

Plasma printing of nanogold on paper substrate for surface-enhanced Raman scattering application

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Abstract: Direct one-step plasma printing of nano-gold is demonstrated using an atmospheric-pressure plasma jet with atomised H₂AuCl₄ solution precursor. Nanogold is deposited on paper with different deposition times, giving different morphologies. Applicability as a SERS (surface-enhanced Raman scattering) platform was demonstrated by the detection of 0.7 amol μm^{-2} of RhB molecules on the paper substrate.

Keywords: Plasma printing, nanogold, SERS, atmospheric-pressure plasma.

1. Introduction

Plasma printing is a rapidly emerging field; it offers controlled deposition of nanostructured phases on a range of substrates, and has wide range of potential manufacturing and fabrication applications [1-3]. Among the numerous opportunities, direct printing of plasmonic metal nanoparticles for SERS (surface-enhanced Raman scattering) is a readily achievable and important application of plasma printing.

With the availability of portable Raman spectrometers, development of low-cost, disposable SERS platforms for on-site screening in biosensing applications has been gaining new momentum. Preparation of high quality metallic nanoparticles such as Ag and Au with optimized size distribution and long-term stability is essential. Particularly for low-cost disposable sensing platforms, wet chemical reduction of a metal precursor using different reducing agents, followed by inkjet printing, has been the usual approach [4]. However, several hours are typically required to grow the metallic nanoparticles, and often additional chemical treatment steps are necessary prior to the inkjet printing.

Plasma-enhanced chemical vapour deposition (PECVD) with a plasma jet can print target material directly from the liquid precursor and provide better film quality and uniformity than conventional wet processes. However, it has not been successfully demonstrated for metallic layer deposition at atmospheric pressure because of the complexities of plasma-metal-precursor interactions. Consequently, post-reduction processes [5] or physical deposition from a colloidal form of nano-metal ink [6] have been viewed as more practical plasma-based approaches to obtain a conducting film or pattern, thereby dispensing with the potential benefits of direct interaction between the plasma and precursor molecules.

By adapting the concept of microfluidic control of liquid precursor from Maguire et al. [7], we have demonstrated a direct plasma printing process on various substrates, including paper. We have further examined the applicability of a deposited nano-gold film, without any

pre-treatment or post-treatment process, as an effective SERS substrate.

2. Experimental

The direct plasma printing system consists of an atmospheric-pressure plasma jet installed on a table-top CNC (computer numerical control) machine, gas and liquid flow rate control units and a high-voltage AC power supply, as shown in Fig. 1. The combination of a syringe pump and parallel-path pneumatic nebuliser provide a stabilised liquid supply. The plasma jet is produced using two parallel ring-shape electrodes surrounding a Pasteur pipet glass tube, as shown in Fig. 1. For atomisation of the the liquid precursor, Ar is supplied through the central gas port, and a supporting He flow is introduced to guide the atomised precursor stream. Nanogold is deposited on a Whatman filter paper at 6 kV, 10 kHz with 20 $\mu\text{l min}^{-1}$ of 1% w/v H₂AuCl₄ aqueous solution further mixed with ethanol in 1:1 volume ratio to enhance atomisation. No pre-treatment or post-treatment was applied. The deposited film was prepared with different process times by scanning the plasma jet. The scanning speed was fixed at 1 mm/s and 5 different samples were prepared with 1, 2, 4, 6 and 10 passes, as shown in Fig. 2.

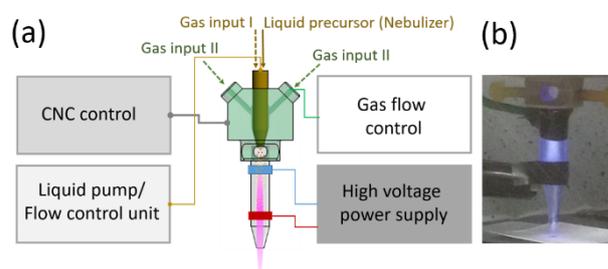


Fig. 1. (a) Schematic of the plasma printing system with atmospheric-pressure plasma jet and (b) close-up image of plasma discharge with paper substrate during the Au deposition process

3. Results and discussion

SERS measurements were performed using a 10^{-5} M Rhodamine B (RhB) solution in ethanol as a Raman indicator. $2 \mu\text{l}$ of the diluted RhB was drop cast on the paper substrate to cover the deposited area and the ethanol was allowed to evaporate, giving an RhB concentration of $0.7 \text{ amol } \mu\text{m}^{-2}$. The Raman spectroscopy was performed using a Renishaw inVia confocal Raman microscope system with He–Ne laser (633 nm) as the excitation source at an incident power of 1.7 mW. As shown in Fig. 2, the RhB was not detected in the reference case (a). Samples on which the nano-gold was deposited showed greatly enhanced detection of RhB. The highest sensitivity was observed in the samples for which 4 and 6 passes had been deposited. This corresponds to 6 s and 9 s deposition at a fixed position, respectively, taking into account the plasma jet diameter of 1.5 mm.

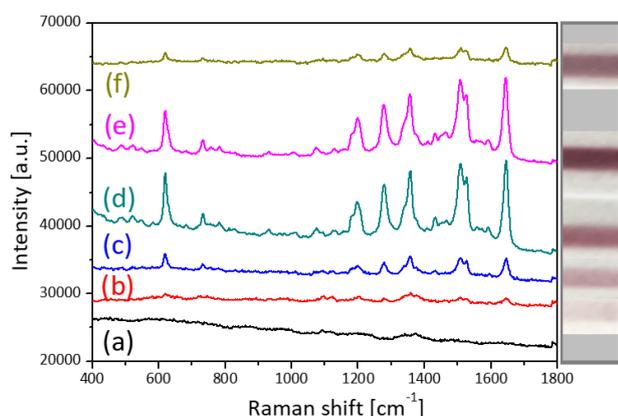


Fig. 2. Left: SERS measurements of Au deposited on paper substrate with $0.7 \text{ amol } \mu\text{m}^{-2}$ of Rhodamine B; results are shown for different deposition times, denoted by the number of scans of the plasma jet (b) 1, (c) 2, (d) 4, (e) 6 and (f) 10 passes at 1 mm/s of speed; these are compared to the reference (a); right: Photos of printed nanogold strip for (b) – (f)

4. Summary

Direct one-step plasma printing of gold on paper substrates for SERS application was demonstrated using an atmospheric-pressure plasma jet with HAuCl_4 precursor. This PECVD-based technique has the potential to be a more flexible and cost-effective approach than existing plasma processes such as post reduction or printing with nano-Au ink and provides better efficiency than conventional wet chemical processing. The applicability as a SERS sensing platform was confirmed by showing that nano-gold deposition on paper substrate enabled the detection of low levels of RhB molecules. The one-step plasma-printing process is expected to be applicable to other soluble metallic precursors, including combinations of precursors, so that composite multifunctional materials can be deposited.

5. References

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