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Highly sensitive and flexible inkjet printed SERS sensors on paper

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ABSTRACT

Surface enhanced Raman spectroscopy (SERS) has the potential to be utilized for the detection of a broad range of chemicals in trace quantities. However, because of the cost and complexity of SERS devices, the technology has been unable to fill the needs of many practical applications, in particular the need for rapid, portable, on-site detection in the field. In this work, we review a new methodology for trace chemical detection using inkjet-printed SERS substrates on paper. The detection performance of the inkjet-printed SERS devices is demonstrated by detecting 1,2-Bis(4-pyridyl)ethylene (BPE) at a concentration as low as 1.8 ppb. We then illustrate the primary advantages of paper SERS substrates as compared to conventional SERS substrates. By leveraging lateral flow concentration, the detection limit of paper SERS substrates can be further improved. Two real-world applications are demonstrated. First, the inkjet-printed SERS substrates are used as "dipsticks" for detecting the fungicide malachite green in water. Then, the flexible paper-based SERS devices are used as swabs to collect and detect trace residues of the fungicide thiram from a surface. We predict that the combination of ultra-low-cost fabrication with the advantages of easy-to-use dipsticks and swabs and the option of lateral flow concentration position ink-jet printed SERS substrates as a technology which will enable the application of SERS in solving critical problems for chemical detection in the field.

1. Introduction

Today there is significant interest in the development of portable and highly sensitive chemical analysis techniques for use in the field at the point of sample acquisition. Surface enhanced Raman spectroscopy (SERS) has been intensively studied for applications in chemical detection. SERS offers sensitivity comparable to that of fluorescence spectroscopy [1] while also providing highly specific information about the analyte. In Raman spectroscopy, photons from a laser source are inelastically scattered at frequencies related to the vibrational energies within the analyte molecule, and thus the measured spectrum uniquely identifies the analyte molecule. Although Raman scattering alone is a weak effect, SERS utilizes optical and chemical enhancements from gold or silver nanostructures to provide a tremendous boost to the Raman signal [2–7]. A driving force behind SERS research has been the sum of reports from over a decade ago showing that SERS enables single molecule identification [1,8–10].

Today, the most common method for performing SERS measurements is to deposit a droplet of a liquid sample onto a rigid silicon or glass substrate that has a nanostructured noble metal surface. When the sample dries, analyte molecules within the sample adsorb onto the nanostructured metal surface, where they will experience the plasmonic and chemical enhancement associated with SERS. These SERS-active surfaces can be fabricated through a number of possible techniques, including self assembly [11–14], directed or templated assembly [15–18], thin film growth [19], and nanolithography [20–22]. While nanolithography approaches tend to have high SERS enhancement factors and superior uniformity, they are complex and expensive to produce. Growth and assembly approaches are less expensive, but they suffer from problems of low throughput. Hence the techniques mentioned above are not optimized to meet the needs of widespread, routine detection of chemical species in the field.

Recently, we reported the fabrication of SERS substrates by inkjet printing silver nanostructures onto paper using a low-cost commercially available desktop piezo-based inkjet printer [23]. Other groups have reported the fabrication of SERS devices on paper and other flexible substrates through soaking [24,25] and screen printing [26]. The SERS substrates on cellulose paper demonstrate an enhancement factor of about 10^5–10^7, which is on par with many of the self assembly and directed assembly techniques. In addition, the paper SERS devices have a number of advantages over rigid SERS substrates. First, liquid samples can be quickly loaded into the paper SERS device by capillary forces (wicking) simply by dipping the paper into the sample. Second, powders and

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residues, which are incredibly difficult to detect with rigid substrates or microfluidic devices, can be loaded into the paper SERS device by swabbing the inherently flexible device across a wide-area surface of any topology. Finally, analytes loaded into the paper device through dipping or swabbing can be concentrated into a small SERS sensing region by leveraging the concept of lateral flow paper fluidics. Thus, when combining the low fabrication cost of inkjet printed SERS substrates with the fluid handling properties and ease-of-use of paper-based analytics, this new paradigm represents a significant advancement in on-site analytics, and enables SERS to be much more accessible in terms of cost and usability.

In this work, we illustrate in detail the methods for fabricating paper-based SERS devices and utilizing them for applications in chemical detection. After detailing the methods for utilizing a commercial inkjet printer for fabrication, SERS spectra are presented for a range of molecules on these ink-jet printed substrates. Detection of the common model analyte 1,2-Bis(4-pyridyl)ethylene (BPE) is demonstrated at a concentration as low as 1.8 ppb. The advantage of utilizing the lateral flow concentration capabilities of the paper device are then quantified. Finally, we demonstrate two high-impact applications of the paper SERS devices. First, trace quantities of the fungicide malachite green in water are detected when the sample is loaded simply by dipping the paper SERS device into the water. Second, trace residues of the fungicide thiram are detected by swabbing a surface with a paper SERS device. This collection of results provides an in-depth view of this new low-cost and easy-to-use method for on-site analytical chemistry.

2. Materials and methods

2.1. Inkjet printed SERS substrates

Chromatography paper (0.19 mm thickness) was purchased from Fisher Scientific. Nitrocellulose membranes were purchased from Bio-Rad Laboratories (Hercules, CA). Chloroauric acid was obtained from Alfa Aesar (Ward Hill, MA). Sodium citrate and glycerol were obtained from Sigma–Aldrich (St. Louis, MO). Common commercial reagents were of analytical reagent grade.

The gold colloid is synthesized according to the method of Lee and Meisel [27]. Briefly, 80 mg of chloroauric acid is added to 400 mL of DI water (18.2 MΩ) and brought to boil in an Erlenmeyer flask. While stirring rapidly, 80 mg of sodium citrate is added. The color shifts rapidly to a deep purple. The solution is allowed to boil for 20 min and then removed from heat.

The gold ink is formed by first centrifuging the gold colloid at 6000g to concentrate the nanoparticles. After removing the supernatant the pellet of nanoparticles is suspended in water to achieve a final concentration factor of 100×. Finally, the ink is created by adding glycerol and ethanol to the concentrated nanoparticles, with a final volume ratio of 5:4:1 of concentrated nanoparticles to glycerol to ethanol. In separate work we have reported the use of silver nanoparticle ink as well [23,28].

For printing, the ink is injected into the main reservoir of refillable printing cartridges which have never contained pigmented ink. The open source vector graphics editor, Inkscape, is used to define the SERS-active regions for the printed substrates. An inexpensive consumer piezo-based inkjet printer, the EPSON Workforce 30, is used to print the SERS-active substrates onto untreated chromatography paper, as previously described [23]. Substrates are printed four times to increase the nanoparticle concentration in the paper. The flexibility of ink-jet printing allows arrays of SERS-active regions to be printed in any shape. Fig. 1A shows an array of triangular sensors printed for use in dipsticks. After printing the array, devices are cut from the paper to the appropriate size. Various paper SERS devices are displayed in Fig. 1B–D.

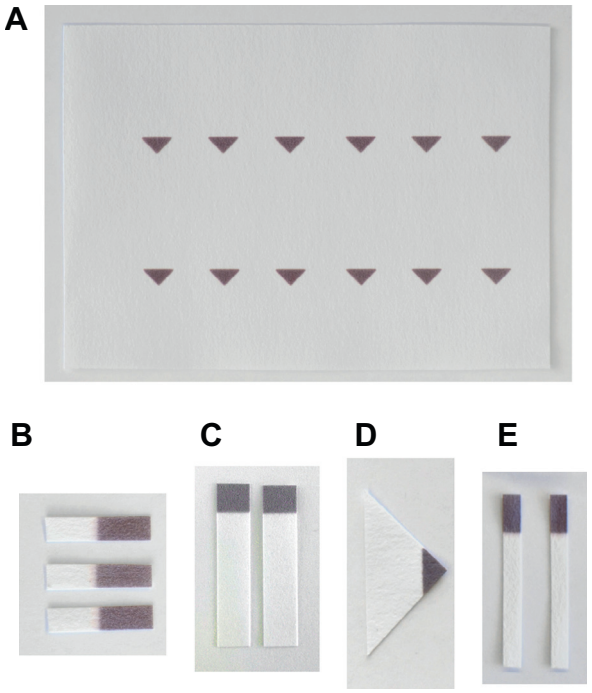

Fig. 1. (A) A printed array of SERS substrates. Printed arrays of SERS substrates can be cut as demanded by the application, with the goal to create a conformation that most benefits analyte collection, concentration, and detection. (B) Inkjet-printed gold nanoparticles for use as a general SERS substrate. (C) Substrates for use in lateral flow concentration experiments. (D) A substrate with a large wicking region for use as a dipstick. (E) Substrates used as surface swabs.

A scanning electron microscope (SEM) image of a typical ink-jet printed gold substrate is presented in Fig. 2, showing the clustering of gold nanoparticles in the paper fiber pores. This clustering of nanoparticles is responsible for the high SERS activity of the substrates. While the random aggregation of nanoparticles seen in Fig. 2 results in local variability of the SERS signal, the large number of nanoparticle clusters captured within the focused region of the fiber optic probe (~100 μm diameter spot) allows averaging over a multitude of nanoparticle aggregates, lowering variability and enabling quantitative results.

2.2. Analyte preparation

1,2-Bis(4-pyridyl)ethylene (BPE), malachite green oxalate, and thiram were obtained from Sigma–Aldrich (St. Louis, MO). BPE, malachite green, and thiram were dissolved in ethanol, water, and acetone, respectively; all samples were diluted with water to various concentrations for use as test samples.

2.3. SERS measurements

SERS measurements were performed using a 785 nm laser (17 mW) for excitation, a QE65000 (Ocean Optics) portable spectrometer for detection, and a fiber optic probe (InPhotonics) for delivery of laser light and collection of scattered photons (Fig. 3). The 785 nm wavelength was chosen due to the low cost and portability of 785 nm laser diodes, as well as the reduction in background fluorescence gained by operating at long wavelengths. An integration time of one second was used for all measurements; signals represent the average of three measurements. This averaging step reduces the random background noise contributed by the detector; we found that averaging across three signals was sufficient to reduce a large fraction of the noise without contributing