Surface-Enhanced Raman Scattering Active Substrates by Liquid Flame Spray Deposited and Inkjet Printed Silver Nanoparticles

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Surface-enhanced Raman scattering (SERS) active substrates were made via liquid flame spray deposition and inkjet printing of silver nanoparticles. Both processes are suitable for cost-effective fabrication of large-area SERS substrates. Crystal violet (CV) solutions were used as target molecules and in both samples the detection limit was approximately 10 nM. In addition, sintering temperature of the inkjet printed silver nanoparticles was found to have a large effect on the SERS activity with the higher curing temperature of 200°C resulting in contamination layer on silver and cancelation of the SERS signal. This layer was characterized using an X-ray photoelectron spectroscopy (XPS).

Keywords: surface-enhanced Raman scattering (SERS), liquid flame spray, inkjet printing, nanoparticles, surface chemistry, nanophotonics

1. Introduction

Surface-enhanced Raman scattering (SERS) is a powerful, surface-sensitive, non-destructive, and in-situ vibrational spectroscopic technique that is suitable for detection of extremely low concentration analytes.¹ Since the original discovery of SERS on roughened silver electrodes in 1977,²,³ the phenomena has been studied widely in more than 5000 research articles covering fields such as chemistry, physics, and material science.⁴

Raman scattering is sensitive to different vibrational modes of the analyte. Hence, SERS provides a fingerprint of a molecule with enhancement factors over a million compared to the conventional Raman scattering. Such signal enhancement originates both from chemical and electromagnetic effects of which the electromagnetic contribution is several orders of magnitude larger than the chemical one.⁵ The electromagnetic enhancement results from the local electric fields typically excited in metallic nanostructures, which support localized surface plasmon resonance (LSPR). Traditionally LSPRs are observed with metals including silver, gold, and copper that all have the plasmon resonance in the visible wavelength range.

SERS occurs when analytes are brought in the vicinity of the surface of such LSPR active substrate. The excitation of plasmons in metallic nanostructures highly enhances the local electric field strengths. The SERS signal intensity depends on the fourth power of the local field strength and signal enhancement factors up to 10¹⁰–10¹¹ have been reported allowing detection down to a single molecule level.⁶–⁸ Furthermore, the electromagnetic field enhancement can be improved by cascading metallic nanoparticles of different sizes in a self-similar chain as theoretically predicted by Li et al.⁹ The local electric field is focused into an even smaller volume as the electric field cascades along the chain from the larger nanostructure into the smaller one. Therefore, a higher local electric field strength is obtained with a larger enhancement factor than with a single nanoparticle. This was confirmed by a recent experiment with an order of magnitude enhancement using a self-similar trimer antenna of gold nanoparticles instead of a single gold particle.

Advances in nanoscale manufacturing tools within the last two decades have resulted in a transformation of SERS from a topic of purely academic interest to a practical analytical tool. Various nanostructures ranging from tip-enhanced Raman spectroscopy (TERS)¹⁰ to shell-isolated nanoparticle enhanced Raman spectroscopy (SHINERS)¹¹ have been suggested recently; for a review of these advances, see Ref. 5. However, the cost of such nanoscale structures is typically too high for practical applications as in many cases the analyte can stain the substrate. Therefore, there is a large demand for low-cost, large-area disposable or recyclable SERS substrates.

Various paths have been taken to achieve such low-cost SERS substrates. First, one can design a renewable SERS substrate by combining metal nanostructures to, for example, TiO₂ structures that can be cleaned by ultraviolet light via photocatalytic activation as suggested by Li et al.¹² Alternatively one can develop a cost-effective manufacturing technique to make the SERS substrate. Here we take the latter approach, and utilize two different routes for generation of low-cost, large-area SERS substrates. A liquid flame spray (LFS) process has been used to coat large areas with nanoparticles on various substrates including paperboard.¹⁸–²⁰ In the LFS process a liquid precursor

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The formed nanoparticle size can be controlled via the process parameters including the flow rates of the gases and precursor, precursor concentration, and deposition time and distance from the substrate. An additional benefit of the LFS process is that the generated nanoparticles can be collected on a moving web, which allows large areas to be coated via roll-to-roll process flow. Here we use LFS to deposit silver nanoparticles for SERS on glass substrates. We also use inkjet printing with commercially available silver ink to fabricate large-area SERS substrates. All printed samples are cured in an oven after printing and we also study the effects of curing temperature on SERS activity.

We believe that the developed SERS sensor platforms will find many applications in detection of extremely small amounts of analytes ranging from bacteria and pathogens to enhanced security with detection of explosives and toxic industrial chemicals in the future.

2. Experimental: Materials and Methods

2.1 Sample preparation

Figure 1 shows the two used methods for silver nanoparticle deposition on the glass substrate: Fig. 1(a) shows a schematic picture of the LFS nanoparticle deposition process and Fig. 1(b) displays the used piezoelectric Dimatix inkjet printer in preparation of the SERS active substrates.

2.1.1 LFS silver nanoparticle deposition

Silver nanoparticle deposition on glass substrate was carried out using an LFS process. Silver nitrate (AgNO₃, 99.9+%, Alfa Aesar) precursor in water solution was fed into the flame with different process parameters. Two different particle sizes were deposited. The silver concentration of 750 mg/ml in the precursor and gas flow ratios of 551/min (H₂) and 51/min (O₂) were used to synthesize silver nanoparticles with an average diameter of 90 nm. Precursor feed rate was fixed to 4 ml/min. For deposition of 30 nm silver nanoparticles the silver concentration in the precursor was reduced to 500 mg/ml with the gas flow ratios of 401/min (H₂) and 201/min (O₂). Precursor feed rate was fixed to 2 ml/min. Direct nanoparticle deposition on glass substrate was carried out using a specially designed deposition tube.

2.1.2 Inkjet printing and curing of the silver nanoparticle surface

Inkjet samples were printed on a typical microscope glass. The silver ink contained silver nanoparticles with diameters from 20 to 50 nm dispersed in ethanol, ethylene glycol, and glycerol (Sun Chemicals U5603). The inkjet printing was performed using a piezoelectric Dimatix DMP-2800 (Fujifilm Dimatix) with a drop-on-demand mode. Single nozzle with a 10 pl drop volume and 45, 60, and 85 μm drop spacing (DS) were applied on glass substrate. The printed samples were cured for 30 min in an oven with temperature of 120°C to guarantee ink setting and drying on the substrate. A curing temperature of 200°C was also tested.

Both LFS deposited and inkjet printed samples were imaged using a scanning electron microscopy (SEM) with a Carl Zeiss Ultra-55 microscope.

2.2 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) spectra of inkjet printed and oven cured glass samples were acquired using a PHI Quantum 2000 X-ray photoelectron spectrometer (Physical Electronics Instruments, USA) equipped with a monochromatic Al Kα X-ray source operated at 25 W. A combination of electron flood and ion bombarding was used to enhance charge compensation. All samples were irradiated with monoenergetic X-rays for 10 min with a pass energy of 184 eV for survey analysis causing photoelectrons to be emitted from the sample surface with an emission current of 2 mA using 45° take-off angle from the sample surface. Three different spots with a diameter of approximately 100 μm were measured for each sample.

For high resolution carbon C 1s peak and silver Ag 3d peak spectra were recorded with a pass energy of 29.35 eV after 10 min of measurement. A mixed Gaussian–Lorentzian character and Shirley background were used for curve fitting of high resolution peaks. The pressure in the main chamber was maintained at 2 × 10⁻⁷ Torr during spectra acquisition.

2.3 Raman spectroscopy

Raman spectroscopy was carried out with a spectrometer (Andor Shamrock 303) and a cooled charge-coupled device (CCD) camera (Newton 940P). The Raman excitation was...