

The Development of a Portable Arsenic Detector Based on Surface-Enhanced Raman Spectroscopy for Rapid on-Site Testing of Groundwater

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ABSTRACT

The combination of high toxicity and widespread occurrence has created a pressing need for effective monitoring of arsenic in groundwater. In this paper, we discuss the development and performance of a field deployable monitoring tool based on surface enhanced Raman spectroscopy (SERS) that can be used for rapid on-site detection and quantification of arsenic in groundwater. More specifically, we discuss (1) the fabrication of close-packed metal nanoparticle film in large scale as SERS substrate via a two-phase interfacial self-assembly process; (2) the fabrication of a SERS sampling module that can house the SERS substrate and also attaches to a fiberoptic Raman probe; and (3) the detection of ppb level arsenic using the assembled portable SERS system. Because of the low cost associated with the SERS sensor materials and fabrications, they can be manufactured as disposable products so that any possible contaminants from analytes (i.e., arsenic) deposited from previous measurements can be avoided.

Keywords: arsenic, groundwater, ppb, SERS, nanoparticle, LSPR, fiberoptic, portable, on-site

1 INTRODUCTION

Arsenic [1] is a well-known toxic chemical that the Environmental Protection Agency (EPA) and the World Health Organization (WHO) list as a known carcinogen. It enters drinking water supplies from natural deposits in the earth or from agricultural and industrial practices, and is one of the most common contaminants in groundwater worldwide. Arsenic can directly cause cancers of the skin, lungs, and bladder, in both humans and animals. The WHO and US guidelines recommend the arsenic values in drinking water to be no more than 10 $\mu\text{g/L}$ (10 ppb).

Although laboratory analysis has been used to measure arsenic in collected groundwater samples, due to the time and cost associated with sample collection, packaging, shipping and instrumental analysis, there is a necessity for development of simple and rapid methods for field assays. The ideal field deployable sensor would be able to detect arsenic reliably in the low ppb concentration range, *in situ*, on-site, with little or no sample preparation, and with no interferences. One technology that meets many of these criteria is surface-enhanced Raman spectroscopy (SERS) spectroscopy [2]. Since the discovery of significant

enhancements of Raman scattering by metallic surfaces or metal nanostructures, SERS has been explored broadly in many different fields in the past decades [2]. Different from conventional Raman spectroscopy the signal intensity obtained from SERS (whereby analytes are adsorbed onto a noble metal surface prior to analysis) is significantly “enhanced”, rendering it suitable for trace analysis. Recent experimental observations have indicated that SERS enhancements, in certain situations can go as high as 10^{14} times, elevating SERS to single molecular sensitivity [3, 4].

The signal enhancement of SERS is proportional to the average over the surface of the metal particle of the local field $|E(\omega)|^2$ at the pump frequency ω multiplied by $|E(\omega')|^2$ at the Stokes-shifted frequency ω' . Recently, Zou *et al* [5] and a few other groups have reported that based on electrostatics calculations, $|E|^2$ enhancements of 10^7 are possible when ordered nanoparticle (size >50 nm) arrays are used as SERS substrates which leads to the possibility of field enhancements of 10^{14} or larger without invoking chemical enhancement effects. This result was due to the combination of local field enhancement associated with plasmon excitation in the nanogaps between metal nanoparticles and long range photonic interactions arising only from ordered array of particles [5]. The effect of the periodic array is to further enhance the field by about an order of magnitude above that obtained from the isolated dimer. For SERS sensing device application, large-scale nanoparticle assemblies are desired as the total numbers of “hot spots”, i.e., the nanogaps/nanojunctions between neighboring nanoparticles, are now dramatically increased and spread over the entire assembled macrosized structures or films. This greatly improves the efficiency of signal observation for single molecule SERS detection. However, due to the difficulty in preparing large scale (e.g., several square inches) ordered nanoparticle assembly film, it has been difficult to experimentally demonstrate that SERS signals could be modulated or controlled by long-range plasmonic interactions.

Recently through our research and development efforts funded by a NIH SBIR program, Agiltron has demonstrated the use of a low-cost, facile two-phase interfacial self-assembly process to repeatedly and controllably produce ultrasensitive SERS substrates containing arrays of nanogaps (or nanojunctions) as “hot-spots” in large scale. This method can be applied to different types of metal nanoparticles despite the difference in their material compositions, the shapes, and size dispersity. In this paper, based on the use of this type of high sensitive SERS substrates, we discuss our development of a field

deployable SERS system and its potential application for rapid on-site detection and quantification of arsenic in groundwater.

2 EXPERIMENTAL

2.1 Silver Nanoparticle Preparations

Based on the original polyol method [6], we have developed a facile process that can be used to produce quasi-spherical silver nanoparticles with narrow diameter distribution in large quantities. In a typical procedure, 170 g of polyvinylpyrrolidone (PVP, MW 40,000) is dissolved in 1 liter ethylene glycol and heated up to 160 °C in an oil bath, until it turned from colorless to light yellow. Then, 17 g of AgNO₃ pre-dissolved in another 1 liter ethylene glycol was added into the above solution, and the reaction is allowed to proceed for 4 h at this temperature before it completes. The colloidal dispersion is cooled down to room temperature. This process will produce silver nanoparticles with an average size of 50 nm.

2.2 Close-Packed Nanoparticle Film Fabrication

For fabricating close-packed metal nanoparticle film, a silver nanoparticle dispersion in water or ethylene glycol is first prepared and then mixed with toluene or any other immiscible hydrophobic organic solvents to form a two-layer liquid system where all the silver nanoparticles are initially dispersed in water (or ethylene glycol). By adding an excess amount of a thiol material such as 11-Mercaptoundecanoic acid into the liquid system (i.e., from the upper toluene layer) the thiols will attach to the surface of the silver nanoparticles (existed at the water-toluene interface) as a complete and molecular thick self-assembled monolayer (SAM). The thiol-modified silver nanoparticles can gradually self-assemble at the ethylene glycol-toluene interface and appear as a shiny mirror-like thin interfacial layer. If a suitable amount of an alcohol such as ethanol is added into this two-layer system to adjust its surface tension property, an almost one-phase system can eventually be formed while maintains the silver shiny appearance throughout the “outer layer” of the new one-phase system. This silver shiny appearance, which is usually only observable for a continuous metal film structure, indicates both long range and short range optical and electronic coupling from the close-packed nanoparticles within the “shiny” film. By casting a drop of this dispersion on a supporting substrate such as a glass slide or a wafer, dipping and withdrawing a substrate, monolayer or multilayers of ordered close-packed silver nanoparticle film with its size of a square inch or larger can be transferred and prepared.

For SERS sensing device applications, the adhesion strength of the SERS film on the substrates and its durability is always an important factor. In our studies, we

pre-treated the substrate (glass and silicon wafer) with a self-assembled monolayer of mercapto silane as linker molecules for covalently attaching the transferred metal particle film onto the substrate via thiol linkage.

2.3 Fabrication of an Attachable SERS Sampling Module

In order to achieve real-time SERS measurement for liquid samples, we have developed/fabricated an “Add-On” SERS sampling module that can be attached to the Raman probe end and inserted into the liquid directly for spectra collection. The dimension of the sampling module was designed in such a way that after its attachment to the end of the laser probe, the position of the SERS chip – fixed inside the module – is precisely set at the focal point of the laser light with maximized signal intensity. A water (liquid) accessible hole is designed with a cover cap so that the laser radiation is enclosed within the sampling system (e.g. zero external laser emission), thus this device is totally eye-safe under all operating conditions. An optical window is placed inside the water chamber to separate the water from the Raman probe. The package design is modular and can be easily taken apart to replace the SERS chip when needed.

For the development of a deployable SERS system we used the PeakSeeker™ portable fiberoptic Raman spectrometer – Agiltron’s most practical and easy-to-use commercial Raman spectrometer. It has a total weight of less than 8 pounds and can be powered by an internal rechargeable lithium ion battery or an included AC/DC adapter suitable for on-site operation and long term data acquisition. The fiber optic probe is used to transmit the excitation light from the laser to the sample and the Raman emissions to the spectrometer.

2.4 Detections of ppb Level Arsenic Using the Assembled Portable SERS System

Solutions containing a fixed concentration (500 ppb) of polyvinylpyrrolidone (PVP) (as an internal standard) and various amounts (1 to 500 ppb) of Na₂HAsO₄ were prepared and tested. During the measurements, the SERS sampling module (containing the SERS chip) was inserted into the solution samples directly for spectra collection. A PeakSeeker™ portable Raman spectrometer with an excitation wavelength of 785 nm was employed for the study.

3 RESULTS AND DISCUSSION

Figure 1 shows a Transmission Electronic Microscope (TEM) image of silver nanoparticles made from our polyol preparations. As indicated in this image, silver nanoparticles made from these large scale preparations can still exhibit extremely high yield and purity. These silver nanoparticles were then processed using the two-phase

interfacial self-assembly method (as described in the Experimental section) to produce the close-packed silver nanoparticle films. As shown in Figure 2, after the addition of a suitable amount of ethanol, an almost one-phase system was formed which exhibited a silver shiny appearance throughout the “outer layer”. By casting a drop of this dispersion on a supporting substrate such as a glass slide or a wafer, dipping and withdrawing a substrate, monolayer or multilayers of ordered close-packed silver nanoparticle film with its size of a square inch or larger can be transferred and prepared. A Scanning Electronic Microscope (SEM) image of such a film is shown in Figure 3A. Similar to the structures of colloidal photonic crystals, the combined use of monodispersed spherical building units and the self-assembly process ensures the production of near-perfect close-packed nanojunction arrays in high numbers. Because of close-packed nanoparticle structure in the film, by using thiol molecules of different chain lengths to form the spacer layer between two touching particles, the metal-thiol-thiol-metal distance can be controlled accordingly. Thiols such as 11-Mercaptoundecanoic acid has a chain length of less than 1.5 nm, which gives a final metal-metal distance of <3 nm for the close packed nanoparticles. Besides functioning as molecular spacers, the thiols used in this process also have several other key functions: (1) to assist/promote the self-assembly process to form close-packed structure during the SERS film preparation; (2) to protect the SERS substrates (e.g., silver) from surface deterioration thereby extending their lifetimes

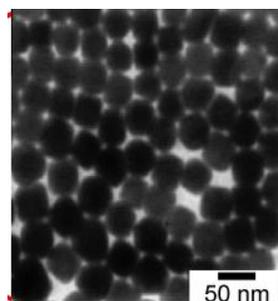


Figure 1: TEM image of the nanoparticles with their diameters around 50 nanometers.

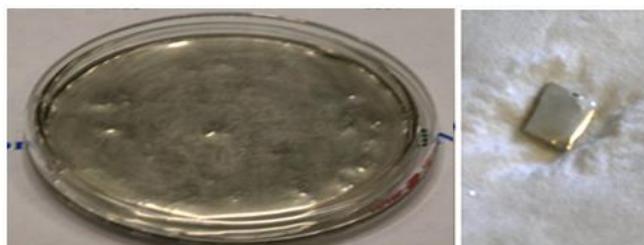


Figure 2. (Left) Formation of a large self-assembled close-packed silver nanoparticle film with a shiny silvery appearance in a glass dish. (Right) a “being-dried” SERS substrate made from the film shown on left on a diced silicon chip.

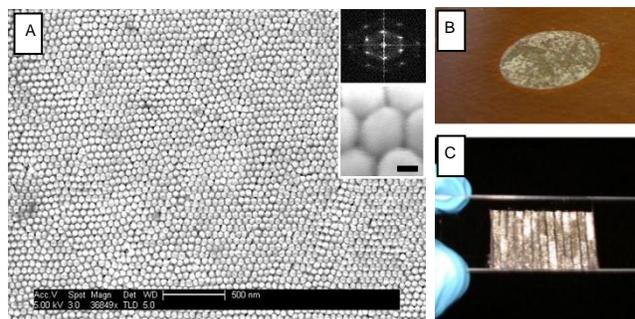


Figure 3: (A) SEM image of a close-packed silver nanoparticle (~50 nm in diameter) superlattice film. The right top inset shows a diffraction pattern obtained from fast Fourier transform of the same SEM image indicating the long range order of the formed film. The right lower inset (scale bar = 20 nm) shows a close-up view of the nanoparticles in the close-packed structures which indicates the spherical nanoparticles are physically in touch with each other. The close-packed ordered nanoparticle structure can be prepared in large scale as (B) inch size SERS films or (C) macro pattern arrays.

[7]; and (3) to attract analytes of interest close to the silver nanostructure surface for maximal SERS enhancements. The close-packed ordered-nanoparticle film obtained from this process can be facily made in inch sizes (Figure 3B) and prepared in macro-patterns (Figure 3C).

We have designed and fabricated an “Add-On” SERS sampling module that can be attached to the Raman probe end and inserted into the liquid directly for spectra collection. Figure 4 shows the final assembled deployable SERS system. Our fabricated SERS sampling module had a small form factor and was constructed of rugged and

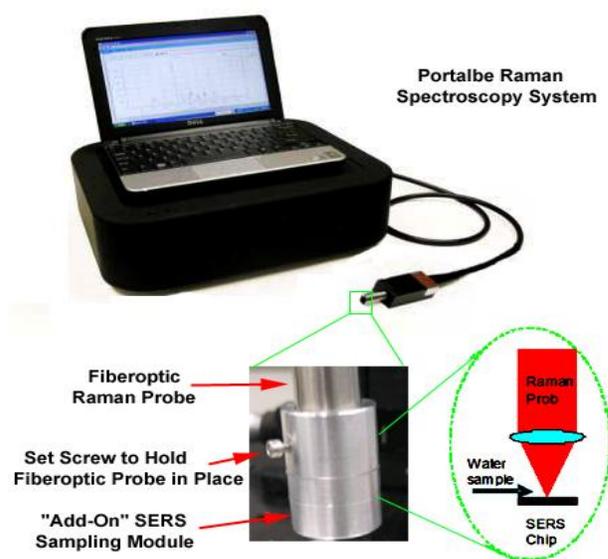


Figure 4. The portable SERS system for rapid on-site detection of arsenic in groundwater.

chemically-resistant stainless steel material. The SERS chip is situated on a holding stage inside the sampling module and pre-aligned to the laser focal point of the fiberoptic Raman probe.

With the availability of both fiberoptic Raman spectrometer and high sensitive SERS chips, we have evaluated their application for trace arsenic detection in water. Figure 5 shows the resultant Raman spectra collected from these solution samples of different arsenic concentrations. The peak at 660 cm^{-1} is associated with the C-C ring stretch of PVP and the peak at $\sim 770\text{ cm}^{-1}$ corresponds to the ν_1 (A1) symmetric As-O. Figure 5B shows the linear dose response of our SERS chip for increasing concentrations between 1 and 500 ppb. This simple dependence allows for quantitative determination of arsenate concentration at levels that are an order of

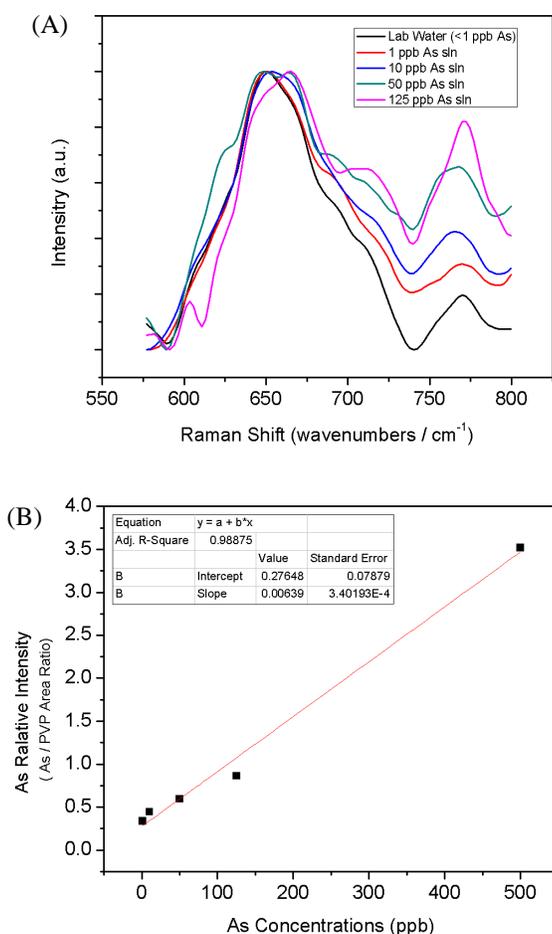


Figure 5. Detection and quantification of trace arsenate (and PVP) in solutions using Agiltron's portable fiberoptic Raman spectrometer and SERS chip. (A) Raman spectra obtained from 5 samples containing a fixed concentration of PVP and different amount of arsenate. (B) The observed linear relation between the relative intensity (As:PVP) of arsenate peak as shown in (A) and its concentrations (1-500 ppb).

magnitude below the current EPA and WHO guidelines. Clearly, the result shown in Figure 5 demonstrated the capability of using the deployable SERS system (comprised of Agiltron's portable fiberoptic Raman spectrometer and SERS chip hosted in the sampling module) to distinguish and detect As (V) at a concentration level as low as 1 ppb. It is worth noting that because of the high sensitivity associated with our SERS chip, the sub-ppb level of As (V) existing in the (control) lab water system was also detected and showed up in the spectra.

4 CONCLUSIONS

In this paper, we demonstrated the detection of 1 ppb level arsenic in water samples using a portable SERS system. More specifically, we (1) demonstrated a facile self-assembly process for close-packed nanoparticle SERS films fabrication; (2) demonstrated the fabrication of a SERS sampling module for direct measurements in water samples; and (3) demonstrated the detection of 1 ppb level arsenic using the assembled portable SERS system. Our method for fabricating close-packed nanoparticle film can be applied to different types of metal nanoparticles for SERS applications despite the difference in their material compositions, shapes, size and dispersity. As the cost (<\$1 per chip) associated with our current SERS film materials/fabrications is low, we can manufacture our SERS chips as disposable products so that any possible contaminations from analytes deposited from previous measurement can be avoided.

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