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Rapid Single Step Atmospheric Pressure Plasma Jet deposition of a SERS active surface

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Abstract: This report details a new novel approach to depositing minute Ag particles in a regular array, comparing particle size, enhancement factor and cost with a commercial substrate and the standard colloidal silver particle method. Quantification of SERS will be displayed using 4MBA and R6G. Also detailed is the ability of our SERS substrate regeneration using plasma cycles. Using cycling of oxygen and hydrogen plasma, we can desorb the target analyte from the surface, reducing the SERS signal to the previous pre-analyte signal.

Keywords: Surface-enhanced Raman scattering, atmospheric pressure plasma jet, deposition, analyte.

1. Introduction

Surface-Enhanced Raman Spectroscopy (SERS) is a highly sensitive detection technique with enormous potential for chemical and biological sensing [1]. The enhancement of the Raman signal is due to localised surface plasmon resonance (LSPR) for substrates such as silver and gold, resulting in orders of magnitude greater signal [2,3]. The critical parameter is control of the surface nanostructure to optimise this remarkable enhancement, which provides non-destructive detection without the need for chemical labelling. The bottleneck for the wide applicability of SERS as a valuable analytical tool is twofold; (1) rapid fabrication with the required nanostructure and (2) the difficulty in recovering a baseline before exposure or re-exposure to the target matrix. Here we describe an atmospheric plasma jet method for rapid single-step deposition of SERS active silver on borosilicate slides and demonstrate the potential of plasma to remove the adsorbed analyte to recover a baseline.

The mechanism of surface enhancement has two factors: electromagnetic (EM) and chemical (CHEM) enhancement. EM enhancement is widely considered the most significant element in enhancing the signal. Albrecht and Creighton attributed the EM enhancement to plasmonic excitation in metal particles in 1975, thus assigning the SERS enhancement factor to enhanced fields from plasmons at a metal surface [4]. The nanoparticle surface structure/features determine the electromagnetic enhancement factor. When a roughened metal surface is irradiated by light, the conductive electrons are delocalised into oscillations to generate the electromagnetic field causing an enhancement in the Raman signal. Since its discovery, the attraction and the potential for creating an analytical device to exploit the remarkable enhancement of signal is clear.

Plasma deposition is a new material deposition method requiring only rudimentary precursors in an aqueous solution. First demonstrated by Alder et al., who deposited silver particles on paper substrates and demonstrated their applicability as SERS substrates [5].

Furthermore, we show initial studies using the plasma jet to clean the surface to provide a pristine surface for analyte adsorption for SERS analysis. This was demonstrated by Ratcliffe et al. (Ratcliffe, Rutten et al. 2007) using atmospheric pressure plasma jets are effective to desorb analytes from a surface for subsequent analysis by mass spectrometry, a technique they called plasma-assisted desorption/ionisation (PADI) [6][7]. Here we adopt this process specifically to desorb the analyte from the surface, with the intention to use this method as part of an analytical approach specifically to restore the baseline and regenerate the surface after measurement.

In this study, we use mercaptobenzoic acid and rhodamine as model analytes; the SERS response from an APPJ plasma deposited silver surface was demonstrated and compared to traditional colloid synthesised silver nanoparticles on glass and a commercially available silver-based SERS substrate.

2. Experimental

Four SERS substrates were compared in this work, a commercially available silver substrate from SERSitive (SS), plasma-deposited silver (PDS) and jet-deposited pre-synthesised spherical silver particles produced via the Turkevich synthesis (ADP).

The APPJ deposited silver SERS substrates on an unmodified borosilicate slide was done as follows. A solution of silver nitrate ($1x10^{-4}$ M) in deionised water (18 MW, ELGA) was injected using a syringe pump (Havard syringe) at a rate of 10mL/hr into a nebuliser. The CETAC nebuliser (Teledyne, US) atomised the solution and is carried through the nebuliser via a drying and cooling chamber operating at 120ºC and 2ºC, respectively. The gas stream containing the dry silver nitrate was then combined with the primary helium (99.9+%, BOC) plasma gas (500 mL/min) and fed into an in-house designed and built plasma jet assembly. Mass flow controllers controlled all flow rates (Brooks, UK).

The plasma was ignited at the stainless-steel electrode tip positioned in a 440 µM I.D. ceramic nozzle. The electrode was driven by a 14 W radio frequency generator operating at 13.56 MHz. The driving signal was pulse width moderated at 18 kHz, with a 50 % duty cycle. The driving signal was passed through a matching network consisting of a variable inductor to equate the high 50 Ω output impedance of the RF generator. The plasma exited the ceramic nozzle, to form a stable plume extending 8-10 mm from the tip of the nozzle. A 1500 mL/min nitrogen sheath gas surrounded the plume to reduce air entrainment, aid plasma stability and produce more exact SERS active spots. The plasma jet chamber was mounted on a three-axis motion stage for accurate spatial positioning. The deposition pattern was a consecutive spot arrangement forming a 2D array, Fig. 1; each spot was formed residence time of three seconds before moving to the next site.

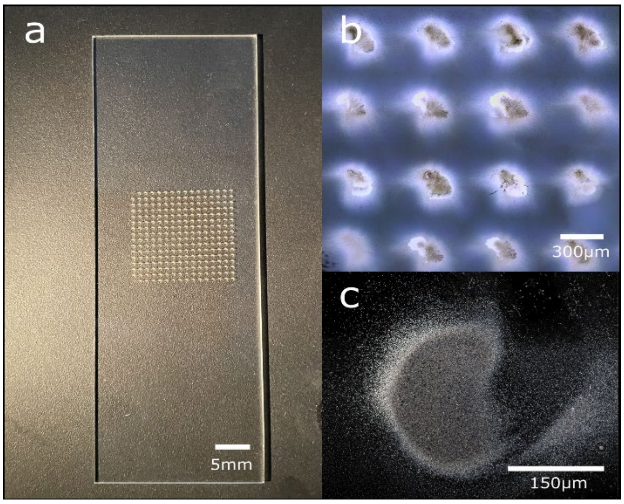

Figure 1. (a) the 16 x 16 2 D array of the silver-based SERS substrate on a borosilicate glass slide. (b) Increased magnification image of the 16 x 16 array depicting a 4 x 4 array. (c) High magnification image of single silver deposition spot.

Jet-deposited pre-synthesised spherical silver particles were carried out using the APPJ assembly described above, with the RF supply disconnected, for ease and the ability to deposit reproducible patterns on borosilicate slides. Solution of the pre-synthesised silver particles was introduced into the nebuliser at a flow rate of 10 ml/hr, and using the same flow rate of helium through the jet assembly, the particles were physically impacted on the surface for a residence time of three seconds - the synthesis of these particles is by the Turkevich method [8]. 4-MBA was introduced onto the SERS substrate using a 4-MBA (1x10^{-4} M) solution of methanol (HPLC grade, Fischer). A 0.1 ml aliquot was spread on the substrate, and the methanol was allowed to evaporate for one minute. Rhodamine was deposited in the same way.

All Raman spectra were recorded with a Renishaw inVia confocal Raman microscope with an argon-ion laser excitation source (514.5 nm). The spectra were recorded at ambient temperature between 100 cm^{-1} to 3200 cm^{-1} Raman shift range. Each spectra sample point was selected in a fair and non-biased way, with each Raman spectra presented being an average of a minimum of three spectra at different points to eliminate spot bias. Each spectrum was baseline corrected using the ‘baseline’ package in R.

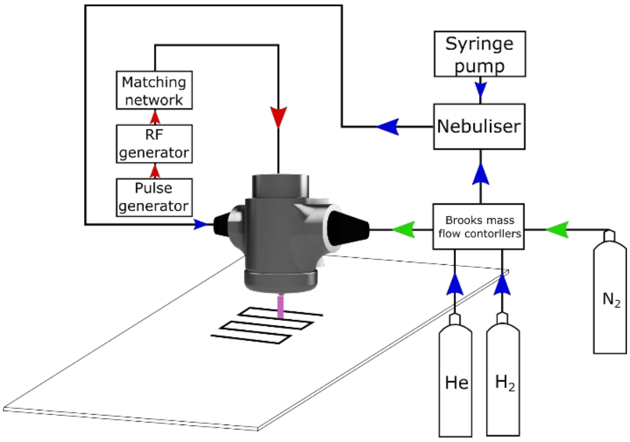

Figure 2. An illustration depicting the setup for plasma deposition, showing all components present culminating in plasma deposition on a borosilicate slide.

3. Results and discussion

The SERS activity of the substrate PDS was comparable in enhancement to other well-established techniques to create SERS active sites. The SERS spectra of different substrates were investigated using 4-mercaptobenzoic acid (4MBA) as a test molecule. 4MBA binds strongly through its thiol group to the Ag surface. The SERS enhancement of PDS is shown in Fig 3. (c), a comparison of the SERS signal to ADP (a) and commercial substrates SS (b) and signal. Also shown in Fig. 3 are each substrate's respective background spectra before adding 4MBA. Using 4MBA, the most extensive SERS enhancement is seen by the well-known Tuchevich colloid procedure ADP, followed by the commercial substrate SS, and then our plasma deposition procedure PDS. The most pronounced bands are 1080 and 1580 cm^{-1}, assigned to v_{8a} and v_{12} aromatic ring vibrations; the 1580 cm^{-1} peak was used for enhancement calculations in Fig. 3.

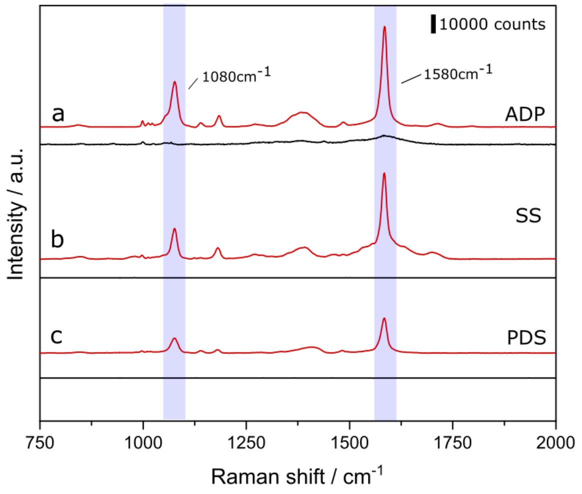

Figure 3. (a) Raman spectra of 100mM 4-mercaptobenzoic acid (red) and baseline corrected background (black) for ADP (a), SS (b), and PDS (c) surfaces.

Table 1. Various substrate enhancement factors

Substrate	Turkevich (ADP)	SERSitive (SS)	Plasma (PDS)
Enhancement factor	1.2 x 10^{7}	9.9 x 10^{6}	4.1 x 10^{6}
Standard error	5.7 x 10^{5}	1.2 x 10^{6}	1.88 x 10^{5}

The SERS response of a plasma-deposited silver surface on a borosilicate slide depends upon the enhancement factor of each individual substrate. The EM effect depends upon the substrate's microstructure; thus, the surface morphology of the silver deposit is key to the correct function as a SERS surface [9]. SEM images are used to analyse both size and morphology. Ag particle distribution shows a concentrated collection of Ag particles which establish an enhancement factor and produce the SERS effect. It is assumed that these spherical microstructures ultimately contribute to plasmon excitation. Herein, we showcase the technique for the novel deposition of silver particles rather than displaying substrates with extraordinary enhancement factors.

With plasma jet deposition, it’s possible to precisely pattern a surface by reproducing multiple silver islands in an array. This APPJ setup allows for the deposit of 100-150 µm diameter spots from PDS. When carrying out SERS, precise aerosol deposition through a 440 µm ID nozzle is seen in Fig 2. The area of active Ag particles is reduced by 100 times by utilising the APPJ's set-up and nozzle. This reduction in active SERS area may sound unfavourable, however, this is advantageous for precise addressable deposition and opens the possibility of multi-analyte analysis.

To some degree, SERS-based detection or measurement of gas-phase volatile molecules relies on the capacity to recover a baseline response. The response depends on the physi or chemisoption onto the surface; these analyte molecules need to be removed for the baseline recovery. Often this is circumvented by one-off measurement surfaces. It has been shown that plasma jets can desorb small molecules off the surface without damaging it. Using the same APPJ set-up, two passes with the helium plasma gas containing 4% oxygen and a separate pass with 4% hydrogen were found effective in removing all the analyte from the surface, evidenced by no residual SERS signal after each of the steps.

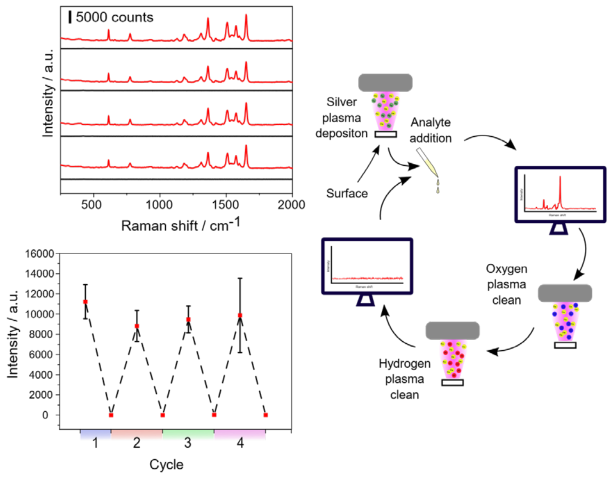

Figure 4. Numerous Raman spectra showing baseline recovery and subsequent R6G SERS signal regeneration on a borosilicate slide, with an illustration depiction of the plasma regeneration process.

The surface is largely unaffected by the plasma exposure, as the SERS response can be restored once the analyte is reintroduced to the surface. The surface starts to break down by oxygen plasma after several cleaning cycles, where the silver particles become aggregated and sinter together under the high electron temperature of the plasma. One cycle consists of an addition of analyte followed by two passes of oxygen, then hydrogen plasma, separately. Replicate recovery of baseline followed by reintroduction is shown in Fig. 4. This procedure can be used for repeated SERS analysis using multiple different analytes – leading to the formation of a SERS reusable substrate.

4. Conclusion

In summary, a new novel approach to an existing technique has been showcased. The technique of SERS has been enhanced by one-step SERS substrate active deposition from a metal salt using an APPJ. The SERS intensity is comparable to known regular methods of SERS substrate synthesis and 'off-shelf' commercial substrates. Comparable SERS signal from substrates produced in an easy one-step synthesis is a significant advantage over previous techniques in time spent and ease of use. The significant advantage is the ability to regenerate a clean background for our SERS substrates, introducing the reusability of the SERS substrates. Using this setup, significant advancements can be made within the SERS field.

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