mg/L, which provides a rapid and sensitive method for the detection of synthetic pigment.

ACKNOWLEDGMENT

The authors would like to thank a Project Funded by the National Natural Science Foundation of China (Grant No. 61575087), the Natural Science Foundation of Jiangsu Province (Grant No. BK20151164), and the National Training Programs of Innovation and Entrepreneurship for Undergraduates (Grant No. 201610320070). We thank for the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD).

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