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DETECTION OF A SUDAN DYE AT LOW CONCENTRATIONS BY SURFACE-ENHANCED RAMAN SPECTROSCOPY USING SILVER NANOPARTICLES

DAO TRAN CAO[1,3,†], LUONG TRUC QUYNH NGAN[1], CAO TUAN ANH[2] AND KIEU NGOC MINH[1,3]

[1]*Institute of Materials Science Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet, Hanoi, Vietnam*

[2]*Tan Trao University, Trung Mon, Yen Son, Tuyen Quang, Vietnam*

[3]*Graduate University of Science and Technology, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet, Hanoi, Vietnam*

[†]*E-mail:* dtcao@ims.vast.ac.vn

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Abstract. *Sudan dyes are red colorants banned from use for food due to their toxic properties. However, because of the cheapness, they are sometimes adulterated into food illegally. Small amounts, including traces, of Sudan dyes in food can be detected by surface-enhanced Raman spectroscopy (SERS). However, due to Sudan's fluorescence, this detection requires the use of appropriate excitation laser wavelengths and SERS substrates. At present, to identify Sudan dyes with SERS, 785 nm excitation laser wavelength is used along with some types of SERS substrates, such as electropolished aluminum foil or gold-silver core-shell colloidal nanoparticles. In this report we show that an array of silver nanoparticles that have been chemically deposited on silicon surface is also a good SERS substrate for Sudan I (a type of Sudan dyes) detection. Using the aforementioned SERS substrate in combination with 785 nm sample excitation, we were able to detect Sudan I to concentrations as low as 1 ppb.*

Keywords: SERS; Sudan dyes; silver nanoparticles.

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

I. INTRODUCTION

Sudan dyes are organic compounds that contain the azo group, which means that they contain the N=N bond in the molecular structure. Usually there are 4 types of Sudan, including Sudan I, II, III and IV. Their molecular formulas are $C_{16}H_{12}N_2O$, $C_{18}H_{16}N_2O$, $C_{22}H_{16}N_4O$ and $C_{24}H_{20}N_4O$, respectively. These dyes are used to produce colors such as rich red, red-orange or orange-yellow for the dyed product. On the daily practice, the main application of Sudan dyes is to coloring plastics, textiles, oil paints, printing products... Sudan dyes have been classified as carcinogenic and mutagenic compounds by International Agency for Research on Cancer [1, 2], so they have been banned for foodstuff coloring. However, they are cheap and easy to obtain, for this reason they are sometimes used illegally as an adulterant in food stuffs and cosmetics for imparting a bright red color. This is particularly common in developing countries, where laws are not strictly followed wherever and whenever.

Numerous techniques have been employed to identify Sudan dyes in food products, most of which involve the use of chromatographic methods coupled with various detectors [3–5]. Among them the combination method of high-performance liquid chromatography and mass spectrometry (HPLC-MS) is the most widely used one. But the application of this method becomes somewhat limited as it is a time-consuming and expensive technique. An alternative method that can be used to identify Sudan dyes as well as many other molecules in general is Raman scattering. However, on the one hand the signal of Raman scattering is often very weak, so it is difficult to apply this method to detect trace amounts of molecules. On the other hand, in general, dyes are very powerful fluorescents, so the fluorescent signal can obscure the Raman scattering signal. Both of these problems will be solved if instead of normal Raman scattering, surface-enhanced Raman scattering (SERS) will be used. SERS is a method in which the molecules of the analyte are adsorbed onto a metal surface that is rough at the nanoscale. Thanks to the presence of this nano-rugged metal surface, the intensity of Raman scattering signals of analyte molecules is greatly enhanced, the enhancement can reach millions of times. SERS also has another important advantage, that it is a fluorescence quenching technique [6]. This fact is particularly significant when we want to detect strong fluorescence substances such as dyes. In addition, the use of the Raman spectrometer systems with the excitation laser of a long wavelength, e. g. 785 nm or 1064 nm, will also drastically reduce the fluorescence.

In the literature there have been some reports of using SERS technique to detect Sudan dyes of low concentrations or traces of Sudan dyes in foodstuffs [7–11]. In those works, the authors of [7, 8] used SERS substrates made from electropolished aluminum foil to detect Sudan I, while researchers of [9, 10] identified Sudan dyes by SERS Au-Ag core-shell substrates. In [11] the technique used to analyze Sudan I in food is more complicated, it is a combination of thin layer chromatography (TLC) with SERS, in which SERS substrate is made of gold nanoparticles. In this report we would like to demonstrate that Sudan I can also be detected to very low concentrations (about 1 ppb) with a very simple SERS substrate, which is the array of silver nanoparticles (AgNPs) chemically deposited on silicon. The fabrication of AgNPs on silicon (AgNPs@Si) SERS substrates by dipping silicon wafer into an aqueous solution containing silver nitrate ($AgNO_3$) and hydrofluoric acid (HF) has been proposed over a dozen years ago [12, 13]. This is a very simple technique of chemical deposition but produces an effective SERS substrate. In this report we will use this approach.

II. EXPERIMENT

The fabrication of AgNPs@Si arrays has been carried out similarly as described in [12,13]. In brief, AgNPs have been deposited chemically on the surface of silicon by dipping silicon wafer into an aqueous solution containing soluble $AgNO_3$ and HF. Silicon used was the boron-doped *p*-type single crystalline (100) Si with resistivity of 0.1-10 ohm.cm. However, silicon is only used as a substrate for AgNPs to adhere to it chemically, so silicon with other characteristics may also be appropriate. The reagents used were of the analytical reagent grade with concentrations as follows: $AgNO_3$ – 99.8%, HF – 40%. The water used was deionized water. At first, the silicon wafer was cut into 6×6 mm^2 samples. Next, the silicon samples were cleaned with acetone to wash off any grease. The silicon samples were then immersed in an aqueous solution of 5 vol.% HF for 5 min to remove surface silicon oxide. After rinsing with deionized water, the silicon samples were immersed in an aqueous solution containing 0.14 M HF and 5 mM $AgNO_3$ for 15 min at room temperature to obtain AgNPs deposited on silicon surfaces. The structure and morphology of the obtained AgNPs were examined by scanning electron microscopy (SEM). The used electron microscope is S-4800 Field Emission Scanning Electron Microscope (Hitachi, Japan).

Sudan dye used is Sudan I (standard stain) purchased from BDH Chemicals Ltd. (Poole, England). For SERS measurements, Sudan I (in the form of powder) was dissolved with a mixture of acetonitrile and water (at a ratio of 1: 1, v/v) to a concentration of 1000 ppm to produce stock solution. Then the stock solution was diluted with the above mixture of acetonitrile and water to concentrations of 10, 1, 0.1, 0.01 and 0.001 ppm (4.03×10^{-5} M to 4.03×10^{-9} M). In the next step 25 μl solution of each concentration is taken and dripped onto an AgNPs@Si SERS substrate. The samples were then allowed to dry naturally in air at room temperature.

The Raman spectra were recorded by a portable Raman spectrometer (model BWS475-785H of the i-Raman Pro family produced by B&W Tek Inc., USA) with 785 nm excitation laser. The spectrometer provides a Raman spectrum over the range of 65 to 2800 cm^{-1} with a spectral resolution of better than 3.5 cm^{-1}. The full laser power at the probe excitation position is 427 mW and the laser spot size is 105 μm (for the objective lens magnification of 20×). In current study each acquisition of Raman spectrum was carried out for 3×10 sec with 8% of the full laser power used (i.e. about 34 mW).

III. RESULTS AND DISCUSSION

Figure 1 shows an array of AgNPs that has been deposited chemically on the silicon surface in the aqueous solution containing 5 mM of $AgNO_3$ and 0.14 M of HF for 15 min at room temperature, but with two different magnifications so that the structure and morphology of AgNPs can be seen in more detail. From Fig. 1 we can see that the AgNPs produced are almost spherical or slightly long, with fairly uniform sizes in the range of 50–80 nm. On the surface of a substrate, AgNPs are distributed evenly.

The chemical deposition of AgNPs on silicon surface that was performed above is essentially a redox process. In this process the silver ion (Ag^+) is reduced to elemental silver, while the silicon is oxidized to SiO_2. In order for the aforementioned process to occur in a sustainable manner, HF must be introduced into the deposition solution to dissolve the generated SiO_2. From this we can see that the growth rate of AgNPs strongly depends on the ratio between $AgNO_3$ and HF concentrations in the deposition solution. If the ratio of HF/$AgNO_3$ concentration is too low,

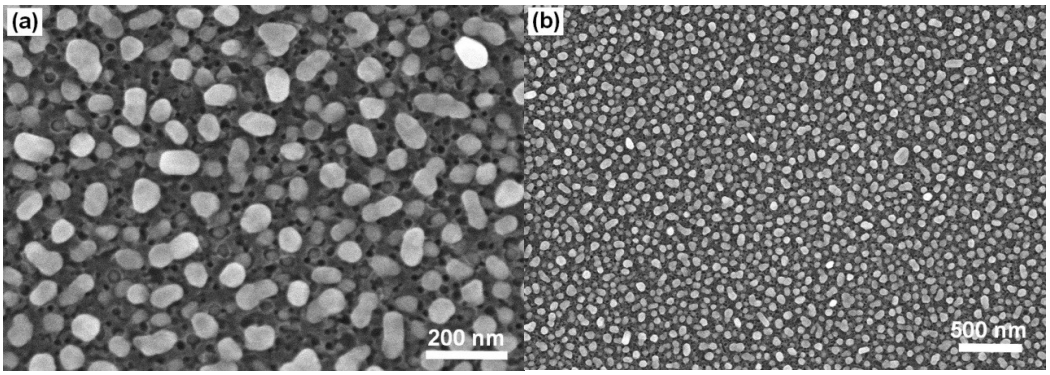

Fig. 1. SEM images with two different magnifications of one AgNPs array that has been deposited chemically on Si in the aqueous solution containing 5 mM of $AgNO_3$ and 0.14 M of HF for 15 min.

the growth of AgNPs will occur very slowly. In the opposite case, AgNPs will quickly become large and easily peel off the silicon surface. In this study we have found that with a 15 min deposition time, the optimal $HF/AgNO_3$ concentration ratio is 140 mM /5 mM. This ratio is different but comparable with the results of [12], where the AgNPs deposition time was 10 min. In [13] the authors used a ratio of 5 M /10 mM, i.e. they used extremely high HF concentration, so they had to use very short deposition times, only about 5-20 sec.

On the next step, the AgNPs@Si arrays, which have been fabricated as described above were used as SERS substrates to detect Sudan I at very low concentrations. The result of this work is illustrated by Fig. 2 and Fig. 3. Figure 2 shows the SERS spectra of Sudan I diluted with a mixture of acetonitrile and water (at a ratio of 1:1, v/v) to concentrations of 10, 1, 0.1, 0.01 and 0.001 ppm (note that 0.001 ppm = 1 ppb) using the AgNPs@Si arrays as the substrate. In addition, on Fig. 2 the Raman spectrum of Sudan I powder is also shown. Figure 3 shows the Sudan I SERS spectra at concentrations of 0.1, 0.01 and 0.001 ppm, which have been shown in Fig. 2, but represented with a higher magnification of the intensity to make the details of the spectra more visible. From Fig. 2 and Fig. 3, at first, we can see that the recorded Raman peaks coincide with the peaks of Sudan I that other authors have published [10]. This allows to confirm that the powder whose Raman spectrum has been recorded is actually Sudan I. Next, we observe that the SERS spectrum of Sudan I (at least at high enough concentrations, e.g. 10 ppm) is consistent with its corresponding Raman spectrum and contains all major characteristic peaks. However, changes in relative intensities and red or blue shift of characteristic peaks were observed in the SERS spectrum of Sudan I compared to its conventional Raman spectrum counterpart. The changes in the intensities and shifts of the position of characteristic peaks are a common phenomenon for SERS spectra. This has happened due to the interaction between molecules of analyte and SERS substrate surface [14, 15]. Regarding the origin of the recorded peaks, it is believed that the peak at around 1225 cm^{-1} is due to C–O stretching vibration and CCH scissoring bending of naphthalene ring, the peak at around 1388 cm^{-1} is due to C=N stretching vibration and C–H in-plane bending, the peak at around 1492 cm^{-1} is due to C=N, N–N stretching vibration, and N–H in-plane bending vibration, and the peak at around 1596 cm^{-1} is due to the C–C scissoring bending from the benzene

ring and N=N stretching vibration [16, 17]. Among these characteristic peaks, the peak at around 1596 cm^{-1} is the most prominent. This peak can be taken as a representative for Sudan I. We can then see that according to Fig. 2 and Fig. 3, Sudan I can be detected to concentrations as low as 1 ppb with prepared AgNPs@Si substrate.

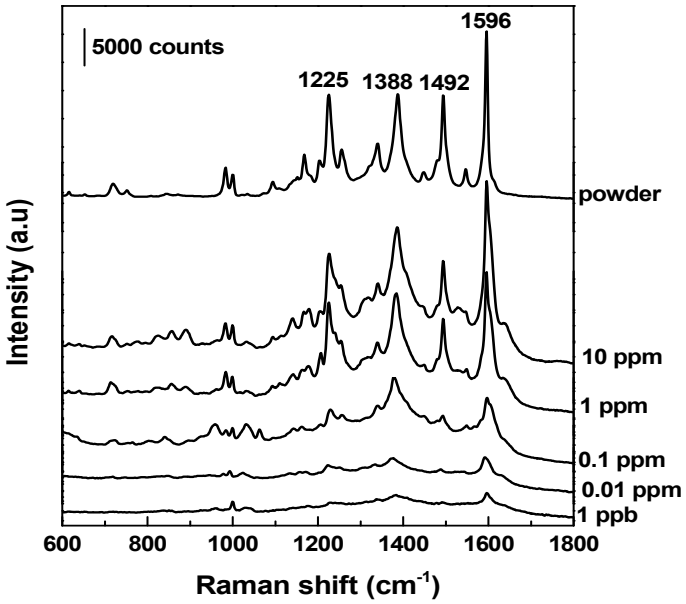

Fig. 2. Raman spectrum of Sudan I powder and SERS spectra of Sudan I at concentrations of 10, 1, 0.1, 0.01 and 0.001 ppm (diluted with a mixture of acetonitrile and water (at a ratio of 1:1, v/v)).

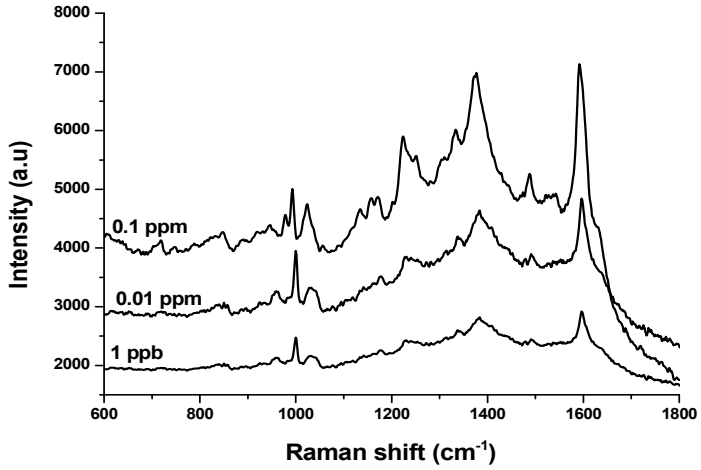

Fig. 3. SERS spectra of Sudan I at concentrations of 0.1, 0.01 and 0.001 ppm, which have been shown in Fig. 2, are re-presented with a higher magnification of the intensity to reveal the spectra in more detail.

To the best of our knowledge, so far in the literature there have been no reports of using AgNPs@Si arrays as SERS substrates to detect Sudan I. In published reports, to identify Sudan I with trace concentrations by SERS, either electropolished aluminum foil [7, 8], or Au-Ag core-shell colloidal nanoparticles [9, 10] were used as SERS substrates. In general, to have such SERS substrates, the fabrication methods are more complicated than the AgNPs@Si array fabrication method we used in this study. Furthermore, in the aforementioned reports the detection limit for Sudan I in the standard solution in the best case was only about 0.01 ppm [8], while our AgNPs@Si SERS substrate could detect Sudan I with concentrations as low as 1 ppb.

IV. CONCLUSIONS

In summary, the results of this study have shown that Sudan I can be detected via SERS technique to concentrations as low as 1 ppb without requiring complicated SERS substrates. A simple SERS substrate, which is made from silver nanoparticles deposited chemically on a silicon surface, is sufficient for this purpose. Furthermore, the uniformity and repeatability of AgNPs@Si substrates are good enough to distinguish different Sudan I concentrations.

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