Sensors & Actuators: B. Chemical 271 (2018) 122–127

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Investigation of silver nanorods as reusable SERS-active substrates for trace level detection of 2-MIB volatile organic compound

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ARTICLE INFO

Keywords:
Silver nanorods
SERS
2-MIB
Sensing
Reusability

ABSTRACT

Silver nanorod arrays deposited on a silicon wafer by employing the DC magnetron sputtering system have been investigated as reproducible and reusable SERS-active substrates. 2-Methylisoborneol (2-MIB) is used as a test molecule to exploit the uniformity, reproducibility and reusability of the fabricated substrates. SERS chips are found to be reusable by simple washing with DI water. Quantitative measurements show a good correlation between the intensity and molar concentration of 2-MIB. SERS chips can detect 2-MIB as low as 1 ppt, limit of detection. The present method is a single package of high SERS performance, large-scale production, ultra-sensitive, uniform, reproducible and reusable.

1. Introduction

Surface-enhanced Raman Scattering (SERS) is a powerful spectroscopic technique for the ultrasensitive and selective detection of chemical and biochemical analytes using plasmonic nanostructures [1–12]. Coinage metals (Cu, Ag, Au) are the most commonly used SERS substrates because of their optical properties which can enhance the Raman signal enormously and also bio-compatibility [13,14]. The high enhancement of Raman signals was explained by electromagnetic (EM) and chemical enhancement (CE) mechanisms. EM results from the intense electromagnetic field enhanced by the localized surface plasmon resonances (LSPRs) around the metal nanostructures, which are capable of generating many hot-spots [15]. By contrast, CE is associated with the charge distribution between the adsorbate and metal nanoparticles. SERS studies on the geometry (particle size, shape, interparticle separation) of the nanostructures have widely been examined because of the EM shows high enhancement (10^6-10^8) compared to the CE (10-10^2) [16–19]. SERS technique has been demonstrated for single molecule detection [20]. SERS find many applications in the field of analytical chemistry [21], biological sciences [22], forensic sciences [23], environmental analysis [24] and clinical diagnosis [25] due to high sensitivity and selectivity of the technique.

In order to get wider acceptance as a quantitative analytical technique, the enormous amount of effort has been put into the development of the SERS substrates with a great amount of uniformity and sensitivity [26,27]. Lithography is the efficient technique to fabricate the substrates with uniformity and homogeneity, even though; it is difficult to fabricate well-ordered nanostructures with abundant hot-spots and also has the disadvantages like low throughput and high cost [28,29]. The general drawback of SERS substrates are lack of reproducibility of the Raman signal and could not be reused [30]. The poor reproducibility and reusability of the SERS-substrates have restricted to cost-effective sensors for practical applications.

Worldwide, many people are not accessible to the safe drinking water is an important issue because it is an essential ingredient for human health and development [31]. Water contaminant can be physical, chemical, biological, radiological, etc. The physical contaminant can be sediment or organic material suspended in the water of rivers, lakes, etc. Chemical contaminants are elements or compounds such as nitrogen, bleach, salts, pesticides, metals, toxins produced by bacteria, human/animal drugs. Biological/microbiological contaminants are bacteria, viruses, protozoan and parasites. Radiological contaminants are Cesium, Plutonium and Uranium. Water contaminants detection studies were done by different authors [32–34] using SERS. Among these, mercury (Hg) is one of the top ten hazardous environmental pollutants. Even very low concentrated Hg consumption can cause numerous health problems. Mercury traces in the water have been addressed through Raman/SERS method by many researchers [35–37]. In drinking water, many of these contaminants were filtered out during the process. Majority of the complaints from the consumer is about taste and odor of drinking water. 2-Methylisoborneol (2-MIB) and Geosmin are responsible for poor taste and odor.

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https://doi.org/10.1016/j.snb.2018.05.110
Received 19 September 2017; Received in revised form 11 May 2018; Accepted 18 May 2018

2-MIB is one of the principal organoleptic, musty odor volatile compounds presents in the freshwater, produced by cyanobacteria and actinomycetes. Though it is reported non-toxic, smell and poor taste leads to the consumer rejection. However, it may be the indicator of the presence of severely toxic cyanobacteria byproducts such as microcystins. 2-MIB can also cause serious problems and revenue losses in aquaculture fisheries by accumulating on fish tissues that result in the musty odor of unacceptable flavor and also increase the harvesting time leads to increase in production costs. Human detection threshold level of 2-MIB is 15 ng/L (ppt) [38]. Many methods have been examined, each with specific limitation. Closed-loop striping gas chromatography-mass spectrometer (GC–MS) effectively isolates the 2-MIB but it needs more pretreatment processing excess of 3.5 h [39], large sample volume and intensive preparation is required in liquid–liquid extractions [40]. Cryogenic coolants, consumable membranes and magnets are required in membrane-assisted solvent extraction (MASE) method and is expensive [41]. Detection and quantification of 2-MIB at ultrasensitive (in the range of 10 ppt) levels in aqueous systems require the use of a sensitive and selective method. Considering the importance of the rapid and sensitive determination, simple operation and high-throughput analysis, SERS is the ideal technique to detect the target molecules. We aimed at fabricating a rapid, sensitive and cost-effective device for industrial application to detect 2-MIB. In our earlier works [23,42], we reported an efficient approach to fabricate silver nanorod based SERS-active substrates with physical vapor deposition method (DC magnetron sputtering). The substrates sensitivity was tested with various analytes viz. trace perchlorate in industrial explosive emulsion and methamphetamine/amphetamine in human urine and exhibited high performance. These substrates are (OnSpec: NECTEC SERS Chips https://www.nectec.or.th/en/innovation/product-innovation/onspec-forensic.html) commercializing for real-world application. In the present contribution, we have investigated the reusability and ultra-sensitive detection of 2-MIB on our SERS-chips. In addition to this, sensitivity, uniformity and reproducibility of the SERS-chips were explored in the present contribution. The fabricated SERS-chips exhibit good SERS reproducibility and ultrasensitive detection of 1 ppt 2-MIB analyte in aqueous solution. The SERS-chips were offered high uniformity and reusability with three cycles of cleaning and sensing. The method can be implemented in the industries of drinking water and aquaculture fisheries effectively.

2. Experimental details

SERS-active thin-film samples of silver nanorod structures were deposited on silicon wafers by a DC magnetron sputtering system. A 3-inch high-purity (99.99%) silver material (K.J. Lesker make) was used as a sputtering target. During the fabrications, a DC power supply at 0.4 A and 340 V was used to deposit the silver nanostructures, with a deposition rate of ~1.0 nm/s, as calibrated by the spectroscopic ellipsometer (J.A. Woollam; HTC-190). A glancing-angle deposition (GLAD) technique was used during the fabrications in order to promote the vertically aligned Ag nanorods, which were spread out with high porosity. The physical structures and porosity were verified by a field-emission scanning electron microscope (FE-SEM; Hitachi, S-5200). Immediately after the deposition, the SERS chips were handled with a great care, while being cleaved into small pieces, mounted on glass slides, and finally stored in nitrogen-filled metalized bags. For the SERS measurements of 2-MIB, the analyte solution purchased from Sigma-Aldrich ~10 mg/mL in methanol, ≥98% (GC), was prepared in a concentration range from 100 parts per billion (100 ppb) down to 1 part per trillion (1 ppt). A 2.5 μL analyte solution was dropped on the SERS chip, and allowed to dry in an ambient atmosphere. The Raman measurements were carried out with a Raman spectrometer (Renishaw; InVia Reflex) with laser excitation wavelengths of 532 nm, 633 nm and 785 nm. All the Raman spectra were collected and processed via the WiRE™ 4.2 software associated with the Raman system.

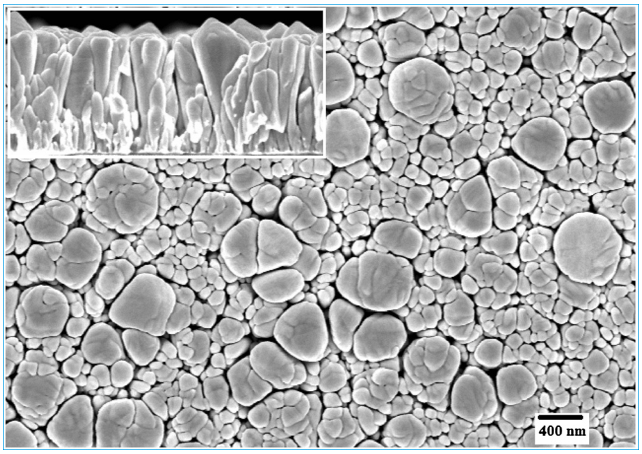

Fig. 1. FESEM image of top view of vertically aligned silver nanorod arrays on silicon wafer. Inset shows the cross-sectional view.

To evaluate the performance of the fabricated substrates as potential SERS-active substrates for real application, analyte molecule of 2-MIB dropped on the SERS-chips and allowed to dry prior to acquire the Raman spectra. First considerations were focused on the three Raman spectra from 2-MIB on the SERS-chips measured with different laser sources (532, 633, and 785 nm), whose excitations yielded completely different spectral Raman responses. For comparison, a Raman spectrum, collected from the 532 nm laser source, for the blank SERS-chip without any test molecule was included. For practical utility studies 100 μL of 2-MIB (1 ppm) spiked in the 1 mL of tap water and mineral water.

3. Results and discussion

Fig. 1 shows the FESEM image of bird's-eye view of vertically aligned silver nanorod (AgNR) arrays deposited on a silicon wafer and the inset shows the cross-sectional view. Hereafter, AgNR substrates referred as SERS-chips. The micrographs confirm the presence of the nanorods on the silicon wafer. ImageJ software was used to estimate the dimension and distribution of AgNR. The dimensions of the AgNR are found to be 1 μm (majority) in length and width of ~200–600 nm and average separation estimated to be ~27 nm. The average widths present on the substrates were 160 ± 48 nm and 520 ± 110 nm. The different size distributions can create abundant hot-spots on the substrates which are very crucial to enhance the Raman signals. Two size distributions SERS-substrates were reported in our previous report which enables the detection of crystal violet up to attomole concentration level [20]. Similar nanostructures with a less variation in the silver nanorod size have been previously reported with high sensitivity to traces of chemical molecules, i.e., methamphetamine/amphetamine in human urine specimens [23] and industrial-grade emulsion explosives [42], based on specific laser wavelength and test molecules. In this work, however, the nanostructures were proposed to be investigated and utilized for the trace-level detections of 2-MIB based on several laser excitation wavelengths of interest.

Fig. 2 illustrates baseline-corrected Raman spectra of the 2-MIB traces on the SERS-chips, based on the different laser sources (532 nm, 633 nm and 785 nm). The 532 nm laser exposed on the blank and the 2-MIB-dropped SERS-chips gave similar spectral results of several Raman peaks, corresponding to backgrounds from the SERS-active surface. Importantly, at only this excitation, the measured spectrum from the 2-MIB on the SERS-chip clearly exhibits an additional intense Raman line at ~986 cm^{-1}, which should clearly indicate the presence of 2-MIB characteristics. In contrast to the previous report, our fabricated SERS substrates work efficiently with NIR wavelength [23,42]. In order to further verify this conflict, the 2-MIB traces on the SERS chips were re-